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(54) Title: HOT MELT ADHESIVES, METHODS FOR THEIR MANUFACTURE AND USE (57) Abstract Hot melt adhesive compositions having enhanced adhesive qualities are provided by blending a base polymer with at least one liquid resin and at least one solid resin. Methods to produce such compositions are also provided.		

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5 **TITLE:** **HOT MELT ADHESIVES, METHODS FOR THEIR
 MANUFACTURE AND USE**

FIELD OF THE INVENTION

 This invention relates to hot melt adhesive compositions, methods for
10 making hot melt adhesive compositions, and articles using hot melt adhesive
 compositions.

BACKGROUND OF THE INVENTION

 A hot melt adhesive (HMA) is a thermoplastic mixture that is flowable
15 when heated, but cools to a solid after application. Typically the HMA is
 essentially free of water or solvent. It is common to incorporate low molecular
 weight additives in a HMA to increase its fluidity at the application temperature or
 allow a reduction in application temperature resulting in a lower cost process
 and/or modification of the mechanical properties of the adhesive such as bond
20 strength and low temperature flexibility. Typical HMAs comprise a base polymer
 and a tackifier. The most widely used hot melt adhesives are based on
 polyethylene, other polyolefins or mixtures thereof, ethylene-vinyl acetate
 copolymers (EVA), polyamides, polyesters, and block copolymer rubbers. Typical
 additives such as tackifiers, waxes, and oils can be used to modify the flow
25 characteristics and other properties of HMAs.

 Often, tackifiers such as synthetic hydrocarbon resins or derivatives of
 natural rosins are added to these ethylene homopolymers and copolymers to give
 them their adhesive qualities. The strength of the adhesive bond is dependent upon
 the individual properties and the relative amounts of each the base polymer and the
30 tackifier. For example, an adhesive based on EVA, a polar copolymer, blended
 with a natural rosin-based tackifier, also a polar composition, would be expected
 to have superior adhesive performance when compared to an EVA blended with a
 synthetic hydrocarbon-based tackifier, a non-polar compound.

 An article written by M.F. Tse and K.O. McElrath entitled "Relating
35 Adhesive Performance to Copolymer/Tackifier Blend," published in the September
 1988 issue of *Adhesives Age*, mentions using fractions and blends of commercially
 available C₅-C₆ aliphatic resins to produce pressure sensitive adhesives. Likewise,

U.S. Patent No. 4,650,829 also relates to pressure sensitive adhesives based on amorphous triblock copolymers.

U.S. Patent No. 4,973,326 discloses hot melt adhesives comprising resin blends wherein each of the resins is limited only to a maximum glass transition temperature and to content ranges based upon those glass transition temperatures. An object of the invention provides for an HMA having good adhesive performance without requiring an application temperature high enough to damage the substrate.

Adhesives using a non-polar hydrocarbon-based tackifier would be essentially acid-free and have less odor and better color stability when compared to adhesives using polar tackifiers. Also, the use of non-polar tackifier resins provides better handling properties when the molten HMA is in contact with metallic surfaces of processing equipment. Therefore, it would be desirable to develop adhesives using hydrocarbon tackifiers that offer bond strength equal to or better than adhesives comprising solar tackifiers.

SUMMARY OF THE INVENTION

This invention relates to HMA compositions comprising a base polymer and as a tackifier, a blend of at least one solid resin and at least one liquid resin. The base polymer is preferably one or more homopolymers and/or copolymers containing ethylene or propylene. The amounts of the solid and the liquid resins in the blend are preferably such that the tackifier has a composite glass transition temperature of from about 0°C to about 45°C. This invention further relates to methods for producing the novel HMA compositions.

DETAILED DESCRIPTION OF INVENTION

Introduction

It was discovered that both low temperature and high temperature HMA performance characteristics were unexpectedly improved by replacing a solid tackifier in a HMA composition with a liquid/solid resin blend. The novel use of a liquid/solid resin blend as a tackifier instead of a solid resin provides a tackifier component that has a lower glass transition temperature (T_g), a lower weight average molecular weight (M_w), a lower number average molecular weight (M_n), and a broader MWD.

Preparation of Solid Resins

The solid resins used in the blends of this invention are hydrocarbon resins or equivalents thereof produced by known methods. "Solid resin" for the purposes of this patent specification and appended claims is a polymerization product of the monomers and polymerization processes disclosed below that is solid at room temperature (~25°C). In another embodiment, a solid resin can be a resin that has been treated to improve its color or that has been blended with stabilizers or other additive packages that do not substantially alter the adhesive properties of the resin. The solid resins have a M_w in the range of about 350 to about 2100, preferably about 400 to about 1500, more preferably about 400 to about 1200. The preferred solid resins have a T_g in the range of from about 25°C to about 100°C, more preferably from about 35°C to about 85°C, even more preferably from about 40°C to about 70°C. The preferred solid resins are selected from C₅-C₉ aromatic modified aliphatic hydrocarbon resins, C₅-C₉ aromatic modified aliphatic hydrocarbon/terpene resins, and alicyclic diene monomer containing hydrocarbon resins.

In one embodiment, the aromatic modified aliphatic hydrocarbon resins, used as the solid resin are prepared by the polymerization of a mixture of a petroleum cracked distillate generally boiling in the range of from about 25°C to about 80°C and a monovinyl aromatic monomer having 8 or 9 carbon atoms. The polymerization product is characterized as a mixture of components giving a proton distribution such that from about 5 percent to about 30 percent are aromatic protons, from about 0 to about 10 percent are olefinic protons, from about 20 percent to about 50 percent are aliphatic methyl protons, and about 0 to about 30 percent are aromatic methyl protons, as determined by Proton Nuclear Magnetic Resonance spectroscopy (¹H NMR).

The petroleum cracked distillate typically comprises a mixture of saturated and unsaturated monomers. The unsaturated monomers are monoolefins and/or diolefins, and although the unsaturated materials are predominantly C₅, some higher and lower materials such as C₆ olefins and diolefins may be present. The distillate may also contain saturated or aromatic materials which can act as a polymerization solvent.

A preferred monovinyl aromatic monomer is styrene which may have substitution of the hydrogens in the aromatic group. Alternatively alpha-methyl styrene or vinyl toluene may be used as an aromatic monomer. Preferred aromatic monomers are styrene, all methyl styrene isomers, indene, and all methyl indene isomers. It is, however, preferred for lower and thus improved color to use the

pure monomer rather than the commercially available mixtures of vinyl aromatic monomers.

Aromatic modified aliphatic hydrocarbon resins are conveniently prepared by Friedel-Crafts catalyzed polymerization in which the mixture of cracked
5 distillate and monovinyl aromatic monomer are treated with from about 0.25 to about 2.5 weight percent of a catalyst. These resins and their method of manufacture are more generally disclosed in U.S. Patent 4,078,132 and EP 0 318 217 A2, the complete disclosures of which are fully incorporated herein by reference for the purpose of U.S. patent practice. Non-limiting examples of such
10 catalysts are aluminum chloride, aluminum bromide, or solutions, slurries or complexes thereof or borontrifluoride. The polymerization mixture may also include but is not limited to from about 10 to 100 weight percent, based on the weight of the feed mixture, of a chain transfer agent such as a diisobutene oligomer to obtain resins having a narrower molecular weight distribution. These reactions
15 are generally carried out at temperatures in the range of from 0°C to 120°C, preferably from 0°C to 80°C, more preferably from 20°C to 55°C, the conditions being controlled to yield a resin of the preferred ranges of softening points. Residual catalyst is quenched by suitable methods such as addition of methyl alcohol, ethyl alcohol, isopropyl alcohol, or aqueous solutions of these alcohols,
20 and subsequent filtration followed by water and/or caustic washing. The final solution may then be stripped of unreacted hydrocarbons and low molecular weight oils by vacuum or steam distillation.

The most preferred aromatic modified aliphatic hydrocarbon solid resins have ring and ball softening points (ASTM E28-92) in the range of from about 85°
25 C to about 145°C, preferably in the range of from about 90°C to about 130°C, more preferably in the range of from about 90°C to about 115°C, even more preferably in the range of from about 90°C to about 100°C. The preferred aliphatic resins also have a percent aromatic protons in the range of from about 5 to about 30, a percent olefinic protons in the range of from about 0 to about 10, a
30 percent aliphatic methyl protons in the range of about 20 to about 50, and a percent aromatic methyl protons in the range of from about 0 to about 30.

Commercially available but non-limiting examples of aromatic modified aliphatic hydrocarbon solid resins are Escorez® 2000 series (such as but not limited to resins 2101, 2393, 2596) and Escorez® 6000 series (such as but not
35 limited to resin ECR-372B or 6372) available from Exxon Chemical Co., Houston, Texas. Such commercial resins are often sold with antioxidant stabilizers and other additive packages present in small amounts.

In another embodiment, the alicyclic diene monomer containing hydrocarbon solid resins to be blended in this invention include those known as cyclopentadiene-dicyclopentadiene (CPD/DCPD) based petroleum resins which can be produced using the Friedel-Crafts polymerization processes discussed
5 above for solid aromatic modified aliphatic petroleum resins. For CPD/DCPD resins, known thermal polymerization processes are also particularly suitable.

After polymerization, any of these resins may be used as is or may be treated with a decolorizing agent or hydrogenated by known methods to remove substantially all the residual ethylenic and aromatic unsaturation, thus improving
10 the color. Typical hydrogenation results in residual ethylenic or aromatic content of less than 10 proton percent, preferably less than 7 proton percent, more preferably less than 5 proton percent, as determined by ^1H NMR.

For the purposes of this specification and appended claims the term "thermoplastic C_9 aromatic resin" includes but is not limited to those resins
15 produced from pure monomers such as styrene and alkyl-substituted styrenes which are similarly polymerized in Friedel-Crafts catalysts. U.S. Patent Nos. 3,926,878, 4,242,244, 4,276,396, 4,328,090, and 4,629,766, and WO 91/13106 each addressing preparation and/or hydrogenation of alicyclic monomer containing resins are fully incorporated herein for purposes of U.S. patent practice.

20 As discussed in the publications incorporated herein by reference, the solid unhydrogenated or substantially hydrogenated alicyclic monomer containing hydrocarbon resins may contain other monomers in addition to the CPD/DCPD. Other non-limiting examples of monomers are vinyl aromatic, indene, styrene, C_4 - C_5 acyclic conjugated dienes, CPD codimers with conjugated acyclic dienes, C_9 ,
25 substituted C_9 , and other copolymerizable C_4 - C_{10} monomers. Preferable alicyclic monomer containing hydrocarbon solid resins have a ring and ball softening point (ASTM E-28) from about 80°C to about 110°C , a M_w of from about 350 to about 900, a z-average molecular weight (M_z) less than about 1600, a Gardner color less than or equal to about 2, and an aliphatic methyl proton percent in the range of
30 about 5 to about 25 percent based on the total number of protons in the resin. More preferably, the ring and ball softening point is from about 85°C to about 105°C , the M_w is from about 360 to about 700, and the M_z is from about 500 to about 1200, and the Gardner color is less than about 2, more preferably less than about 1.

35 Commercially available, non-limiting examples of resins suitable as alicyclic diene monomer containing hydrocarbon tackifiers include the hydrogenated CPD/DCPD Escorez® 5000 series (such as but not limited to resins 5300, 5320,

and 5380) available from Exxon Chemical Co., Houston, TX; the hydrogenated C₅/C₉ Eastotac® H100 resin available from Eastman Chemical Products, Inc., Kingsport, TN; and the hydrogenated C₉/C₄ Regalite® R91 and R101 resins available from Hercules, Inc., Wilmington, DE, Arkon® P90 and P100 available from Arakawa Inc., Japan. Such commercial resins are often sold with antioxidant stabilizers and/or other additive packages present in small amounts which do not affect the invention of this specification and appended claims.

Additional description, and reference to principal patent disclosures, for both solid aromatic modified aliphatic hydrocarbon resins and alicyclic diene monomer containing hydrocarbon resins is presented in "Hydrocarbon Resins", *Kirk-Othmer Encycl. of Chem. Tech.*, v. 13, pages 717-743 (J. Wiley & Sons, 1995), all the teachings of which are fully incorporated herein by reference for purposes of U.S. patent practice.

15 Preparation of Liquid Resins

The liquid resins used in the blends of this invention are also from the same monomers and by the same methods as disclosed above for the solid resins. The distinction of liquid resins from the solid resins is that the liquid resins have lower molecular weights (M_n and M_w) resulting properties such as lower softening points, glass transition temperatures, and their liquid consistency at room temperature. Preferred liquid resins have a T_g in the range of from about -80°C to about 20°C, preferably from about -60°C to about 0°C, more preferably from about -40°C to about -10°C. In another embodiment, a liquid resin can be a resin that has been treated to improve the color or that has been blended with stabilizers or other additive packages that do not substantially alter the adhesive properties of the resin. The preferred liquid resins have a M_w in the range of about 100 to about 2000, preferably about 200 to about 1000, more preferably about 200 to about 800. The preferred liquid resins to be blended are selected from C₅-C₉ aromatic modified aliphatic hydrocarbon resins, C₅-C₉ aromatic modified aliphatic hydrocarbon/terpene resins, and alicyclic diene monomer containing hydrocarbon resins. In a preferred embodiment, the one or more liquid resins are also compatible with the solid resins with which they are blended; more preferably they will contain the same or similar type monomers.

The most preferred aromatic modified aliphatic hydrocarbon liquid resins have a percent aromatic protons in the range of from about 5 to about 30, a percent olefinic protons in the range of from about 0 to about 10, a percent

aliphatic methyl protons in the range of from about 20 to about 50, and a percent aromatic methyl protons in the range of from about 0 to about 30.

Commercially available but non-limiting examples of aromatic modified aliphatic hydrocarbon liquid resins are Escorez® 2000 series (such as but not limited to Escorez® 2520 available from Exxon Chemical Co., Houston, TX). Such commercial resins are often sold with antioxidant stabilizers and other additive packages present in small amounts.

Preferable alicyclic monomer containing hydrocarbon liquid resins have a M_w of from about 100 to about 2000, a Gardner color less than or equal to about 5, and an aliphatic methyl proton percent in the range of about 5 to about 25 percent based on the total number of protons in the liquid resin. More preferably, the M_w is from about 200 to about 1000, and the Gardner color is less than about 2, more preferably less than about 1.

Commercially available, non-limiting examples of resins suitable as alicyclic diene monomer containing hydrocarbon tackifiers include the hydrogenated CPD/DCPD Escorez® 5000 series (such as but not limited to resin ECR-327 available from Exxon Chemical Co., Houston, TX or Exxon Chemical Belgium, Brussels, Belgium).

U.S. Patent Nos. 4,677,176, 4,684,707, 4,902,766, 4,916,192, and 4,933,409 each addressing preparation of liquid hydrocarbon resins are fully incorporated herein by reference for purposes of U.S. patent practice.

Blending of Solid and Liquid Resins

The liquid/solid resin blend of this invention contains one or more liquid resins and one or more solid resins. The resins useful as blend components are selected from C_5 - C_9 aromatic modified aliphatic hydrocarbon resins, C_5 - C_9 aromatic modified aliphatic hydrocarbon/terpene resins, and alicyclic diene monomer containing hydrocarbon resins. The liquid and solid resins to be blended are preferably selected from similar, thus compatible, types of resins. The solid and liquid resins may be blended by any method commonly known to those skilled in the art. The liquid and solid resins can be blended together in the molten state or can be blended directly with the base polymer and other additives, such as wax, during the preparation of the HMA. Liquid resin can also be injected into the polymerizate of the solid resin as the polymerizate exits the reactor. The solid and liquid resin blend can be subsequently recovered and steam stripped. The order of blending of the liquid resin, solid resin, and other adhesive components is not

critical. The T_g of the resin blends, however, can be targeted to a specific desired value since the blends follow the Fox inverse rule:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} + \dots + \frac{w_n}{T_{gn}}$$

- where w_1 through w_n are the weight fractions of the various blend components based on the weight of the total tackifier blend, T_{g1} through T_{gn} are the glass transition temperatures of the various blend components, and T_g is the glass transition temperature of the blend. The two liquid resins used in the blends of the examples shown below were Escorez® 2520 and ECR-327, glass transition temperatures of -16°C and -13°C, respectively. All temperatures are converted to degrees Kelvin for this calculation. Therefore, calculation of the T_g of 303°K or 30°C for the tackifier of Example 5 is as follows:

$$\frac{1}{T_g} = \frac{0.74}{(273 + 50)} + \frac{0.26}{(273 - 16)}$$

- The tackifier, containing one or more liquid resins and one or more solid resins, preferably has a composite T_g in the range of about 0°C to about 45°C, more preferably about 10°C to about 40°C, even more preferably about 20°C to about 40°C.

Preparation of Base Polymers

- The new HMAs contain a base polymer consisting of one or more ethylene-based or propylene-based polymers having a M_n greater than 10,000. The base polymer can be polyethylene, a copolymer of ethylene and one or more comonomers, polypropylene, a copolymer of propylene and one or more comonomers, or mixtures thereof. Preferably, these ethylene and propylene homopolymers and copolymers have a degree of crystallinity of at least 5 weight percent, more preferably at least 15 weight percent, as measured by DSC.

- In one preferred embodiment, the base polymer comprises ethylene and one or more comonomers. The comonomers may be one or more polar groups such as vinyl acids, vinyl esters, vinyl alcohols, such as ethacrylic acid, crotonic acid, vinyl acetic acid, angelic acid, maleic acid, fumaric acid, ketones, carbon monoxide, 2-hydroxy ethyl acrylate, 2-hydroxy ethyl methacrylate, and the like. Preferred examples of polar comonomers include alkylmethacrylates, alkylacrylates, alkylmethacrylic acids, and alkylacrylic acids. Even more preferable examples of

suitable comonomers include vinyl acetate, acrylic acid, methacrylic acid, methacrylate, ethyl methacrylate, methyl methacrylate, ethyl acrylate, n-butyl acrylate, and methyl acrylate. Preferred copolymers have a comonomer content of less than 38 weight percent, more preferably in the range of from 10 to 33 weight percent, more preferably from 20 to 30 weight percent based upon the weight of the copolymer. These copolymers are produced by many processes known in the art, such as, but not limited to, free radical polymerization, and are available commercially in many forms. For example, ethylene-vinyl acetate copolymers are produced by high pressure free radical polymerization and are available from Exxon Chemical Company, Houston, TX, under the Escorene® trade name. These Escorene® EVA copolymers have weight percent comonomer in the range of from about 14 to about 33 and a melt index in the range of from about 2.3 to about 2500 dg/min. (ASTM D1238, condition E, 190°C and 2.16 kg). The comonomers may also be a mixture of any of the polar moieties described above and non-polar groups described below.

In another embodiment, the base polymer is a copolymer of ethylene or propylene, more preferably ethylene. Preferred comonomers for ethylene are one or more higher alpha-olefins, more preferably one or more C₃ to C₂₀ alpha olefins, preferably one or more C₃ to C₈ alpha olefins, more preferably one or more C₄ to C₆ alpha olefins. Preferred comonomers for propylene are ethylene or one or more higher alpha-olefins, more preferably one or more C₄ to C₂₀ alpha olefins, preferably one or more C₄ to C₈ alpha olefins, more preferably one or more C₄ to C₆ alpha olefins. Ethylene or propylene may also be copolymerized with one or more cyclic olefin monomers, such as norbornene, methyl norbornene, cyclopentene, ethylidene norbornene, cyclopentadiene, and the like, or mixtures of alpha-olefins and cyclic olefins. Examples include but are not limited to copolymers such as ethylene/hexene-1, ethylene/butene-1, ethylene/4-methylpentene-1, ethylene/octene-1, ethylene/norbornene, ethylene/butene-1/hexene-1, and the like. The comonomers are present at 0.5 to 33 mole percent, preferably 1.5 to 25 mole percent, more preferably 5 to 18 mole percent, based on the total ethylene copolymer. These polymers can be prepared in accordance with well-known methods, typically by polymerization with Zeigler-Natta catalysts or single site metallocene catalysts as well as other known catalyst systems.

35 Preparation of HMAs

The HMA compositions of this invention comprise a base polymer, a blend of a hydrocarbon solid and hydrocarbon liquid resins as a tackifier, and optionally

other modifiers. Preferably the liquid resin is present in the range of from about 1 part to about 100 parts by weight per 100 parts by weight of the solid resin, more preferably from about 1 part to about 40 parts, most preferably from about 1 to about 20 parts. Resins to be blended are preferably of a similar, thus more compatible, molecular structure. For example, use of a DCPD-based liquid resin is preferred when a solid DCPD resin is used and a solid aromatic modified aliphatic liquid resin is preferred when a solid aromatic modified aliphatic liquid resin is used.

The copolymer may be present in the HMA composition from about 10 to about 90 weight percent, preferably from about 20 to about 80 weight percent, even more preferably from about 30 to about 60 weight percent, most preferably from about 33 to about 50 weight percent, based upon the total weight of the HMA.

The resin blend tackifier may be present in the HMA composition from about 10 to about 90 weight percent, preferably from about 20 to about 80 weight percent, even more preferably from about 30 to about 60 weight percent, most preferably from about 33 to about 50 weight percent, based upon the total weight of the HMA.

Waxes, antioxidants, and other additives known in the art may be added to the blends of this invention as optional ingredients. These additives include but are not limited to photostabilizers, ultraviolet stabilizers, fillers, plasticizers, lubricants, coloring agents, and the like. These additional ingredients are typically present in the adhesive composition at less than or equal to about 35 weight percent, preferably about 1 to about 25 weight percent, even more preferably about 5 to about 15 weight percent, based upon the total weight of the HMA including the additive.

The components of the adhesive composition may be blended by ordinary methods known in the art for blending ethylene polymers, tackifiers, and the like. For example, an ethylene-vinyl acetate copolymer can be placed in a receptacle, heated, and stirred. Each solid and liquid resin can be added to the receptacle so that a uniform dispersion is obtained. The order in which the HMA components are blended is unimportant. The blends may be produced by mixing the components using any suitable mixing device at a temperature above the melting point of the components, e.g. at 130°C to 180°C for a period of time sufficient to form a homogeneous mixture, normally 1 to 120 minutes depending on the type of mixing device.

Preferred adhesive compositions of the invention have a SAFT of 70°C or higher and show a measurable improvement in T-peel at 25°C to polymeric substrates such as polyethylene, polypropylene, and Mylar™. Preferred adhesive compositions of the invention also have at least a 50% improvement in T-peel relative to adhesive compositions using only a solid resin as a tackifier, more preferably greater than a 100% improvement, even more preferably greater than a 200% improvement. This T-peel improvement is demonstrated at 25°C, preferably additionally as low as 5°C and as high as 45°C, to one or more substrates selected from polypropylene, polyethylene, or Mylar™. Adhesive compositions comprising a tackifier wherein the blended liquid and solid resins have the same or similar monomeric constituents also demonstrate improved low temperature performance, such as T-peel at 0°C and higher. For example, preferred tackifiers are blended from one or more liquid resins and one or more solid resin wherein all the resins in a single tackifier are either aromatic-modified aliphatic or DCPD-based. Additionally, it is preferred that the T_g s of the liquid and the solid resins that are blended have individual T_g s that differ by 40°C or more. Adhesive compositions based upon EVA as a base polymer show the best performance, especially at a vinyl acetate content of less than 30 weight percent based upon the weight of the EVA.

20

Useful Applications

The blends of this invention can then be used as adhesives on substrates such as asphalt, cement, metals (including aluminum), Mylar® (a biaxially-oriented polyethylene terephthalate), polymers (including polyolefins such as rubbers, plastics, thermoplastics), glass, ceramics, wood, paper, rocks, minerals and paint, cardboard, and the like. Preferred examples include polyethylene, polypropylene, and Mylar®. Pressure sensitive adhesives (PSAs), contact adhesives (CAs), and hot melt pressure sensitive adhesives (HMPSAs) may also be improved by use of these novel resin blends. The preferred use is HMA compositions. Such adhesives can be used in final applications such as packaging, laminates, coating materials, bookbindings, upholstery, wood products, and automobiles.

30

EXAMPLES

In order to provide a better understanding of the present invention including representative advantages thereof, the following examples are offered.

35

Testing Procedures

Proton Nuclear Magnetic Resonance (^1H NMR): data is obtained in a Varian VXR 300 MHz spectrometer equipped with a 10 mm broadband probe.

5 The system is configured so that the decoupler channel can be used to observe the proton signals. Acquisition conditions are as follows: pulse angle 30° ; pulse delay 10 seconds; acquisition 2 seconds; spectral width 10,000 hertz; free induction decays collected per sample were 200. Samples of whole resins are dissolved in deuterated chloroform at a concentration of 80 mg/ml and run at 50°C . Chemical

10 shifts are given in ppm and are relative to tetramethylsilane which was set to 0 ppm. Due to the structural complexity of these tackifiers, only generic proton assignments are made. These assignments are useful in assessing differences between samples based on general proton categories. The different proton types were calculated by integrating the signal area in three spectral regions. The

15 aliphatic region is defined as signals between about 0 and about 3.5 ppm. The olefin region is defined as between about 4.5 and about 6.0 ppm. The aromatic region is defined as about 6.2 to about 7.8 ppm. By summing the area of the three regions the percentage of each proton type is calculated by dividing total area into the signal intensity of each region. For aliphatic tackifiers, the unsaturation is

20 expressed in proton percent by ratioing the signal area in the olefinic region to the total proton signal intensity.

The aliphatic region is further divided into different proton types. An estimation of the different types present is done by subdividing the aliphatic region into different areas. The region between about 0.2 and about 1.1 ppm is taken to

25 represent the intensity of methyl groups attached to saturated hydrocarbon moieties and the intensity between about 2.0 and about 3.5 ppm represent benzylic and allylic protons. The percent methyl group content or concentration is calculated by ratioing the area of the methyl signal region to all of the aliphatic intensity and the benzylic/allylic proton concentration was determined by ratioing

30 its area intensity to all of the aliphatic intensity.

Gel Permeation Chromatography (GPC): Samples are run in tetrahydrofuran (THF) at 30°C on a Waters 410 instrument having a five-column set with nominal porosity ranging from 10^5 to 10^2 angstroms. The flow rate is 2.5 ml/min. and the corresponding plate count is 3500 plates per foot for this column

35 combination. Filtered solutions of the tackifiers in THF with a concentration of about 0.5 weight to volume ratio at 30°C are used. The molecular weight average for the resins are reported as polystyrene equivalent numbers. It should be noted

that the molecular weight values reported from GPC are not absolute because precise calibration methods are unavailable for tackifiers.

Ring and Ball Softening Point (s.p.) was measured in accordance with ASTM E28-92.

- 5 Differential Scanning Calorimetry (DSC): The glass transition temperature of the resin blend components was measured using a DuPont Instruments Model 912 differential scanning calorimeter. Samples weighing approximately 10 mg were scanned from -50° to 150°C at a rate of 10°C/min.

- 10 T-Peel Strength: T-peel strength is defined as the average load per unit width of bond line required to produce progressive separation of two bonded adherents. Separation speed is 2 inches (51 mm) per minute. Bonding conditions are described in the examples below.

- 15 Shear Adhesion Failure Temperature (SAFT): SAFT is the temperature at which a specified bond fails when the bonded area is subjected to force parallel to the bonded surfaces. Failure is defined as complete separation of the bonded area. One inch square lap shear bonds to kraft paper are prepared. Samples are hung vertically in an air circulating oven and a 500 gram weight is suspended from the bottom strip. The oven temperature is raised at the rate of 30°C every 15 minutes. The reported SAFT is the average of three readings. Bonding conditions are described in the examples below.

- 20 Peel Adhesion Failure Temperature (PAFT): PAFT is the temperature at which a specified bond fails when the bonded area is subjected to force perpendicular to the bonded surfaces. Failure is defined as complete separation of the bonded area. One inch by 3 inch adhesive bonds to kraft paper are prepared. Samples are configured with the bonded plane oriented horizontally (in peel mode) in an air circulating oven and a 100 gram weight is suspended from the free end of the bond. The oven temperature is raised at the rate of 30°C every 15 minutes. The reported PAFT is the average of three readings. Bonding conditions are described in the examples below.

- 30 Stress-Strain Measurements (e.g. tensile strength, strain at break, yield stress, and yield strain) were performed on an Instron model 4505 testing machine. Specimens for tensile stress-strain studies were made by compression molding the HMA between layers of Teflon-coated aluminum foil for 30 minutes at 150°C to form a molded layer of the HMA 2 mm in thickness. The molded layers were die cut into micro-dumbbell specimens as specified in ASTM D-1708. A crosshead speed of 2 inches (51 mm) per minute was used for each of the examples tested.

The stress was calculated based on the undeformed cross-sectional area of the tensile specimens.

Dynamic Mechanical Thermal Analysis (DMTA) measurements of tensile loss modulus and loss tangent of the adhesive blends were performed using a Rheometric Scientific™ Mark II DMTA in dual cantilever bending mode using the medium size frame and the single point clamp yielding a total free length of 10 mm on each side of the test specimen. Test specimens were prepared as for the stress-strain tests except that specimens 40 mm x 13 mm rectangles cut from the 2 mm thick layer of HMA. Each sample was scanned from -70°C to 100°C increasing the temperature at the rate of 3°C/min and a test frequency of 1 Hz.

Open time is defined to be the maximum time available between the application of the HMA, at 180°C, on a first substrate and the bonding of a second substrate to the first substrate that will still allow a solid seal between the two substrates. Solid seal as defined herein means that when the bond between the two substrates is separated after bonding, the bond is destroyed by failure of the substrate and not failure of the adhesive. A 45 to 55 mg portion of the HMA at 180°C is applied as a bead of 5 cm over the width of a first substrate. At a selected time interval after the application of the HMA, a second substrate is contacted with the first substrate at a pressure of 1.5 bar for a fixed time of 4 seconds. The bond is then separated. This procedure is repeated for time intervals between the application of the HMA and the subsequent destruction of the bond ranging from 1 second to 60 seconds. The open time is the maximum time interval at which the bond is destroyed by failure of the substrate and not of the adhesive. The substrates used were 50 mm x 62 mm section of Bookbinding Cardboard NR 10, available from L. Coosemans, Dworp, Belgium.

Set time is defined as the minimum time required to hold together two bonded substrate surfaces mechanically in order to obtain a solid seal. Solid seal as defined herein means that when the bond between the two substrates is separated after bonding, the bond is destroyed by failure of the substrate and not failure of the adhesive. A 45 to 55 portion of the HMA at 180°C is applied as a 5 cm bead to the width of a first substrate. Using a fixed open time of 1 second, or at 1 second after the application of the HMA to the first substrate, a second substrate is contacted with the first substrate at a pressure of 1.5 bar for a selected time interval between 0.2 and 30 seconds. The bond is then separated. This procedure is repeated for different time intervals between the bonding of the two substrates and the subsequent destruction of the bond. The set time is the minimum time interval at which the bond is destroyed by failure of the substrate

and not of the adhesive. The substrates used were 50 mm x 62 mm section of Bookbinding Cardboard NR 10, available from L. Coosemans, Dworp, Belgium.

HMA Blend Components

- 5 Aristowax® 165 is a petroleum wax with approximate molecular weights of $M_n=410$ and $M_w=460$ and an approximate DSC melting point of 68°C, and is available from Unocal Corp., Los Angeles, California.

- ECR-327 is a liquid dicyclopentadiene-based hydrocarbon resin having a M_w of approximately 340, a M_w/M_n of about 3.3, and a T_g of about -13°C, and is
10 available from Exxon Chemical Company, Houston, Texas, or Exxon Chemical Europe, Brussels, Belgium.

- Escorene® UL-7750 is an ethylene-vinyl acetate copolymer comprising about 28 weight percent vinyl acetate and having approximate molecular weights of $M_n=19,000$ and $M_w=41,000$, a polydispersity of approximately 2.16, a DSC
15 melting point of about 69°C, a melt index of about 32 dg/min., and a density of about 0.934, and is available from Exxon Chemical Company, Houston, Texas.

Escorene® UL04533 is an ethylene-vinyl acetate copolymer comprising about 33 weight percent vinyl acetate and having a melt index of about 45 dg/min., and is available from Exxon Chemical Europe, Brussels, Belgium.

- 20 Escorez® 2393 is a solid aromatic modified aliphatic hydrocarbon resin having a M_w of approximately 1100 and a M_w/M_n of about 2.4, a T_g of about 47°C, and is available from Exxon Chemical Company, Houston, Texas.

- Escorez® 2520 is a liquid aromatic modified aliphatic hydrocarbon resin having a M_w of approximately 430 and a M_w/M_n of about 1.5, a T_g of about -16°C, and is available from Exxon Chemical Company, Houston, Texas.
25

Escorez® 5320 is a solid dicyclopentadiene-based hydrocarbon resin having a M_w of approximately 410 and a M_w/M_n of about 2.6, a T_g of about 66°C, and is available from Exxon Chemical Company, Houston, Texas.

- Escorez® 5380 is a solid dicyclopentadiene-based hydrocarbon resin
30 having a M_w of approximately 370 and a M_w/M_n of about 2.3, a T_g of about 36°C, and is available from Exxon Chemical Company, Houston, Texas.

- Escorez® 6372 is a solid, hydrogenated aromatic modified aliphatic hydrocarbon hydrocarbon resin having a M_w of approximately 1250 and a M_w/M_n of about approximately 1.67, a T_g of about 50°C, and is available from Exxon
35 Chemical Europe, Brussels, Belgium.

Irganox® 1010 is an oxidation inhibitor and thermal stabilizer available from Ciba-Geigy Corp., Ardsley, New York).

HMA Blending and Testing

5 A series of HMA blends was made using as a tackifier either a solid resin alone or a liquid/solid resin blend. In Examples 1-9 below, a series of hot melt adhesives (HMA) based on Escorene® 7750 was formulated using various tackifiers and Aristowax® 165 as a flow modifier. The ratio of components was 45/45/10 respectively by weight in all cases. Also, 0.5 weight percent (based on
10 the weight of the EVA/tackifier/wax mixture) of Irganox® 1010 (available from Ciba-Geigy Corp., Ardsley, New York) was added to the EVA/tackifier/wax mixture as an oxidation inhibitor and thermal stabilizer. Formulations were prepared in stainless steel beakers at a nominal temperature of 150°C with a blanket of nitrogen covering the materials. Once the components had melted in the
15 quiescent state, a propeller type stirrer was used to mix them. Stirring was continued for 30 minutes after visual inspection indicated that a homogeneous blend had been achieved.

Each of the HMA formulations was laid out to form a thin film suitable for bonding. The HMA was heated to 150°C in an oven then laid out on release paper
20 using an eight path applicator to achieve a film that had a nominal thickness of about 0.005" (0.127 mm). The HMA films were used to bond cast films of polypropylene (Escorene® 4252, $M_n = 80,000$, $M_w = 297,000$, melting point = 163°C, thickness = 0.130 mm, available from Exxon Chemical Company, Houston, Texas). Seals were made in a Carver hot press heated to 150°C, the adhesive
25 being sandwiched between polypropylene film using a pressure of approximately 40 p.s.i. (276 kPa) for 10 seconds. The resulting bond was found to be fairly consistent for examples anywhere within the specified range. Molding plates of 1/32" (0.794 mm) aluminum were used to separate the polypropylene film from the platens of the press. After sealing, the bonds were quenched between water
30 cooled platens at a temperature of approximately 25°C using a pressure of approximately 40 p.s.i. (276 kPa). For the purposes of T-peel testing, 0.5" (12.7 mm) strips were cut from the bonded sandwich of polypropylene film and HMA. Test pieces were allowed to age for a minimum of 24 hours prior to evaluating the strength of the bond. T-peel testing was carried out at room temperature on an
35 Instron 4505 testing frame with an extension rate of 2"/minute and a sampling rate of 2 points/second. In the case of adhesives exhibiting only slip/stick failure the T-

peel strength was taken as the average of the peaks on the force/displacement plot. When samples showed evidence of smooth peel the T-peel strength was taken as the average of the regions of smooth peel. In cases where both smooth peel and slip/stick were exhibited by the same sample the average value of the smooth peel is reported. T-peel tests were prepared and performed by the same method for substrates of polyethylene (Escorene® LD-117.08, melt index = 1.5-2.0 dg/min., density = 0.93 g/cm³, thickness = 0.130 mm, available from Exxon Chemical Company, Houston, Texas), Mylar™ (thickness = 0.089 mm, available from Cadillac Plastic and Chemical Company, Houston, Texas), and aluminum (Reynolds® 667, thickness = 0.020 mm, available from Reynolds Metals Co., Richmond, Virginia). For each HMA formulation five bonds were tested and the results averaged. The adhesive performance of the HMA compositions comprising solid resins and liquid/solid resin blends is reported in Tables 1-4.

TABLE 1

Example	1	2	3
Comparative (C)/ Blend (B)	C	B	B
Escorene® 7750, pbw*	45	45	45
Escorez® 2393, pbw	45	35	41
Escorez® 2520, pbw	-	10	4
Aristowax® 165, pbw	10	10	10
Irganox® 1010, pbw	0.5	0.5	0.5
Composite Tackifier T _g , °C	47	31	40
T-peel to PP at 25°C, lb./in. (N/25mm)	1.10 (4.81)	1.99 (8.71)	2.04 (8.93)
T-peel to PP at 0°C, lb./in. (N/25mm)	0.11 (0.48)	0.16 (0.70)	0.21 (0.92)
T-peel to PE at 25°C, lb./in. (N/25mm)	0.20 (0.88)	0.67 (2.93)	0.94 (4.11)
T-peel to Mylar at 25°C, lb./in. (N/25mm)	2.44 (10.7)	2.62 (11.5)	3.83 (16.8)
T-peel to Aluminum at 25°C, lb./in. (N/25mm)	0.80 (3.50)	0.40 (1.75)	1.27 (5.56)
SAFT, °C	64	73	72
PAFT, °C	45	50	56
Tensile Strength at 25°C, p.s.i. (kPa)	870.8 (6,000)	688.4 (4,747)	751.9 (5,184)
Strain at Break at 25°C (%)	650	800	650
Yield Stress at 0°C, p.s.i. (kPa)	1,622 (11,184)	1,227 (8,460)	1135 (7,826)
Yield Strain at 0°C (%)	50	60	60
Tensile Strength at 0°C, p.s.i. (kPa)	2,065 (14,328)	2,308 (15,914)	1,964.5 (13,545)
Strain at Break at 0°C (%)	400	500	400
T _{g1} , °C	-13	nd	-13
T ₁ ', °C	40	nd	38
Open time, s	28	nd	24
Set time, s	3.8	nd	2.8

pbw = parts by weight

nd = no data

PP = polypropylene

PE = polyethylene

5

10

Comparative Example 1 is an adhesive composition comprising only a solid resin as a tackifier. Examples 2 and 3 are each adhesives comprising, as a tackifier, a blend of a liquid resin and the solid resin of comparative Example 1. Examples 2 and 3 demonstrate the overall improvement in the balance of adhesive performance when a portion of the solid resin is replaced with a liquid resin in accordance with the invention.

In particular, the T-peel of Examples 2 and 3 are higher than that of comparative Example 1 for all polymeric substrates (PP, PE, and Mylar™). The minimum increase in T-peel is 7% as shown in Example 2 using a Mylar™ substrate while the maximum increase is 370% as shown in Example 3 using a PE substrate. Examples 2 and 3 demonstrate this increase in T-peel strength at room temperature and at 0°C. Examples 2 and 3 also show improved performance in strain at break and strain at break at low temperature and at room temperature. High temperature performance also improved as demonstrated by the PAFT and SAFT values of Examples 2 and 3 versus comparative Example 1. Tensile strength and yield stress were the only areas where performance was reduced. However, tensile strength and yield stress are essentially measures of cohesive strength, or the ability of a substance resist separation or plastic deformation when subjected to stress. T-peel is a measure of adhesive strength, or the ability of two substances to resist separation from each other when subjected to stress. The objective of a HMA is to hold two substrates together. Therefore, the HMA must have both adhesive strength to stay attached to each substrate and cohesive strength to resist separation of the HMA. The T-peel tests all resulted in adhesive failure. Therefore, the slight drop in tensile strength and yield stress are of no consequence since the HMA ultimately failed adhesively and not cohesively.

TABLE 2

Example	4	5	6	7
Comparative (C)/ Blend (B)	C	B	B	B
Escorene® 7750, pbw	45	45	45	45
Escorez® 6372, pbw	45	33.3	39.6	33
Escorez® 2520, pbw	-	11.7	5.4	-
ECR-327®, pbw	-	-	-	12
Aristowax® 165, pbw	10	10	10	10
Irganox® 1010, pbw	0.5	0.5	0.5	0.5
Composite Tackifier T _g , °C	50	30	40	30
T-peel to PP at 25°C, lb./in. (N/25mm)	0.74 (3.24)	5.20 (22.8)	3.72 (16.3)	3.07 (13.4)
T-peel to PP at 0°C, lb./in. (N/25mm)	0.23 (1.01)	0.19 (0.83)	0.07 (0.31)	0.22 (0.96)
T-peel to PE at 25°C, lb./in. (N/25mm)	0.34 (1.49)	7.20 (31.5)	1.06 (4.64)	1.76 (7.70)
T-peel to Mylar at 25°C, lb./in. (N/25mm)	1.26 (5.51)	1.91 (8.36)	7.54 (33.0)	6.96 (30.5)
T-peel to Aluminum at 25°C, lb./in. (N/25mm)	0.45 (1.97)	1.37 (5.99)	0.95 (4.16)	1.29 (5.64)
SAFT, °C	67	71	72	70
PAFT, °C	59	49	53	49
Tensile Strength at 25°C, p.s.i. (kPa)	1,055 (7,274)	624 (4,302)	730.9 (5,040)	604.8 (4,170)
Strain at Break at 25°C (%)	700	800	700	800
Yield Stress at 0°C, p.s.i. (kPa)	1,466 (10,108)	955.6 (6,589)	1083 (7,467)	1,230 (8,481)
Yield Strain at 0°C (%)	80	80	80	80
Tensile Strength at 0°C, p.s.i. (kPa)	2,011.5 (13,869)	2,022 (13,942)	1,769 (12,197)	2,356 (16,245)
Strain at Break at 0°C (%)	400	550	400	500
T _{g1} , °C	-15	nd	-13	nd
T ₁ ', °C	37	nd	33	nd
Open time, s	27	nd	33	nd
Set time, s	3.8	nd	4.4	nd

- Comparative Example 4 is an adhesive composition comprising only a solid resin as a tackifier. Examples 5-7 are each adhesives comprising, as a tackifier, a blend of a liquid resin and the solid resin of comparative Example 4. Examples 5-7 demonstrate the overall improvement in the balance of adhesive performance a portion of the solid resin is replaced with a liquid resin in accordance with the invention.

In particular, the T-peel of Examples 5-7 are higher than that of comparative Example 4 for all substrates (PP, PE, Mylar™, and aluminum) at 25° C. The minimum increase in T-peel is 111% as shown in Example 6 using an aluminum substrate while the maximum increase is over 2000% as shown in
5 Example 6 using a Mylar™ substrate. Examples 5-7 also show equal or improved performance in yield strain and strain at break at low temperature and at room temperature relative to comparative Example 4. SAFT improved for Examples 5-7 over that of comparative Example 4 while PAFT showed a slight drop.

10 Tensile strength and yield stress of Examples 5-7 were reduced relative to the comparative example. However, as in Examples 2 and 3, since the T-peel tests for Examples 5-7 all resulted in adhesive failure, the HMAs with blended tackifiers outperformed the comparative even though cohesive performance was reduced somewhat.

For comparative Examples 1 and 4 and Examples 3 and 6, T_{g1} is the glass
15 transition temperature of the phase of the HMA rich in the base polymer. T_1' is the glass transition temperature of the phase of the HMA rich in tackifier. T_1' is the temperature at which the maximum value of loss tangent occurs, and T_{g1} is the temperature at which the maximum value of tensile loss module occurs, both as determined by DMTA. T_1' of the HMA comprising the liquid/solid resin blend as a
20 tackifier will be reduced in the range of from 1°C to 20°C below that of an HMA comprising an equal portion of the same solid resin as a tackifier, more preferably in the range of from 5°C to 20°C, even more preferably in the range of from 10°C to 20°C.

Open and set times for comparative Examples 1 and 4 and Examples 3 and
25 6 are included to show that the open and set time performance of the novel HMA compositions is approximately that same as for that of the comparative example while the adhesive performance is greatly improved as discussed above.

TABLE 3

Example	8	9
Comparative (C)/ Blend (B)	C	B
Escorene® 7750, pbw	45	45
Escorez® 5380, pbw	-	38.7
Escorez® 5320, pbw	45	-
ECR-327®, pbw	-	6.3
Aristowax® 165, pbw	10	10
Irganox® 1010, pbw	0.5	0.5
Composite Tackifier T _g , °C	66	28
T-peel to PP at 25°C, lb./in. (N/25mm)	0.46 (2.01)	3.21 (14.0)
T-peel to PP at 0°C, lb./in. (N/25mm)	0.16 (0.70)	0.19 (0.83)
T-peel to PE at 25°C, lb./in. (N/25mm)	0.15 (0.66)	0.77 (3.37)
T-peel to Mylar at 25°C, lb./in. (N/25mm)	0.06 (0.26)	3.72 (16.3)
T-peel to Aluminum at 25°C, lb./in. (N/25mm)	0.42 (1.84)	0.69 (3.02)
SAFT, °C	69	70
PAFT, °C	60	45
Tensile Strength at 25°C, p.s.i. (kPa)	752.8 (5,191)	592.9 (4,088)
Strain at Break at 25°C (%)	400	650
Yield Stress at 0°C, p.s.i. (kPa)	1,787 (12,321)	1,041 (7,178)
Yield Strain at 0°C (%)	50	70
Tensile Strength at 0°C, p.s.i. (kPa)	1,969 (13,576)	1,800 (12,411)
Strain at Break at 0°C (%)	150	400

Comparative Example 8 is an adhesive composition comprising only a solid resin as a tackifier. Example 9 is an adhesive comprising, as a tackifier, a blend of a liquid resin and the solid resin of comparative Example 8. Example 9 demonstrates the overall improvement in the balance of adhesive performance when a portion of the solid resin is replaced with a liquid resin in accordance with the invention..

In particular, the T-peel values of Example 9 are higher than that of comparative Example 8 for all substrates (PP, PE, Mylar™, and aluminum) at 25°C and 0°C. The minimum increase in T-peel is 19% using a PP substrate at 0°C while the maximum increase is over 6000% using a Mylar™ substrate at 25°C. Example 9 also shows improved performance in yield strain and strain at break at low temperature and at room temperature relative to comparative Example 8.

SAFT improved for Example 9 over that of comparative Example 8 while PAFT showed a slight drop.

Tensile strength and yield stress of Example 9 was reduced relative to comparative Example 8. However, as in Examples 2 and 3, since the T-peel tests for Example 9 all resulted in adhesive failure, the HMAs with blended tackifiers outperformed the comparative even though cohesive performance was reduced somewhat.

TABLE 4

Example	10	11
Comparative (C)/ Blend (B)	C	B
Escorene® UL04533, pbw	45	45
Escorez® 6372, pbw	45	39.6
Escorez® 2520, pbw	-	5.4
Aristowax® 165, pbw	10	10
Irganox® 1010, pbw	0.5	0.5
Composite Tackifier T _g , °C	50	40
T-peel to PP at 25°C, lb./in. (N/25mm)	6.47 (28.3)	6.91 (30.2)
T-peel to PE at 25°C, lb./in. (N/25mm)	0.52 (2.28)	1.01 (4.42)
T-peel to Mylar at 25°C, lb./in. (N/25mm).	11.18 (48.9)	11.34 (49.6)
T-peel to Aluminum at 25°C, lb./in. (N/25mm).	2.49 (10.9)	3.63 (15.9)
SAFT, °C	62	66
PAFT, °C	54	52

10

Comparative Example 10 is an adhesive composition comprising only a solid resin as a tackifier. Example 11 is an adhesive comprising, as a tackifier, a blend of a liquid resin and the solid resin of comparative Example 10. Example 11 demonstrated the overall improvement in the balance of adhesive performance when a portion of the solid resin is replaced with a liquid resin in accordance with the invention..

15

In particular, the T-peel values of Example 11 are higher than that of comparative Example 10 for all substrates (PP, PE, Mylar™, and aluminum) at 25°C and 0°C. The minimum increase in T-peel is 1.4% using a Mylar™ substrate at 25°C while the maximum increase was 94% using a PE substrate at 25°C. SAFT improved for Example 11 over that of comparative Example 10 while PAFT showed a slight drop.

20

Examples 2, 3, 5-7, 9, and 11 with the liquid/solid resin blend as a tackifier outperformed there comparative counterparts, Examples 1, 4, 8, and 10, using only a solid resin as a tackifier.

- 5 While the present invention has been described and illustrated by reference to particular embodiments, it will be appreciated by those of ordinary skill in the art that the invention lends itself to variations not necessarily illustrated herein. For example, it is not beyond the scope of this invention to produce by direct polymerization resins equivalent to the resin blends discussed above. Additionally,
- 10 the use of headings and subheadings on paragraphs throughout this document are included as an aid to the reader and should not be construed to limit the scope of the invention in any way. For this reason, then, reference should be made solely to the appended claims for the purposes of determining the true scope of the present invention.

CLAIMS

What is claimed is:

- 5 1. A hot melt adhesive composition comprising:
 - (a) a base polymer; and
 - (b) a tackifier comprising at least one solid resin and at least one liquid resin, said tackifier having a glass transition temperature of from about 0°C to about 45°C.
- 10 2. The composition of claim 1 wherein the base polymer is a polyethylene homopolymer, a copolymer of ethylene and one or more comonomers, or a blends thereof.
- 15 3. The composition of claim 2 wherein the one or more comonomers are selected from the group consisting of vinyl acids, vinyl alcohols, vinyl esters, carbon monoxide, cyclic olefins, and higher alpha olefins.
- 20 4. The composition of claim 1 wherein the copolymer contains less than 38 weight percent of the one or more comonomers based on the weight of the copolymer and said comonomers are selected from the group consisting of vinyl acids, vinyl alcohols, vinyl esters, and carbon monoxide.
- 25 5. The composition of claim 1 wherein the copolymer contains the one or more comonomers in the amount of from 0.5 to 33 mole percent and said comonomers are selected from the group consisting of cyclic olefins and higher alpha olefins.
- 30 6. The composition of claim 1 wherein the base polymer is a polypropylene homopolymer, a copolymer of propylene and one or more comonomers, or mixtures thereof.
- 35 7. The composition of claim 6 wherein the one or more comonomers are selected from the group consisting of ethylene, cyclic olefins, and higher alpha olefins.

8. The composition of claim 1 wherein the total liquid resin content is in the range of from about 10 parts to about 100 parts by weight per 100 parts by weight of the total solid resin content.
- 5 9. The composition of claim 1 wherein at least one of the resins is substantially hydrogenated.
10. The composition of claim 1 wherein the liquid and solid resins are each selected from the group consisting of: C₅-C₉ aromatic modified aliphatic hydrocarbon resins; C₅-C₉ aromatic modified aliphatic hydrocarbon/terpene resins; and alicyclic diene monomer containing hydrocarbon resins;
- 10 11. The composition of claim 1 wherein the base polymer is present in the amount of from 10 weight percent to 90 weight percent, and the tackifier is present in the amount of from 10 weight percent to 90 weight percent.
- 15 12. The composition of claim 1 further comprising one or more additives selected from the group consisting of waxes, antioxidants, photostabilizers, ultraviolet stabilizers, fillers, plasticizers, lubricants, or coloring agents, said additive present in an amount less than or equal to about 35 weight percent based on the weight of the entire composition including the additive.
- 20 13. A hot melt adhesive composition comprising a mixture of:
- 25 (a) a copolymer of ethylene and one or more comonomers, said comonomer being present in the amount of from 10 to 38 weight percent based upon the weight of the copolymer and wherein the one or more comonomers are selected from the group consisting of: vinyl acetate, acrylic acid, methacrylic acid, methacrylate, ethylmethacrylate, methylmethacrylate, ethylacrylate, and methylacrylate; and
- 30 (b) a tackifier comprising at least one solid resin and at least one liquid resin, said liquid and solid resins each selected from the group consisting of: C₅-C₉ aromatic modified aliphatic hydrocarbon resins; C₅-C₉ aromatic modified aliphatic hydrocarbon/terpene resins; and alicyclic diene monomer containing hydrocarbon resins;
- 35

said tackifier having a glass transition temperature from about 0°C to about 45°C.

14. A method for preparing a hot melt adhesive composition comprising
5 blending said tackifier with a base polymer, wherein said tackifier is a blend of at least one liquid resin and at least one solid resin, such that the resulting tackifier has a T_g in the range of from about 0°C to about 45°C.
15. The method of claim 14 wherein each liquid and solid resin is selected from
10 the group consisting of: C₅-C₉ aromatic modified aliphatic hydrocarbon resins; C₅-C₉ aromatic modified aliphatic hydrocarbon/terpene resins; and alicyclic diene monomer containing hydrocarbon resins.
16. The method of claim 14 wherein the base polymer comprises ethylene and
15 one or more comonomers are selected from the group consisting of vinyl acids, vinyl alcohols, vinyl esters, carbon monoxide, and C₃ to C₂₀ alpha olefins.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 96/14407

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C09J123/02 //(C09J123/02,157:02,157:02)

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)

IPC 6 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 practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,4 358 557 (BOGGS BRENDA J) 9 November 1982	1-4,8-16
Y	see column 1, line 54 - column 2, line 47 ---	5-7
X	US,A,4 247 428 (KULKARNI MOHAN V) 27 January 1981 see example 1 ---	1-4,8-16
Y	US,A,3 577 372 (FLANAGAN THOMAS P ET AL) 4 May 1971 see column 2, line 25 - line 47 -----	5-7

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in 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 document 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
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Information on patent family members

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