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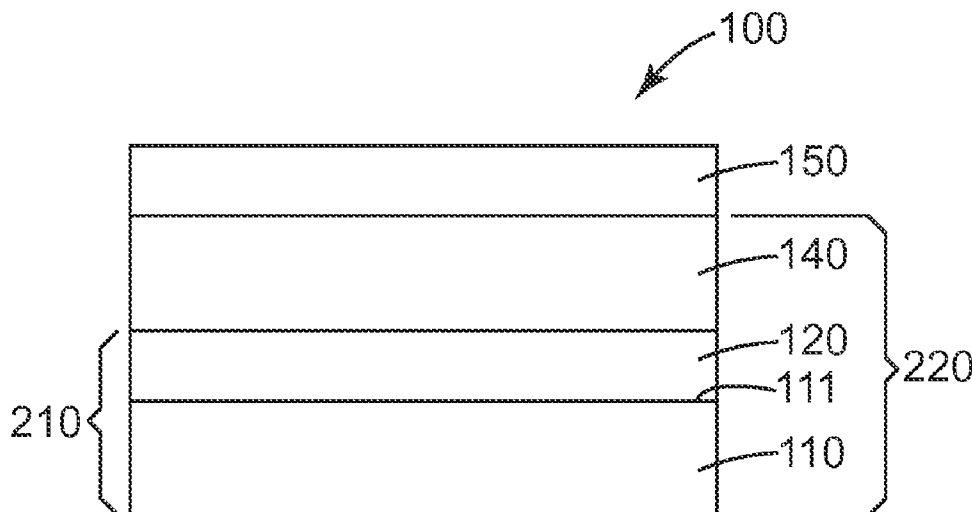
(19) **United States**(12) **Patent Application Publication****Seth et al.**(10) **Pub. No.: US 2015/0037526 A1**(43) **Pub. Date: Feb. 5, 2015**(54) **ADHESIVES COMPRISING CROSSLINKER WITH (METH)ACRYLATE GROUP AND OLEFIN GROUP AND METHODS**(71) Applicant: **3M INNOVATIVE PROPERTIES COMPANY**, St. Paul, MN (US)(72) Inventors: **Jayshree Seth**, Woodbury, MN (US);
Corinne E. Lipscomb, St. Paul, MN (US)(21) Appl. No.: **14/515,062**(22) Filed: **Oct. 15, 2014****Related U.S. Application Data**

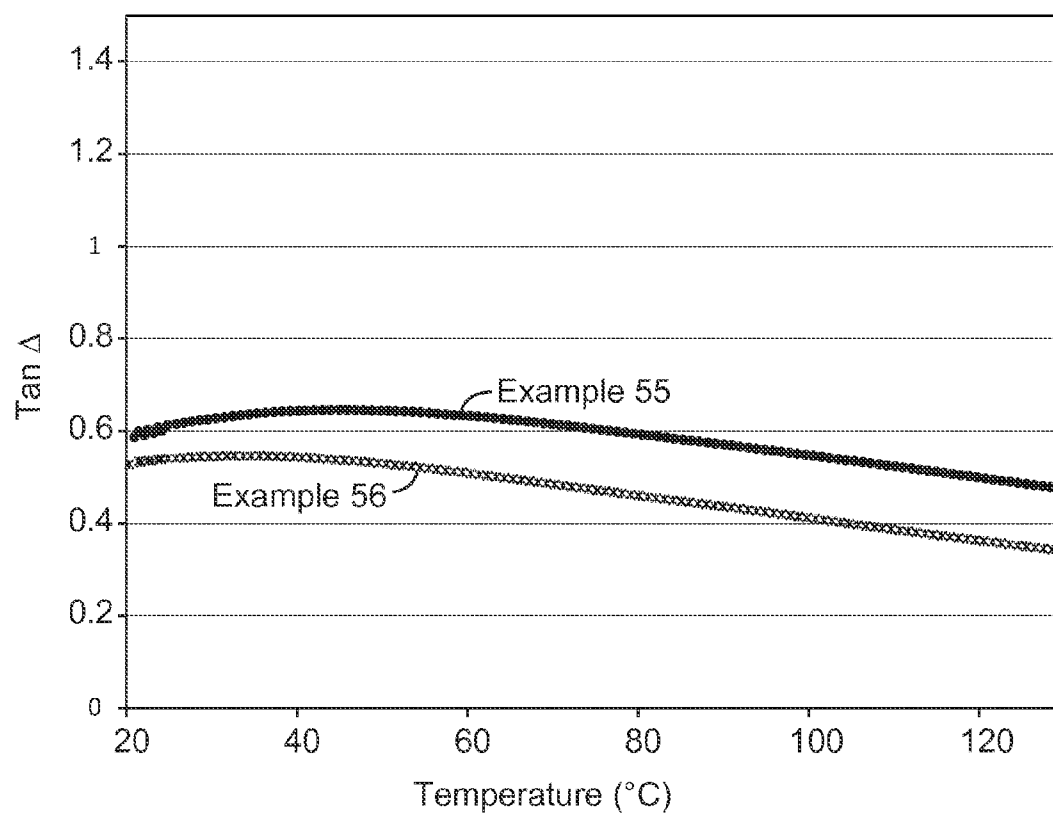
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CPC **C09J 7/0217** (2013.01); **C09J 2433/00** (2013.01)
USPC **428/41.3**(57) **ABSTRACT**

There is provided an article having a release liner and a pressure sensitive adhesive composition disposed along a major surface of the release liner, where the pressure sensitive adhesive composition has at least 50 wt-% of polymerized units derived from alkyl meth(acrylate) monomer(s); and 0.2 to 15 wt-% of at least one crosslinking monomers comprising a (meth)acrylate group and a C₆-C₂₀ olefin group, the olefin group being optionally substituted. In another embodiment, an adhesive composition is described comprising a syrup comprising i) a free-radically polymerizable solvent monomer; and ii) a solute (meth)acrylic polymer comprising polymerized units derived from one or more alkyl(meth)acrylate monomers; wherein the syrup comprises at least one crosslinking monomer or the (meth)acrylic solute polymer comprises polymerized units derived from at least one crosslinking monomer, the crosslinking monomer comprising a (meth)acrylate group and a C₆-C₂₀ olefin group, the olefin group being optionally substituted.



*FIG. 1*

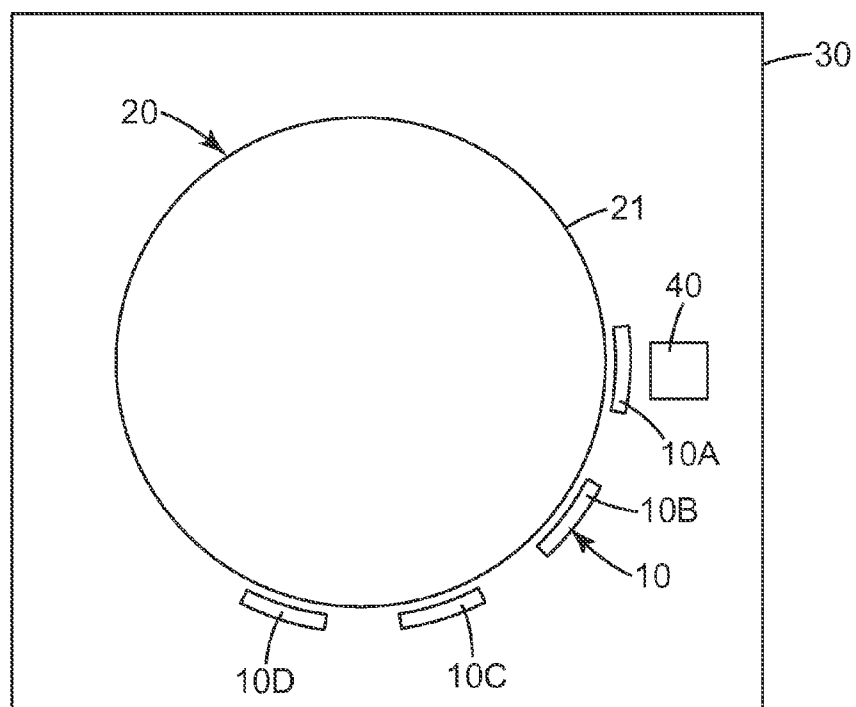


FIG. 2

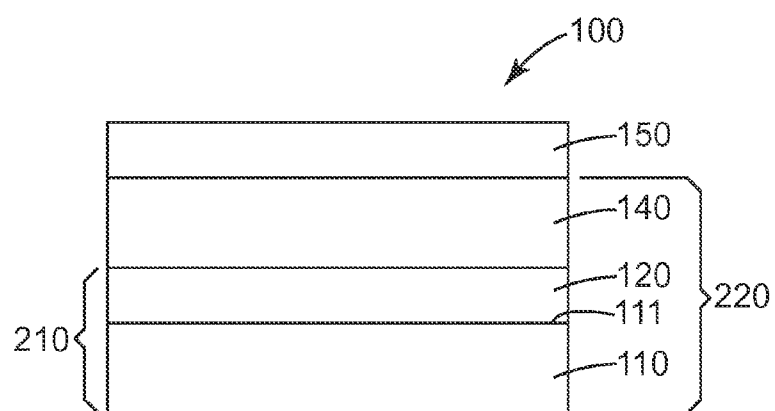


FIG. 3

ADHESIVES COMPRISING CROSSLINKER WITH (METH)ACRYLATE GROUP AND OLEFIN GROUP AND METHODS

BACKGROUND

[0001] As described in WO 2012/177337, there are two major crosslinking mechanisms for acrylic adhesives: free-radical copolymerization of multifunctional ethylenically unsaturated groups with the other monomers, and covalent or ionic crosslinking through the functional monomers, such as acrylic acid. Another method is the use of UV crosslinkers, such as copolymerizable benzophenones or post-added photocrosslinkers, such as multifunctional benzophenones and triazines. In the past, a variety of different materials have been used as crosslinking agents, e.g., polyfunctional acrylates, acetophenones, benzophenones, and triazines. The foregoing crosslinking agents, however, possess certain drawbacks which include one or more of the following: high volatility; incompatibility with certain polymer systems; generation of undesirable color; requirement of a separate photoactive compound to initiate the crosslinking reaction; and high sensitivity to oxygen. A particular issue for the electronics industry and other applications in which PSAs contact a metal surface is the generation of corrosive by-products and the generation of undesirable color.

BRIEF DESCRIPTION OF THE DRAWINGS

[0002] The disclosure may be more completely understood in consideration of the following detailed description of various embodiments of the disclosure in connection with the accompanying figures, in which:

[0003] FIG. 1 depicts the tan delta, the ratio of the shear loss modulus (G'') to the shear storage modulus (G'), as determined by dynamic mechanical analysis.

[0004] FIG. 2 illustrates an exemplary ultraviolet radiation curing chamber useful in some exemplary embodiments of the present disclosure.

[0005] FIG. 3 illustrates an exemplary article including an ultraviolet radiation cured coating according to some exemplary embodiments of the present disclosure.

[0006] While the above-identified drawings, which may not be drawn to scale, set forth various embodiments of the present disclosure, other embodiments are also contemplated, as noted in the Detailed Description. In all cases, this disclosure describes the presently disclosed invention by way of representation of exemplary embodiments and not by express limitations. It should be understood that numerous other modifications and embodiments can be devised by those skilled in the art, which fall within the scope and spirit of this invention.

SUMMARY

[0007] Thus, industry would find advantage in alternative crosslinkers that are substantially free of halogens for use in pressure sensitive adhesives. There is also a need for articles having these adhesives disposed on a major surface of a release liner that is substantially free of metal catalyst.

[0008] In one aspect, the present disclosure provides an article comprising a release liner and a pressure sensitive adhesive composition disposed on a major surface of the release liner, wherein the pressure sensitive adhesive comprises at least 50 wt-% of polymerized units derived from alkyl(meth)acrylate monomer(s); and 0.2 to 15 wt-% of at

least one crosslinking monomer comprising a (meth)acrylate group and a C_6 - C_{20} olefin group, the olefin group being straight-chained or branched and optionally substituted.

[0009] In some embodiments, the present disclosure provides articles such as those according to the previously mentioned aspect in which the release liner is created by applying a layer comprising a (meth)acrylate-functional siloxane to a major surface of a substrate; and irradiating said layer, in a substantially inert atmosphere comprising no greater than 500 ppm oxygen, with a short wavelength polychromatic ultraviolet light source having at least one peak intensity at a wavelength of from about 160 nanometers to about 240 nanometers to at least partially cure the layer, optionally wherein the layer is at a curing temperature greater than 25° C.

[0010] In another aspect, the present disclosure provides an article comprising a release liner and a pressure sensitive adhesive composition disposed on a major surface of the release liner, wherein the pressure sensitive adhesive is a UV curable (meth)acrylic pressure sensitive adhesive that is substantially free of halogens, and further wherein the release liner comprises a UV curable release layer on a major surface of a substrate.

[0011] In yet another aspect, the present disclosure provides an article comprising a release liner and a pressure sensitive adhesive composition disposed on a major surface of the release liner, wherein the pressure sensitive adhesive comprises at least 50 wt-% of polymerized units derived from alkyl(meth)acrylate monomer(s); and 0.2 to 15 wt-% of at least one crosslinking monomer comprising a (meth)acrylate group and a C_6 - C_{20} olefin group, the olefin group being straight-chained or branched and optionally substituted, and further wherein the release liner is derived by applying a layer comprising a (meth)acrylate-functional siloxane to a major surface of a substrate; and irradiating said layer, in a substantially inert atmosphere comprising no greater than 500 ppm oxygen, with a short wavelength polychromatic ultraviolet light source having at least one peak intensity at a wavelength of from about 160 nanometers to about 240 nanometers to at least partially cure the layer, optionally wherein the layer is at a curing temperature greater than 25° C.

DETAILED DESCRIPTION

[0012] The present disclosure describes pressure sensitive adhesives (PSAs) prepared from crosslinkable (e.g. syrup) compositions, as well as articles. The crosslinked pressure-sensitive adhesives provide a suitable balance of tack, peel adhesion, and shear holding power. Further, the storage modulus of the pressure sensitive adhesive at the application temperature, typically room temperature (25° C.), is less than 3×10^5 dynes/cm at a frequency of 1 Hz. In some embodiments, the adhesive is a pressure sensitive adhesive at an application temperature that is greater than room temperature. For example, the application temperature may be 30, 35, 40, 45, 50, 55, or 65° C. In this embodiment, the storage modulus of the pressure sensitive adhesive at room temperature (25° C.) is typically less than 3×10^6 dynes/cm at a frequency of 1 Hz. In some embodiments, the storage modulus of the pressure sensitive adhesive at room temperature (25° C.) is less than 2×10^6 dynes/cm or 1×10^6 dynes/cm at a frequency of 1 Hz.

[0013] Words of orientation such as "atop," "on," "covering," "uppermost," "overlying," "underlying" and the like for describing the location of various layers, refer to the

relative position of a layer with respect to a horizontally-disposed, upwardly-facing substrate. It is not intended that the substrate, layers or articles encompassing the substrate and layers, should have any particular orientation in space during or after manufacture.

[0014] “Layer” refers to any material or combination of materials on or overlaying a substrate.

[0015] “Overcoat” or “overcoated” describes the position of a layer with respect to a substrate or another layer of a multi-layer construction, means that the described layer is atop or overlaying the substrate or another layer, but not necessarily adjacent to or contiguous with either the substrate or the other layer.

[0016] The term “separated by” to describe the position of a layer with respect to another layer and the substrate, or two other layers, means that the described layer is between, but not necessarily contiguous with, the other layer(s) and/or substrate.

[0017] “Syrup composition” refers to a solution of a solute polymer in one or more solvent monomers, the composition having a viscosity from 100 to 8,000 cPs at 25° C. The viscosity of the syrup is greater than the viscosity of the solvent monomer(s).

[0018] “alkyl” refers to straight-chained, branched, and cyclic alkyl groups and includes both unsubstituted and substituted alkyl groups. Unless otherwise indicated, the alkyl groups typically contain from 1 to 20 carbon atoms. Examples of “alkyl” as used herein include, but are not limited to, methyl, ethyl, n-propyl, n-butyl, n-pentyl, isobutyl, t-butyl, isopropyl, n-octyl, 2-octyl, n-heptyl, ethylhexyl, cyclopentyl, cyclohexyl, cycloheptyl, adamantyl, and norbornyl, and the like. Unless otherwise noted, alkyl groups may be mono- or polyvalent.

[0019] The term heteroalkyl refers to an alkyl group, as just defined, having at least one catenary carbon atom (i.e. in-chain) replaced by a catenary heteroatom such as O, S, or N.

[0020] The term olefin group refers to an unsaturated aliphatic straight-chained, branched, or cyclic (i.e. unsubstituted) hydrocarbon group having one or more double bonds. Those containing one double bond are commonly called alkenyl groups. In some embodiments, the cyclic olefin group comprises less than 10 or 8 carbon atoms, such as in the case of cyclohexenyl. In some embodiments, the olefin group may further comprise substituents as will subsequently be described. The olefin group is typically monovalent.

[0021] “Renewable resource” refers to a natural resource that can be replenished within a 100 year time frame. The resource may be replenished naturally or via agricultural techniques. The renewable resource is typically a plant (i.e. any of various photosynthetic organisms that includes all land plants, inclusive of trees), organisms of Protista such as seaweed and algae, animals, and fish. They may be naturally occurring, hybrids, or genetically engineered organisms. Natural resources such as crude oil, coal, and peat which take longer than 100 years to form are not considered to be renewable resources.

[0022] “Catenated heteroatom” means an atom other than carbon (for example, oxygen, nitrogen, or sulfur) that replaces one or more carbon atoms in a carbon chain (for example, so as to form a carbon-heteroatom-carbon chain or a carbon-heteroatom-heteroatom-carbon chain);

[0023] “Cure” means conversion to a crosslinked polymer network (for example, through catalysis);

[0024] “Fluoro-” (for example, in reference to a group or moiety, such as in the case of “fluoroalkylene” or “fluoroalkyl” or “fluorocarbon”) or “fluorinated” means only partially fluorinated such that there is at least one carbon-bonded hydrogen atom;

[0025] “Fluorochemical” means fluorinated or perfluorinated;

[0026] “Heteroorganic” means an organic group or moiety (for example, an alkyl or alkylene group) containing at least one heteroatom (preferably, at least one catenated heteroatom);

[0027] “Hydrosilyl” refers to a monovalent moiety or group comprising a silicon atom directly bonded to a hydrogen atom (for example, the hydrosilyl moiety can be of formula $\text{—Si(R)}_{3-p}\text{(H)}_p$, where p is an integer of 1, 2, or 3 and R is a hydrolyzable or non-hydrolyzable group (preferably, non-hydrolyzable) such as alkyl or aryl);

[0028] “Hydroxysilyl” refers to a monovalent moiety or group comprising a silicon atom directly bonded to a hydroxyl group (for example, the hydroxysilyl moiety can be of formula $\text{—Si(R)}_{3-p}\text{(OH)}_p$, where p is an integer of 1, 2, or 3 and R is a hydrolyzable or non-hydrolyzable group (preferably, non-hydrolyzable) such as alkyl or aryl);

[0029] “Isocyanato” means a monovalent group or moiety of formula —NCO ;

[0030] “Mercapto” means a monovalent group or moiety of formula —SH ;

[0031] “Oligomer” means a molecule that comprises at least two repeat units and that has a molecular weight less than its entanglement molecular weight; such a molecule, unlike a polymer, exhibits a significant change in properties upon the removal or addition of a single repeat unit;

[0032] “Oxy” means a divalent group or moiety of formula —O— ; and

[0033] “Perfluoro-” (for example, in reference to a group or moiety, such as in the case of “perfluoroalkylene” or “perfluoroalkyl” or “perfluorocarbon”) or “perfluorinated” means completely fluorinated such that, except as may be otherwise indicated, there are no carbon-bonded hydrogen atoms replaceable with fluorine.

[0034] “Intensity peak” refers to a local maximum in an emission spectrum for a UV radiation source when plotted as emission intensity as a function of emission wavelength. The emission spectrum may have one or more intensity peaks over the wavelength range covered by the emission spectrum. Thus, an intensity peak need not correspond to the maximum emission intensity peak over the entire wavelength range covered by the emission spectrum.

[0035] “Polychromatic UV radiation,” “polychromatic UV light,” “short wavelength polychromatic UV radiation,” and “short wavelength polychromatic UV light” all refer to ultraviolet radiation or light having an emission wavelength of 400 nm or less wherein the emission spectrum includes at least two intensity peaks, with at least one intensity peak occurring at no greater than 240 nanometers (nm).

[0036] “Substantially inert atmosphere” refers to an atmosphere having an oxygen content of no greater than 500 ppm.

[0037] “Substantially free of halogens” refers to a pressure sensitive adhesive in composition which a substance containing a halogen atom is not used intentionally as a main component.

[0038] “Substantially free of metal catalyst” refers to a release composition in which a substance containing a metal catalyst is not used intentionally as a main component.

[0039] “(Meth)acrylic” or “(meth)acrylic-functional” includes materials that include one or more ethylenically unsaturated acrylic- and/or methacrylic-functional groups, e.g. $-AC(O)C(R)=CH_2$, preferably wherein A is O, S or NR', wherein R' is a hydrogen atom or a hydrocarbon group; and R is a 1-4 carbon lower alkyl group, H or F. Herein, “(meth)acryloyl” is inclusive of (meth)acrylate and (meth)acrylamide. Herein, “(meth)acrylic” includes both methacrylic and acrylic.

Herein, “(meth)acrylate” includes both methacrylate and acrylate.

[0040] “Siloxane” includes any chemical compound composed of units of $-O-Si-O-$ and having the generalized formula R'_2SiO , wherein R' is a hydrogen atom or a hydrocarbon group.

[0041] “(Co)polymer” or “(co)polymeric” includes homopolymers and copolymers, as well as homopolymers or copolymers that may be formed in a miscible blend, e.g., by coextrusion or by reaction, including, e.g., transesterification. The term “copolymer” includes random, block, graft, and star copolymers.

[0042] “Cure” or “curable” refers to a process that causes a chemical change, e.g., a reaction to solidify a layer or increase its viscosity.

[0043] “Cured (co)polymer layer” or “cured (co)polymer” includes both cross-linked and uncross-linked (co)polymers.

[0044] “Cross-linked” (co)polymer refers to a (co)polymer whose (co)polymer chains are joined together by covalent chemical bonds, usually via cross-linking molecules or groups, to form a network (co)polymer. A cross-linked (co)polymer is generally characterized by insolubility, but may be swellable in the presence of an appropriate solvent.

[0045] “Unaged peel adhesion” refers to peel adhesion measured according to the release test described herein on a release surface maintained at a temperature of no more than 25° C. at no more than 75% relative humidity for no more than 24 hours before the measurement. Preferably, the unaged peel adhesion is measured on a release surface within one hour of preparation of the release surface.

[0046] “Aged peel adhesion” refers to peel adhesion measured according to the release test described herein on a release surface aged for at least seven days at 90° C. and 90% relative humidity.

[0047] When a group is present more than once in a formula described herein, each group is “independently” selected unless specified otherwise.

[0048] The adhesive comprises a (meth)acrylic polymer prepared from one or more monomers common to acrylic adhesives, such as a (meth)acrylic ester monomers (also referred to as (meth)acrylate acid ester monomers and alkyl (meth)acrylate monomers) optionally in combination with one or more other monomers such as acid-functional ethylenically unsaturated monomers, non-acid-functional polar monomers, and vinyl monomers.

[0049] The (meth)acrylic polymer comprises one or more (meth)acrylate ester monomers derived from a (e.g. non-tertiary) alcohol containing from 1 to 14 carbon atoms and preferably an average of from 4 to 12 carbon atoms.

[0050] Examples of monomers include the esters of either acrylic acid or methacrylic acid with non-tertiary alcohols such as ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 3-methyl-1-butanol, 1-hexanol, 2-hexanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, 2-ethyl-1-butanol, 3,5,5-

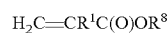
trimethyl-1-hexanol, 3-heptanol, 1-octanol, 2-octanol, isooctylalcohol, 2-ethyl-1-hexanol, 1-decanol, 2-propylheptanol, 1-dodecanol, 1-tridecanol, 1-tetradecanol, and the like. In some embodiments, a preferred (meth)acrylate ester monomer is the ester of (meth)acrylic acid with isooctyl alcohol.

[0051] In some favored embodiments, the monomer is the ester of (meth)acrylic acid with an alcohol derived from a renewable source. A suitable technique for determining whether a material is derived from a renewable resource is through ^{14}C analysis according to ASTM D6866-10, as described in US2012/0288692. The application of ASTM D6866-10 to derive a “bio-based content” is built on the same concepts as radiocarbon dating, but without use of the age equations. The analysis is performed by deriving a ratio of the amount of organic radiocarbon (^{14}C) in an unknown sample to that of a modern reference standard. The ratio is reported as a percentage with the units “pMC” (percent modern carbon).

[0052] One suitable monomer derived from a renewable source is 2-octyl(meth)acrylate, as can be prepared by conventional techniques from 2-octanol and (meth)acryloyl derivatives such as esters, acids and acyl halides. The 2-octanol may be prepared by treatment of ricinoleic acid, derived from castor oil, (or ester or acyl halide thereof) with sodium hydroxide, followed by distillation from the co-product sebacic acid. Other (meth)acrylate ester monomers that can be renewable are those derived from ethanol and 2-methyl butanol. In some embodiments, the (e.g. pressure sensitive) adhesive composition (e.g. (meth)acrylic polymer and/or free-radically polymerizable solvent monomer) comprises a bio-based content of at least 25, 30, 35, 40, 45, or 50 wt-% using ASTM D6866-10, method B. In other embodiments, the (e.g. pressure sensitive) adhesive composition comprises a bio-based content of at least 55, 60, 65, 70, 75, or 80 wt-%. In yet other embodiments, the (e.g. pressure sensitive) adhesive composition comprises a bio-based content of at least 85, 90, 95, 96, 97, 99 or 99 wt-%.

[0053] The (e.g. pressure sensitive) adhesive (e.g. (meth)acrylic polymer and/or solvent monomer) comprises one or more low T_g (meth)acrylate monomers, having a T_g no greater than 10° C. when reacted to form a homopolymer. In some embodiments, the low T_g monomers have a T_g no greater than 0° C., no greater than -5° C., or no greater than -10° C. when reacted to form a homopolymer. The T_g of these homopolymers is often greater than or equal to -80° C., greater than or equal to -70° C., greater than or equal to -60° C., or greater than or equal to -50° C. The T_g of these homopolymers can be, for example, in the range of -80° C. to 20° C., -70° C. to 10° C., -60° C. to 0° C., or -60° C. to -10° C.

[0054] The low T_g monomer may have the formula



wherein R¹ is H or methyl and R⁸ is an alkyl with 1 to 22 carbons or a heteroalkyl with 2 to 20 carbons and 1 to 6 heteroatoms selected from oxygen or sulfur. The alkyl or heteroalkyl group can be linear, branched, cyclic, or a combination thereof.

[0055] Exemplary low T_g monomers include for example ethyl acrylate, n-propyl acrylate, n-butyl acrylate, isobutyl acrylate, t-butyl acrylate, n-pentyl acrylate, isoamyl acrylate, n-hexyl acrylate, 2-methylbutyl acrylate, 2-ethylhexyl acrylate, 4-methyl-2-pentyl acrylate, n-octyl acrylate, 2-octyl acrylate, isooctyl acrylate, isononyl acrylate, decyl acrylate,

isodecyl acrylate, lauryl acrylate, isotridecyl acrylate, octadecyl acrylate, and dodecyl acrylate.

[0056] Low T_g heteroalkyl acrylate monomers include, but are not limited to, 2-methoxyethyl acrylate and 2-ethoxyethyl acrylate.

[0057] In some embodiments, the (e.g. pressure sensitive) adhesive (e.g. (meth)acrylic polymer and/or free radically polymerizable solvent monomer) comprises low T_g monomer(s) having an alkyl group with 6 to 20 carbon atoms. In some embodiments, the low T_g monomer has an alkyl group with 7 or 8 carbon atoms. Exemplary monomers include, but are not limited to, 2-ethylhexyl methacrylate, isooctyl methacrylate, n-octyl methacrylate, 2-octyl methacrylate, isodecyl methacrylate, and lauryl methacrylate. Likewise, some heteroalkyl methacrylates such as 2-ethoxy ethyl methacrylate can also be used.

[0058] In some embodiments, the (e.g. pressure sensitive) adhesive (e.g. (meth)acrylic polymer and/or solvent monomer) comprises a high T_g monomer, having a T_g greater than 10° C. and typically of at least 15° C., 20° C. or 25° C., and preferably at least 50° C. Suitable high T_g monomers include, for example, t-butyl acrylate, methyl methacrylate, ethyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, s-butyl methacrylate, t-butyl methacrylate, stearyl methacrylate, phenyl methacrylate, cyclohexyl methacrylate, isobornyl acrylate, isobornyl methacrylate, norbornyl(meth)acrylate, benzyl methacrylate, 3,3,5-trimethylcyclohexyl acrylate, cyclohexyl acrylate, N-octyl acrylamide, and propyl methacrylate or combinations.

[0059] In some embodiments, the (meth)acrylic polymer is a homopolymer. In other embodiments, the (meth)acrylic polymer is a copolymer. Unless specified otherwise, the term polymer refers to both a homopolymer and copolymer.

[0060] The T_g of the copolymer may be estimated by use of the Fox equation, based on the T_gs of the constituent monomers and the weight percent thereof.

[0061] The alkyl(meth)acrylate monomers are typically present in the (meth)acrylic polymer in an amount of at least 85, 86, 87, 88, 89, or 90 up to 95, 96, 97, 98, or 99 parts by weight, based on 100 parts by weight of the total monomer or polymerized units. When high T_g monomers are included in a pressure sensitive adhesive, the adhesive may include at least 5, 10, 15, 20, to 30 parts by weight of such high T_g monomer(s). When the (e.g. pressure sensitive) adhesive composition is free of unpolymerized components, such as tackifier, silica, and glass bubbles, the parts by weight of the total monomer or polymerized units is approximately the same as the wt-% present in the total adhesive composition. However, when the (e.g. pressure sensitive) adhesive composition comprises such unpolymerized components, the (e.g. pressure sensitive) adhesive composition can comprises substantially less alkyl (meth)acrylate monomer(s) and crosslinking monomer. The (e.g. pressure sensitive) adhesive composition comprises at least 50 wt-% of polymerized units derived from alkyl(meth)acrylate monomers. In some embodiments, the pressure sensitive adhesive composition comprises at least 50, 55, 60, 65, 70, 75, 80, 85, or 90 parts by weight, based on 100 parts by weight of the total monomer (or wt-% of the total adhesive composition) of one or more low T_g monomers. For embodied methods wherein the adhesive is not a pressure sensitive adhesive, the adhesive may comprise 50, 55, 60, 65, 70, 75, 80, 85, or 90 parts by weight, based on 100 parts by weight of the total monomer (or wt-% of the total adhesive composition) of one or more high T_g monomers. The (meth)acrylic

polymer may optionally comprise an acid functional monomer (a subset of high T_g monomers), where the acid functional group may be an acid per se, such as a carboxylic acid, or a portion may be salt thereof, such as an alkali metal carboxylate. Useful acid functional monomers include, but are not limited to, those selected from ethylenically unsaturated carboxylic acids, ethylenically unsaturated sulfonic acids, ethylenically unsaturated phosphonic acids, and mixtures thereof. Examples of such compounds include those selected from acrylic acid, methacrylic acid, itaconic acid, fumaric acid, crotonic acid, citraconic acid, maleic acid, oleic acid, β-carboxyethyl(meth)acrylate, 2-sulfoethyl methacrylate, styrene sulfonic acid, 2-acrylamido-2-methylpropane-sulfonic acid, vinylphosphonic acid, and mixtures thereof.

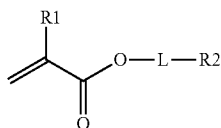
[0062] Due to their availability, acid functional monomers are generally selected from ethylenically unsaturated carboxylic acids, i.e. (meth)acrylic acids. When even stronger acids are desired, acidic monomers include the ethylenically unsaturated sulfonic acids and ethylenically unsaturated phosphonic acids. In some embodiments, the acid functional monomer is generally used in amounts of 0.5 to 15 parts by weight, preferably 0.5 to 10 parts by weight, based on 100 parts by weight total monomer or polymerized units. In some embodiments, the (meth)acrylic polymer and/or PSA comprises less than 1.0, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, 0.1 or 0 wt-% of polymerized units derived from acid-functional monomers such as acrylic acid.

[0063] The (meth)acrylic copolymer may optionally comprise other monomers such as a non-acid-functional polar monomer. Representative examples of suitable polar monomers include but are not limited to 2-hydroxyethyl(meth)acrylate; N-vinylpyrrolidone; N-vinylcaprolactam; acrylamide; mono- or di-N-alkyl substituted acrylamide; t-butyl acrylamide; dimethylaminoethyl acrylamide; N-octyl acrylamide; poly(alkoxyalkyl)(meth)acrylates including 2-(2-ethoxyethoxy)ethyl(meth)acrylate, 2-ethoxyethyl(meth)acrylate, 2-methoxyethoxyethyl(meth)acrylate, 2-methoxyethyl methacrylate, polyethylene glycol mono(meth)acrylates; alkyl vinyl ethers, including vinyl methyl ether; and mixtures thereof. Preferred polar monomers include those selected from the group consisting of 2-hydroxyethyl(meth)acrylate and N-vinylpyrrolidone. The non-acid-functional polar monomer may be present in amounts of 0 to 10 or 20 parts by weight, or 0.5 to 5 parts by weight, based on 100 parts by weight total monomer. In some embodiments, the (meth)acrylic polymer and/or PSA comprises less than 1.0, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, 0.1 or 0 wt-% of polymerized units derived from non-acid polar monomers.

[0064] When used, vinyl monomers useful in the (meth)acrylate polymer include vinyl esters (e.g., vinyl acetate and vinyl propionate), styrene, substituted styrene (e.g., α-methyl styrene), vinyl halide, and mixtures thereof. As used herein vinyl monomers are exclusive of acid functional monomers, acrylate ester monomers and polar monomers. Such vinyl monomers are generally used at 0 to 5 parts by weight, preferably 1 to 5 parts by weight, based on 100 parts by weight total monomer or polymerized units. In some embodiments, the (meth)acrylic polymer and/or PSA comprises less than 1.0, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, 0.1 or 0 wt-% of polymerized units derived from vinyl monomers.

[0065] In some embodiments, the polymer contains no allyl ether, vinyl ether or vinyl ester monomer units.

[0066] The adhesive further comprises a crosslinking monomer comprising a (meth)acrylate group and a C₆-C₂₀ olefin group. The olefin group comprises at least one hydrocarbon unsaturation. In some embodiments, the olefin group comprises substituents. The crosslinking monomer may have the formula



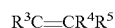
R1 is H or CH₃,

[0067] L is an optional linking group; and

R2 is a C₆-C₂₀ olefin group, the olefin group being optionally substituted.

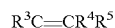
[0068] For embodiments wherein the crosslinking monomer comprises a (e.g. divalent) linking group, the linking group (i.e. L) typically has a molecular weight no greater than 1000 g/mole and in some embodiments no greater than 500 g/mole, 400 g/mole, 300 g/mole, 200 g/mole, 100 g/mole, or 50 g/mole.

[0069] In some embodiments, the crosslinking monomer comprises a (meth)acrylate group and an optionally substituted C₆-C₂₀ olefin group comprising a terminal hydrocarbon unsaturation. In this embodiment the hydrocarbon unsaturation has the formula:



wherein R⁴ and R⁵ are H and R³ is H or (e.g. C₁-C₄) alkyl. Undecenyl(meth)acrylate includes such terminal unsaturation.

[0070] In other embodiments, the crosslinking monomer comprises a (meth)acrylate group and an optionally substituted C₆-C₂₀ olefin group comprising at least one hydrocarbon unsaturation in the backbone of the optionally substituted C₆-C₂₀ olefin group. In this embodiment, the hydrocarbon unsaturation has the formula:



[0071] wherein R⁴ and R⁵ are independently alkyl and R³ is H or (e.g. C₁-C₄) alkyl. In some embodiments, R⁴ and R⁵ are each methyl. In this embodiment, R⁴ or R⁵ is the terminal alkyl group of the C₆-C₂₀ olefin group. Citronellyl(meth)acrylate, geraniol(meth)acrylate and farnesol(meth)acrylate include a hydrocarbon unsaturation of this type.

[0072] In some embodiments, the crosslinking monomer comprises a (meth)acrylate group and an optionally substituted C₆-C₂₀ olefin group comprising two or more hydrocarbon unsaturations in the backbone. Some illustrative crosslinking monomers include for example geraniol(meth)acrylate (e.g. 3,7-dimethylocta-2,6-dienyl]prop-2-enoate) and farnesol(meth)acrylate (e.g. 3,7,11-trimethyldodeca-2,6,10-trienyl]prop-2-enoate).

[0073] In yet another embodiment of a hydrocarbon unsaturation in the backbone of the optionally substituted C₆-C₂₀ olefin group, R³ and R⁴ are independently H or (e.g. C₁-C₄) alkyl and R⁵ is a terminal alkyl group having up to 18 carbon atoms. Oleyl(meth)acrylate includes a hydrocarbon unsaturation of this type.

[0074] In typical embodiments, the substituted C₆-C₂₀ olefin group does not comprise a carbonyl group. Thus, the (meth)acrylate group is the only group of the crosslinking monomer that comprises a carbonyl group. Thus, the crosslinking monomer is free of other groups that comprise a carbonyl such as an aldehyde, ketone, carboxylic acid, ester, amide, enone, acryl halide, acid anhydride, and imide. Hence, the crosslinking monomer comprises or consists of two types of polymerizable functional groups, i.e. a single (meth)acrylate group and one or more hydrocarbon unsaturations.

[0075] The optionally substituted C₆-C₂₀ olefin group may be a straight-chain, branched, or cyclic. Further, the hydrocarbon unsaturation may be at any position.

[0076] When the crosslinking monomer comprises a single hydrocarbon unsaturation, the unsubstituted C₆-C₂₀ olefin group may be characterized as an alkenyl group. In some embodiments, the alkenyl group has a straight chain. In some embodiments, the alkenyl group has branched chain, commonly comprising pendent methyl groups bonded to a straight chain.

[0077] Some illustrative crosslinking monomers comprising an alkenyl group include citronellyl(meth)acrylate, 3-cyclohexene methyl(meth)acrylate, undecenyl(meth)acrylate, and oleyl acrylate. Other C₆-C₂₀ alkenyl groups include 1-hexenyl, 2-hexenyl, 3-hexenyl, 4-hexenyl, 5-hexenyl, 1-methyl-1-pentenyl, 2-methyl-1-pentenyl, 3-methyl-1-pentenyl, 4-methyl-1-pentenyl, 1-methyl-2-pentenyl, 2-methyl-2-pentenyl, 3-methyl-2-pentenyl, 4-methyl-2-pentenyl, 1-methyl-3-pentenyl, 2-methyl-3-pentenyl, 3-methyl-3-pentenyl, 4-methyl-3-pentenyl, 1-methyl-4-pentenyl, 2-methyl-4-pentenyl, 3-methyl-4-pentenyl, 4-methyl-4-pentenyl; 1,1-dimethyl-2-butenyl; 1,1-dimethyl-3-butenyl; 1,2-dimethyl-1-butenyl; 1,2-dimethyl-2-butenyl; 1,2-dimethyl-3-butenyl; 1,3-dimethyl-1-butenyl; 1,3-dimethyl-2-butenyl; 1,3-dimethyl-3-butenyl; 2,2-dimethyl-3-butenyl; 2,3-dimethyl-1-butenyl; 2,3-dimethyl-2-butenyl; 2,3-dimethyl-3-butenyl; 3,3-dimethyl-1-butenyl; 3,3-dimethyl-2-butenyl; 1,1,2-trimethyl-2-propenyl; and also the isomers of heptenyl, octenyl, and nonenyl.

[0078] Cyclic alkenyl groups included cyclohexenyl as well as dicyclopentenyl.

[0079] Provided that the C₆-C₂₀ olefin group comprises at least one hydrocarbon unsaturation, the C₆-C₂₀ olefin group may optionally comprise substituents. The substituents are chosen such that the crosslinking monomer comprises at least one hydrocarbon unsaturation available for crosslinking, as evident by a measurable and preferably substantial increase in shear values.

[0080] In some embodiments, the C₆-C₂₀ olefin group comprises pendent substituents. For example, when the C₆-C₂₀ olefin group comprises two or more hydrocarbon unsaturations, one or more of the additional hydrocarbon unsaturations can be reacted to append pendent substituents onto the C₆-C₂₀ olefin group backbone.

[0081] In other embodiments, the C₆-C₂₀ olefin group can comprise substituents such as a heteroatom (e.g. oxygen) or a (e.g. divalent) linking group (i.e. "L") between the (meth)acrylate group and C₆-C₂₀ olefin group. For example, the starting alcohol can be chain extended before reacting on the (meth)acrylate group. In some embodiments, the starting alcohol is chain extended with one or more alkylene oxide groups, such as ethylene oxide, propylene oxide, and combinations thereof. One illustrative crosslinking monomer of this type is the ester of (meth)acrylic acid of an ethoxylated and/or

propoxylated unsaturated fatty alcohol. Some of such ethoxylated and/or propoxylated unsaturated fatty alcohols are commercially available as non-ionic surfactants. Thus, L comprises or consists of alkylene (e.g. ethylene) oxide repeat units. One illustrative fatty alcohol of this type is available from Croda as "Brij O2". Such ethoxylated alcohol comprises a mixture of molecules (wherein n is 1 or 2) having the general formula



[0082] The crosslinking monomers can be prepared by reacting the corresponding alcohol with acryloyl chloride, methylene chloride and triethylamine, or a combination thereof, such as set forth in the examples. The crosslinking monomers can also be prepared by direct esterification with acrylic acid.

[0083] The concentration of crosslinking monomer comprising a (meth)acrylate group and an optionally substituted C_6 - C_{20} olefin group is typically at least 0.1, 0.2, 0.3, 0.4 or 0.5 wt-% and can range up to 10, 11, 12, 13, 14, or 15 wt-% of the (e.g. pressure sensitive) adhesive composition. However, as the concentration of such crosslinking monomer increases, the peel adhesion (180° to stainless steel) can decrease. Thus, in typically embodiments, the concentration of crosslinking monomer comprising a (meth)acrylate group and an optionally substituted C_6 - C_{20} olefin group is no greater than 9, 8, 7, 6, or 5 wt-% and in some favored embodiments, no greater than 4, 3, 2, or 1 wt-%.

[0084] In some embodiments, the crosslinking monomer comprises a branched C_6 - C_{20} having less than 18, or 16, or 14, or 12 carbon atoms, such as in the case of citronellyl acrylate and geraniol acrylate. In this embodiment, a pressure sensitive adhesive can be obtained having high shear values (i.e. greater than 10,000 minutes at 70° C.) in combination with high adhesion with as little as 0.5 wt-% of such crosslinking monomer. As the chain length of the branched C_6 - C_{20} group increases, the amount of crosslinking monomer needed to provide the same number of crosslinks increases. For example, in the case of farnesol acrylate at least 0.7 wt-% or 0.8 wt-% resulted in high shear values. In the case of cyclic C_6 - C_{20} olefin groups, such as in the case of cyclohexane methyl acrylate, at least 2, 3, 4, or 5 wt-% resulted in high shear values. In the case of crosslinking monomers comprising a straight-chain C_6 - C_{20} such as in the case of undecenyl acrylate and oleyl acrylate, high shear values in combination with high adhesion was obtained with about 1 wt-%. Lower concentrations of undecenyl acrylate and optionally substituted oleyl acrylate are surmised to also provide a good balance of properties.

[0085] The (e.g. pressure sensitive) adhesive composition may comprise a single crosslinking monomer comprising a (meth)acrylate group and (optionally substituted) C_6 - C_{20} olefin group or a combination of two or more of such crosslinking monomers. Further, the crosslinking monomer may comprise two or more isomers of the same general structure.

[0086] In favored embodiments, the crosslinked adhesive composition comprises high shear values to stainless steel or orange peel drywall, i.e. greater than 10,000 minutes at 70° C., as determined according to the test methods described in the examples. The crosslinked pressure sensitive adhesive can exhibit a variety of peel adhesion values depending on the intended end use. In some embodiments, the 180° degree peel adhesion to stainless steel is least 15 N/dm. In other embodiments, the 180° degree peel adhesion to stainless steel is least

20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, or 75 N/dm. The 180° degree peel adhesion to stainless steel is typically no greater than 150 or 100 N/dm. Such peel adhesive values are also attainable when adhered to other substrates.

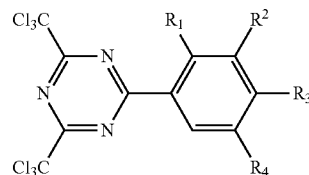
[0087] In some embodiments, such as in the case of optionally substituted citronellyl(meth)acrylate and oleyl(meth)acrylate, the crosslinking monomer is a bio-based material. Thus, the use of such crosslinking monomer is amenable to increasing the total content of biobased material of the adhesive. Further, since the crosslinking monomer comprises an olefin group comprising at least 6 carbon atoms, when the hydrocarbon unsaturation does not crosslink, the crosslinking monomer can serve the function of a low Tg monomer. This can be amenable to utilizing higher concentrations of such crosslinking monomer. Further, the crosslinking monomer does not form corrosive by-products and has good color stability. In some embodiments, the b* of the adhesive after exposure to UV or heat, as described in greater detail in the test method described in the examples, is less than 1 or 0.9, or 0.8, or 0.7, or 0.6, or 0.5, or 0.4, or 0.3. In some embodiments, the b* of the adhesive after exposure to UV and heat, as described in greater detail in the test method described in the examples, is less than 2, or 1.5, or 1, or 0.9, or 0.8, or 0.7, or 0.6, or 0.5, or 0.4, or 0.3.

[0088] The (e.g. pressure sensitive) adhesive may optionally comprise another crosslinker in addition to the crosslinker having a (meth)acrylate group and optionally substituted C_6 - C_{20} olefin group. In some embodiments, the (e.g. pressure sensitive) adhesive comprises a multifunctional (meth)acrylate.

[0089] Examples of useful multifunctional (meth)acrylate include, but are not limited to, di(meth)acrylates, tri(meth)acrylates, and tetra(meth)acrylates, such as 1,6-hexanediol di(meth)acrylate, poly(ethylene glycol)di(meth)acrylates, polybutadiene di(meth)acrylate, polyurethane di(meth)acrylates, and propoxylated glycerin tri(meth)acrylate, and mixtures thereof.

[0090] Generally the multifunctional (meth)acrylate is not part of the original monomer mixture, but added subsequently after the formation of the (meth)acrylic polymer. If used, the multifunctional (meth)acrylate is typically used in an amount of at least 0.01, 0.02, 0.03, 0.04, or 0.05 up to 1, 2, 3, 4, or 5 parts by weight, relative to 100 parts by weight of the total monomer content.

[0091] In some embodiments, the (e.g. pressure sensitive) adhesive may further comprise a chlorinated triazine crosslinking compound. The triazine crosslinking agent may have the formula.



wherein R_1 , R_2 , R_3 and R_4 of this triazine crosslinking agent are independently hydrogen or alkoxy group, and 1 to 3 of R_1 , R_2 , R_3 and R_4 are hydrogen. The alkoxy groups typically have no greater than 12 carbon atoms. In favored embodiments, the alkoxy groups are independently methoxy or ethoxy. One representative species is 2,4-bis(trichloromethyl)-6-(3,4-bis

(methoxy)phenyl)-triazine. Such triazine crosslinking compounds are further described in U.S. Pat. No. 4,330,590.

[0092] In some embodiments, the (e.g. pressure sensitive) adhesive comprises predominantly (greater than 50%, 60%, 70%, 80%, or 90% of the total crosslinks) or exclusively crosslinks from the crosslinking monomer that comprises a (meth)acrylate group and an optionally substituted C₆-C₂₀ olefin group. In such embodiment, the (e.g. pressure sensitive) adhesive may be free of other crosslinking compounds, particularly aziridine crosslinkers, as well as multifunctional (meth)acrylate crosslinkers, chlorinated triazine crosslinkers and melamine crosslinkers.

[0093] The (meth)acrylic copolymers and adhesive composition can be polymerized by various techniques including, but not limited to, solvent polymerization, dispersion polymerization, solventless bulk polymerization, and radiation polymerization, including processes using ultraviolet light, electron beam, and gamma radiation. The monomer mixture may comprise a polymerization initiator, especially a thermal initiator or a photoinitiator of a type and in an amount effective to polymerize the comonomers.

[0094] A typical solution polymerization method is carried out by adding the monomers, a suitable solvent, and an optional chain transfer agent to a reaction vessel, adding a free radical initiator, purging with nitrogen, and maintaining the reaction vessel at an elevated temperature (e.g. about 40 to 100° C.) until the reaction is complete, typically in about 1 to 20 hours, depending upon the batch size and temperature. Examples of typical solvents include methanol, tetrahydrofuran, ethanol, isopropanol, acetone, methyl ethyl ketone, methyl acetate, ethyl acetate, toluene, xylene, and an ethylene glycol alkyl ether. Those solvents can be used alone or as mixtures thereof.

[0095] Useful initiators include those that, on exposure to heat or light, generate free-radicals that initiate (co)polymerization of the monomer mixture. The initiators are typically employed at concentrations ranging from about 0.0001 to about 3.0 parts by weight, preferably from about 0.001 to about 1.0 parts by weight, and more preferably from about 0.005 to about 0.5 parts by weight of the total monomer or polymerized units.

[0096] Suitable initiators include but are not limited to those selected from the group consisting of azo compounds such as VAZO 64 (2,2'-azobis(isobutyronitrile)), VAZO 52 (2,2'-azobis(2,4-dimethylpentanenitrile)), and VAZO 67 (2,2'-azobis(2-methylbutyronitrile)) available from E.I. du Pont de Nemours Co., peroxides such as benzoyl peroxide and lauroyl peroxide, and mixtures thereof. The preferred oil-soluble thermal initiator is (2,2'-azobis(2-methylbutyronitrile)). When used, initiators may comprise from about 0.05 to about 1 part by weight, preferably about 0.1 to about 0.5 part by weight based on 100 parts by weight of monomer components in the pressure sensitive adhesive.

[0097] The polymers prepared from solution polymerization have pendent unsaturated groups that can be crosslinked by a variety of methods. These include addition of thermal or photo initiators followed by heat or UV exposure after coating. The polymers may also be crosslinked by exposure to electron beam or gamma irradiation.

[0098] One method of preparing (meth)acrylic polymers includes partially polymerizing monomers to produce a syrup composition comprising the solute (meth)acrylic polymer and unpolymerized solvent monomer(s). The unpolymerized solvent monomer(s) typically comprises the same monomer

as utilized to produce the solute (meth)acrylic polymer. If some of the monomers were consumed during the polymerization of the (meth)acrylic polymer, the unpolymerized solvent monomer(s) comprises at least some of the same monomer(s) as utilized to produce the solute (meth)acrylic polymer. Further, the same monomer(s) or other monomer(s) can be added to the syrup once the (meth)acrylic polymer has been formed. Partial polymerization provides a coatable solution of the (meth)acrylic solute polymer in one or more free-radically polymerizable solvent monomers. The partially polymerized composition is then coated on a suitable substrate and further polymerized.

[0099] In some embodiments, the crosslinking monomer is added to the monomer(s) utilized to form the (meth)acrylic polymer. Alternatively or in addition thereto, the crosslinking monomer may be added to the syrup after the (meth)acrylic polymer has been formed. The (meth)acrylate group of the crosslinker and other (e.g. (meth)acrylate) monomers utilized to form the (meth)acrylic polymer preferentially polymerize forming an acrylic backbone with the pendent C₆-C₂₀ olefin group. Without intending to be bound by theory, it is surmised that at least a portion of the carbon-carbon double bonds of the pendent C₆-C₂₀ olefin group crosslink with each other during radiation curing of the syrup. Other reaction mechanisms may also occur.

[0100] The syrup method provides advantages over solvent or solution polymerization methods; the syrup method yielding higher molecular weight materials. These higher molecular weights increase the amount of chain entanglements, thus increasing cohesive strength. Also, the distance between cross-links can be greater with high molecular syrup polymer, which allows for increased wet-out onto a surface.

[0101] Polymerization of the (meth)acrylate solvent monomers can be accomplished by exposing the syrup composition to energy in the presence of a photoinitiator. Energy activated initiators may be unnecessary where, for example, ionizing radiation is used to initiate polymerization. Typically, a photoinitiator can be employed in a concentration of at least 0.0001 part by weight, preferably at least 0.001 part by weight, and more preferably at least 0.005 part by weight, relative to 100 parts by weight of the syrup.

[0102] A preferred method of preparation of the syrup composition is photoinitiated free radical polymerization. Advantages of the photopolymerization method are that 1) heating the monomer solution is unnecessary and 2) photoinitiation is stopped completely when the activating light source is turned off. Polymerization to achieve a coatable viscosity may be conducted such that the conversion of monomers to polymer is up to about 30%. Polymerization can be terminated when the desired conversion and viscosity have been achieved by removing the light source and by bubbling air (oxygen) into the solution to quench propagating free radicals. The solute polymer(s) may be prepared conventionally in a non-monomeric solvent and advanced to high conversion (degree of polymerization). When solvent (monomeric or non-monomeric) is used, the solvent may be removed (for example by vacuum distillation) either before or after formation of the syrup composition. While an acceptable method, this procedure involving a highly converted functional polymer is not preferred because an additional solvent removal step is required, another material may be required (a non-monomeric solvent), and dissolution of the high molecular weight, highly converted solute polymer in the monomer mixture may require a significant period of time.

[0103] The polymerization is preferably conducted in the absence of solvents such as ethyl acetate, toluene and tetrahydrofuran, which are non-reactive with the functional groups of the components of the syrup composition. Solvents influence the rate of incorporation of different monomers in the polymer chain and generally lead to lower molecular weights as the polymers gel or precipitate from solution. Thus, the (e.g. pressure sensitive) adhesive can be free of unpolymerizable organic solvent.

[0104] Useful photoinitiators include benzoin ethers such as benzoin methyl ether and benzoin isopropyl ether; substituted acetophenones such as 2,2-dimethoxy-2-phenylacetophenone photoinitiator, available the trade name IRGACURE 651 or ESACURE KB-1 photoinitiator (Sartomer Co., West Chester, Pa.), and dimethylhydroxyacetophenone; substituted α -ketols such as 2-methyl-2-hydroxy propiophenone; aromatic sulfonyl chlorides such as 2-naphthalene-sulfonyl chloride; and photoactive oximes such as 1-phenyl-1,2-propanedione-2-(O-ethoxy-carbonyl)oxime. Particularly preferred among these are the substituted acetophenones.

[0105] Preferred photoinitiators are photoactive compounds that undergo a Norrish I cleavage to generate free radicals that can initiate by addition to the acrylic double bonds. The photoinitiator can be added to the mixture to be coated after the polymer has been formed, i.e., photoinitiator can be added to the syrup composition. Such polymerizable photoinitiators are described, for example, in U.S. Pat. Nos. 5,902,836 and 5,506,279 (Gaddam et al.).

[0106] Such photoinitiators preferably are present in an amount of from 0.1 to 1.0 part by weight, relative to 100 parts by weight of the total syrup content. Accordingly, relatively thick coatings can be achieved when the extinction coefficient of the photoinitiator is low.

[0107] The syrup composition and the photoinitiator may be irradiated with activating UV radiation to polymerize the monomer component(s). UV light sources can be of two types: 1) relatively low light intensity sources such as blacklights, which provide generally 10 mW/cm² or less (as measured in accordance with procedures approved by the United States National Institute of Standards and Technology as, for example, with a UVIMAP UM 365 L-S radiometer manufactured by Electronic Instrumentation & Technology, Inc., in Sterling, Va.) over a wavelength range of 280 to 400 nanometers; and 2) relatively high light intensity sources such as medium pressure mercury lamps which provide intensities generally greater than 10 mW/cm², preferably 15 to 450 mW/cm². Where actinic radiation is used to fully or partially polymerize the syrup composition, high intensities and short exposure times are preferred. For example, an intensity of 600 mW/cm² and an exposure time of about 1 second may be used successfully. Intensities can range from 0.1 to 150 mW/cm², preferably from 0.5 to 100 mW/cm², and more preferably from 0.5 to 50 mW/cm².

[0108] The degree of conversion can be monitored during the irradiation by measuring the index of refraction of the polymerizing medium as previously described. Useful coating viscosities are achieved with conversions (i.e., the percentage of available monomer polymerized) in the range of up to 30%, preferably 2% to 20%, more preferably from 5% to 15%, and most preferably from 7% to 12%. The molecular weight (weight average) of the solute polymer(s) is typically at least 100,000 or 250,000 and preferably at least 500,000 g/mole or greater.

[0109] When preparing (meth)acrylic polymers described herein, it is expedient for the photoinitiated polymerization reactions to proceed to virtual completion, i.e., depletion of the monomeric components, at temperatures less than 70° C. (preferably at 50° C. or less) with reaction times less than 24 hours, preferably less than 12 hours, and more preferably less than 6 hours. These temperature ranges and reaction rates obviate the need for free radical polymerization inhibitors, which are often added to acrylic systems to stabilize against undesired, premature polymerization and gelation. Furthermore, the addition of inhibitors adds extraneous material that will remain with the system and inhibit the desired polymerization of the syrup composition and formation of the crosslinked pressure-sensitive adhesives. Free radical polymerization inhibitors are often required at processing temperatures of 70° C. and higher for reaction periods of more than 6 to 10 hours.

[0110] The pressure-sensitive adhesives may optionally contain one or more conventional additives. Preferred additives include tackifiers, plasticizers, dyes, antioxidants, UV stabilizers, and (e.g. inorganic) fillers such as (e.g. fumed) silica and glass bubbles.

[0111] In some embodiments, the pressure sensitive adhesive comprises fumed silica. Fumed silica, also known as pyrogenic silica, is made from flame pyrolysis of silicon tetrachloride or from quartz sand vaporized in a 3000° C. electric arc. Fumed silica consists of microscopic droplets of amorphous silica fused into (e.g. branched) three-dimensional primary particles that aggregate into larger particles. Since the aggregates do not typically break down, the average particle size of fumed silica is the average particle size of the aggregates. Fumed silica is commercially available from various global producers including Evonik, under the trade designation "Aerosil"; Cabot under the trade designation "Cab-O-Sil", and Wacker Chemie-Dow Corning. The BET surface area of suitable fumed silica is typically at least 50 m²/g, or 75 m²/g, or 100 m²/g. In some embodiments, the BET surface area of the fumed silica is no greater than 400 m²/g, or 350 m²/g, or 300 m²/g, or 275 m²/g, or 250 m²/g. The fumed silica aggregates preferably comprise silica having a primary particle size no greater than 20 nm or 15 nm. The aggregate particle size is substantially larger than the primary particle size and is typically at least 100 nm or greater.

[0112] The concentration of (e.g. fumed) silica can vary. In some embodiments, such as for conformable pressure sensitive adhesives, the adhesive comprises at least 0.5, 1.0, 1.1, 1.2, 1.3, 1.4, or 1.5 wt-% of (e.g. fumed) silica and in some embodiments no greater than 5, 4, 3, or 2 wt-%. In other embodiments, the adhesive comprises at least 5, 6, 7, 8, 9, or 10 wt-% of (e.g. fumed) silica and typically no greater than 20, 19, 18, 17, 16, or 15 wt-% of (e.g. fumed) silica.

[0113] In some embodiments, the pressure sensitive adhesive comprises glass bubbles. Suitable glass bubbles generally have a density ranging from about 0.125 to about 0.35 g/cc. In some embodiments, the glass bubbles have a density less than 0.30, 0.25, or 0.20 g/cc. Glass bubbles generally have a distribution of particles sizes. In typical embodiments, 90% of the glass bubbles have a particle size (by volume) of at least 75 microns and no greater than 115 microns. In some embodiments, 90% of the glass bubbles have a particle size (by volume) of at least 80, 85, 90, or 95 microns. In some embodiments, the glass bubbles have a crush strength of at

least 250 psi and no greater than 1000, 750, or 500 psi. Glass bubbles are commercially available from various sources including 3M, St. Paul, Minn.

[0114] The concentration of glass bubbles can vary. In some embodiments, the adhesive comprises at least 1, 2, 3, 4 or 5 wt-% of glass bubbles and typically no greater than 20, 15, or 10 wt-% of glass bubbles.

[0115] The inclusion of glass bubbles can reduce the density of the adhesive. Another way of reducing the density of the adhesive is by incorporation of air or other gasses into the adhesive composition. For example the (e.g. syrup) adhesive composition can be transferred to a frother as described for examples in U.S. Pat. No. 4,415,615; incorporated herein by reference. While feeding nitrogen gas into the frother, the frothed syrup can be delivered to the nip of a roll coater between a pair of transparent, (e.g. biaxially-oriented polyethylene terephthalate) films. A silicone or fluorochemical surfactant is included in the frothed syrup. Various surfactants are known including copolymer surfactants described in U.S. Pat. No. 6,852,781.

[0116] In some embodiments no tackifier is used. When tackifiers are used, the concentration can range from 5 or 10 wt-% to 40, 45, 50, 55, or 60 wt-% of the (e.g. cured) adhesive composition.

[0117] Various types of tackifiers include phenol modified terpenes and rosin esters such as glycerol esters of rosin and pentaerythritol esters of rosin that are available under the trade designations "Nuroz", "Nutac" (Newport Industries), "Permalyn", "Staybelite", "Foral" (Eastman). Also available are hydrocarbon resin tackifiers that typically come from C5 and C9 monomers by products of naphtha cracking and are available under the trade names "Piccotac", "Eastotac", "Regalrez", "Regalite" (Eastman), "Arkon" (Arakawa), "Norsolene", "Wingtack" (Cray Valley), "Nevtack", LX (Neville Chemical Co.), "Hikotac", "Hikorez" (Kolon Chemical), "Novares" (Rutgers Nev.), "Quintone" (Zeon), "Escorez" (Exxonmobile Chemical), "Nures", and "H-Rez" (Newport Industries). Of these, glycerol esters of rosin and pentaerythritol esters of rosin, such as available under the trade designations "Nuroz", "Nutac", and "Foral" are considered biobased materials.

[0118] Depending on the kinds and amount of components, the pressure sensitive adhesive can be formulated to have a wide variety of properties for various end uses.

[0119] In one specific embodiment, the adhesive composition and thickness is chosen to provide a synergistic combination of properties. In this embodiment, the adhesive can be characterized as having any one or combination of attributes including being conformable, cleanly removable, reusable, reactivatable, and exhibiting good adhesion to rough surfaces.

[0120] Thus, in some embodiments, the PSA is conformable. The conformability of an adhesive can be characterized using various techniques such as dynamic mechanical analysis (as determined by the test method described in the examples) that can be utilized to determine that shear loss modulus (G''), the shear storage modulus (G'), and tan delta, defined as the ratio of the shear loss modulus (G'') to the shear storage modulus (G'). As used herein "conformable" refers to the (e.g. first) adhesive exhibiting a tan delta of at least 0.4 or greater at 25° C. and 1 hertz. In some embodiments, the (e.g. first) adhesive has tan delta of at least 0.45, 0.50, 0.55, 0.65, or 0.70 at 25° C. and 1 hertz. The tan delta at 25° C. and 1 hertz of the (e.g. first) adhesive is typically no greater than 0.80 or 1.0. In some embodiments, the tan delta of the (e.g. first)

adhesive is no greater than 1.0 at 1 hertz and temperatures of 40° C., 60° C., 80° C., 100° C. and 120° C. In some embodiments, the first adhesive layer has tan delta of at least 0.4 or greater at 1 hertz and temperatures of 40° C., 60° C., 80° C., 100° C. and 120° C.

[0121] The PSA and adhesive coated articles can exhibit good adhesion to both smooth and rough surfaces. Various rough surfaces are known including for example textured drywall, such as "knock down" and "orange peel"; cinder block, rough (e.g. Brazilian) tile and textured cement. Smooth surfaces, such as stainless steel, glass, and polypropylene have an average surface roughness (R_a) as can be measured by optical interferometry of less than 100 nanometer; whereas rough surfaces have an average surface roughness greater than 1 micron (1000 nanometers), 5 microns, or 10 microns.

[0122] Surfaces with a roughness in excess of 5 or 10 microns can be measured with stylus profilometry. Standard (untextured) drywall has an average surface roughness (R_a), of about 10-20 microns and a maximum peak height (R_t using Veeco's Vison software) of 150 to 200 microns. Orange peel and knockdown drywall have an average surface roughness (R_a) greater than 20, 25, 30, 35, 40, or 45 microns and a maximum peak height (R_t) greater than 200, 250, 300, 350, or 400 microns. Orange peel drywall can have an average surface roughness (R_a) of about 50-75 microns and a maximum peak height (R_t) of 450-650 microns. Knock down drywall can have an average surface roughness (R_a) greater than 75, 80, or 85 microns, such as ranging from 90-120 microns and a maximum peak height (R_t) of 650-850 microns. In typical embodiments, R_a is no greater than 200, 175, or 150 microns and R_t is no greater than 1500, 1250, or 1000 microns. Cinder block and Brazilian tile typically have a similar average surface roughness (R_a) as orange peel drywall.

[0123] Although many conformable adhesives exhibit good initial adhesion to a rough surface, the PSA and articles described herein can exhibit a shear (with a mass of 250 g) to orange peel dry wall of at least 500 minutes. In some embodiments, the PSA and articles can exhibit a shear (with a mass of 250 g) to orange peel dry wall of at least 1000, 2000, 3000, 4000, 5000, 6000, 7000, 8000, 9000 or 10,000 minutes.

[0124] The PSA and adhesive coated articles can be cleanly removable from paper. By "cleanly removable from paper" it is meant that the paper does not tear and the paper does not have any staining or adhesive residue after removal of the adhesive from the paper when tested (according to Test Method 3 set forth in the examples). The 90° peel values to paper (according to Test Method 3, set forth in the examples) is typically at least 25 and no greater than 200 or 175 N/dm. In some embodiments, the 90° peel value to paper no greater than 50, 45, or 40 N/dm.

[0125] The PSA and adhesive coated articles can be reusable. By reusable it is meant that PSA and/or adhesive coated article can repeatedly be removed and readhered to paper at least 1, 2, 3, 4, or 5 times. In some embodiments, it can be readhered to paper at least 5, 10, 15, or 20 times while maintaining at least 80%, 85%, or 90% of the initial peel adhesion (according to the "Reusability" test further described in the examples).

[0126] Further, in some embodiments, the adhesive can be reactivatable, i.e. contaminants can be removed by cleaning the adhesive layer(s) with soap and water, such as by the test methods described in WO 96/31564; incorporated herein by reference.

[0127] The adhesives of the present invention may be coated upon a variety of flexible and inflexible backing materials using conventional coating techniques to produce adhesive-coated materials. Flexible substrates are defined herein as any material which is conventionally utilized as a tape backing or may be of any other flexible material. Examples include, but are not limited to plastic films such as polypropylene, polyethylene, polyvinyl chloride, polyester (polyethylene terephthalate), polycarbonate, polymethyl(meth)acrylate (PMMA), cellulose acetate, cellulose triacetate, and ethyl cellulose. Foam backings may be used. In some embodiments, the backing is comprised of a bio-based material such as polylactic acid (PLA).

[0128] Backings may also be prepared of fabric such as woven fabric formed of threads of synthetic or natural materials such as cotton, nylon, rayon, glass, ceramic materials, and the like or nonwoven fabric such as air laid webs of natural or synthetic fibers or blends of these. The backing may also be formed of metal, metalized polymer films, or ceramic sheet materials may take the form of any article conventionally known to be utilized with pressure-sensitive adhesive compositions such as labels, tapes, signs, covers, marking indicia, and the like.

[0129] Backings can be made from plastics (e.g., polypropylene, including biaxially oriented polypropylene, vinyl, polyethylene, polyester such as polyethylene terephthalate), nonwovens (e.g., papers, cloths, nonwoven scrims), metal foils, foams (e.g., polyacrylic, polyethylene, polyurethane, neoprene), and the like. Foams are commercially available from various suppliers such as 3M Co., Voltek, Sekisui, and others. The foam may be formed as a coextruded sheet with the adhesive on one or both sides of the foam, or the adhesive may be laminated to it. When the adhesive is laminated to a foam, it may be desirable to treat the surface to improve the adhesion of the adhesive to the foam or to any of the other types of backings. Such treatments are typically selected based on the nature of the materials of the adhesive and of the foam or backing and include primers and surface modifications (e.g., corona treatment, surface abrasion). Suitable primers include for example those described in EP 372756, U.S. Pat. No. 5,534,391, U.S. Pat. No. 6,893,731, WO2011/068754, and WO2011/38448.

[0130] In some embodiments, the backing material is a transparent film having a transmission of visible light of at least 90 percent. The transparent film may further comprise a graphic. In this embodiment, the adhesive may also be transparent.

[0131] The above-described compositions can be coated on a substrate using conventional coating techniques modified as appropriate to the particular substrate. For example, these compositions can be applied to a variety of solid substrates by methods such as roller coating, flow coating, dip coating, spin coating, spray coating knife coating, and die coating. The composition may also be coated from the melt. These various methods of coating allow the compositions to be placed on the substrate at variable thicknesses thus allowing a wider range of use of the compositions. Coating thicknesses may vary as previously described. The syrup composition may be of any desirable concentration for subsequent coating, but is typically 5 to 20 wt-% polymer solids in monomer. The desired concentration may be achieved by further dilution of the coating composition, or by partial drying. Coating thicknesses may vary from about 25 to 1500 microns (dry thickness). In typical embodiments, the coating thickness ranges

from about 50 to 250 microns. When the multilayer PSA or article is intended to be bonded to a rough surface, the thickness of the adhesive layer typically ranges from the average roughness (Ra) to slightly greater than the maximum peak height (Rt).

[0132] The adhesive can also be provided in the form of a pressure-sensitive adhesive transfer tape in which at least one layer of the adhesive is disposed on a release liner for application to a permanent substrate at a later time. The adhesive can also be provided as a single coated or double coated tape in which the adhesive is disposed on a permanent backing.

[0133] For a single-sided tape, the side of the backing surface opposite that where the adhesive is disposed is typically coated with a suitable release material. Release materials are known and include materials such as, for example, silicone, polyethylene, polycarbamate, polyacrylics, and the like. For double coated tapes, another layer of adhesive is disposed on the backing surface opposite that where the adhesive of the invention is disposed. The other layer of adhesive can be different from the adhesive of the invention, e.g., a conventional acrylic PSA, or it can be the same adhesive as the invention, with the same or a different formulation. Double coated tapes are typically carried on a release liner. Additional tape constructions include those described in U.S. Pat. No. 5,602,221 (Bennett et al.), incorporated herein by reference. In some embodiments, the pressure sensitive adhesive and a release layer in the release liner are both UV curable compositions. Any conventional coating technique can be used to "wet cast" and UV cure the pressure sensitive adhesive directly onto the UV cured release layer of the release liner. Optionally the UV cured pressure sensitive adhesive is "dry laminated" to the LTV cured release layer of the release liner.

[0134] It is desirable to provide tight side release values of 20 grams/inch or more. It is also desirable to provide a release ratio (tight side adhesion strength/easy side adhesion release strength) of 3 or more. A release ratio of 3 or more contributes to the desired release behavior wherein the adhesive consistently releases first from the easy side of the liner then subsequently from the tight side of the liner. It is further desirable to provide both such characteristics simultaneously.

[0135] Release materials, such as those useful in the presently disclosed release liners, include UV curable compositions made using techniques disclosed in US 2013/0059105 (Wright), which is hereby incorporated by reference. In some embodiments, the present disclosure describes a method for producing a release liner from an at least partially cured layer (optionally a fully cured layer), the method including applying a layer comprising a (meth)acrylate-functional siloxane to a surface of a substrate, and irradiating the layer in a substantially inert atmosphere with a short wavelength polychromatic ultraviolet light source having a peak intensity at a wavelength of from about 160 (+/-5) nanometers (nm) to about 240 (+/-5) nm to at least partially cure the layer. Optionally, the layer is at a curing temperature greater than 25° C.

[0136] Thus, in some exemplary embodiments, the material comprising the layer may be heated to a temperature greater than 25° C. during or subsequent to application of the layer to the substrate. Alternatively, the material comprising the layer may be provided at a temperature of greater than 25° C., e.g. by heating or cooling the material comprising the layer before, during, and/or after application of the layer to the substrate. Preferably, the layer is at a temperature of at least 50° C., 60° C., 70° C., 80° C., 90° C., 100° C., 125° C.,

or even 150° C. Preferably the layer is at a temperature of no more than 250° C., 225° C., 200° C., 190° C., 180° C., 170° C., 160° C., or even 155° C.

[0137] Methods of the present disclosure involve applying a layer comprising a (meth)acrylate-functional siloxane to a major surface of a substrate. Generally, the materials comprising the layer may be oils, fluids, gums, elastomers, or resins, e.g., friable solid resins. Generally, lower molecular weight, lower viscosity materials are referred to as fluids or oils, while higher molecular weight, higher viscosity materials are referred to as gums; however, there is no sharp distinction between these terms. Elastomers and resins have even higher molecular weights than gums and typically do not flow. As used herein, the terms “fluid” and “oil” refer to materials having a dynamic viscosity at 25° C. of no greater than 1,000,000 mPa·sec (e.g., less than 600,000 mPa·sec), while materials having a dynamic viscosity at 25° C. of greater than 1,000,000 mPa·sec (e.g., at least 10,000,000 mPa·sec) are referred to as “gums.”

[0138] In order to obtain the low thicknesses generally desirable for some silicone coatings, e.g., silicone release materials, it is often necessary to dilute high molecular weight materials with solvents in order to coat or otherwise apply them to a substrate. In some embodiments, it may be preferable to use low molecular weight silicone oils or fluids, including those having a dynamic viscosity at 25° C. of no greater than 200,000 mPa·sec, no greater than 100,000 mPa·sec, or even no greater than 50,000 mPa·sec.

[0139] In some embodiments, it may be useful to use materials compatible with common solventless coating operations, including, e.g., those having a kinematic viscosity at 25° C. of no greater than 50,000 centistokes (cSt), e.g., no greater than 40,000 cSt, or even no greater than 20,000 cSt. In some embodiments, it may be desirable to use a combination of silicone materials, wherein at least one of the silicone materials has a kinematic viscosity at 25° C. of at least 5,000 centistokes (cSt), e.g., at least 10,000 cSt, or even at least 15,000 cSt. In some embodiments, it may be desirable to use materials in the layer having a kinematic viscosity at 25° C. of between 1000 and 50,000 cSt, e.g., between 5,000 and 50,000 cSt, or even between 10,000 and 50,000 cSt.

[0140] In general, depending on the selected material comprising the layer, including its viscosity, any known coating method may be used. Exemplary coating methods include roll coating, spray coating, dip coating, gravure coating, bar coating, vapor coating, and the like. Once coated, the silicone material is exposed to short wavelength ultraviolet radiation.

[0141] In accordance with the method of the disclosure, the (meth)acrylate-functional siloxane may be coated via any of a variety of conventional coating methods, such as roll coating, knife coating, or curtain coating. The low viscosity (co) polymerization mixtures are preferably coated by means specifically adapted to deliver thin release layers, preferably through the use of precision roll coaters and electrospray methods such as those described in U.S. Pat. Nos. 4,748,043 and 5,326,598 (both to Seaver et al.). Higher viscosity mixtures which can be coated to higher thickness (e.g., up to about 500 μm) can be provided by selecting higher molecular weight oligomeric starting materials. Oligomeric or (co)polymeric starting materials can also be thickened with adjuvants (e.g. thickeners), including but not limited to particulate fillers such as colloidal silica and the like, prior to coating.

[0142] In some exemplary embodiments of any of the foregoing, the layer is applied at a thickness of about 0.1 (+/-0.05)

micrometer (μm) to about 5 (+/-0.1) μm prior to irradiation with the short wavelength polychromatic light source. In certain exemplary embodiments, the layer is applied at a thickness of at least about 0.2 (+/-0.05) μm , 0.3 (+/-0.05) μm , 0.4 (+/-0.05) μm , or even 0.5 (+/-0.05) μm ; to about 4 (+/-0.1) μm , 3 (+/-0.1) μm , 2 (+/-0.1) μm , or even 1 (+/-0.1) μm , prior to irradiation with the short wavelength polychromatic light source.

[0143] In other exemplary embodiments, the at least partially cured layer or even the fully cured layer may have a thickness of 0.1 (+/-0.05) micrometer (μm) to about 5 (+/-0.1) μm . In certain exemplary embodiments, the at least partially cured layer or even the fully cured layer has a thickness of at least about 0.2 (+/-0.05) μm , 0.3 (+/-0.05) μm , 0.4 (+/-0.05) μm , or even 0.5 (+/-0.05) μm ; to about 4 (+/-0.1) μm , 3 (+/-0.1) μm , 2 (+/-0.1) μm , or even 1 (+/-0.1) μm .

[0144] In any of the foregoing exemplary embodiments, applying the layer to the surface of the substrate includes applying a discontinuous coating. In other words, the layer need not cover the entire major surface of the substrate, and only a portion of the substrate surface may be covered by the layer. For example, the layer may be applied to the substrate as a single strip or stripe, or as a plurality of strips or stripes, as a plurality of dots, or in any other discernible pattern.

[0145] Exemplary methods of the present disclosure include UV-radiation curing of the layer, by irradiating the layer, in a substantially inert atmosphere containing no greater than 500 ppm oxygen, with radiation (e.g. light) emitted from a short wavelength polychromatic ultraviolet light source having a peak intensity at a wavelength of from about 160 (+/-5) nanometers (nm) to about 240 (+/-5) nm, to at least partially cure the layer.

[0146] Substantially inert atmospheres are particularly useful in embodiments in which the UV-radiation source has radiant output at wavelengths of less than 200 nm. In such embodiments, oxygen gas present in the environment may absorb the UV radiation, thereby substantially preventing the radiation from reaching the target surface. Thus, in any of the foregoing exemplary embodiments, the substantially inert atmosphere includes no greater than 500 ppm oxygen. In some of the foregoing exemplary embodiments, the substantially inert atmosphere includes no greater than 400 ppm oxygen, 300 ppm oxygen, 200 ppm oxygen, or even 100 ppm oxygen. In some of the foregoing exemplary embodiments, the substantially inert atmosphere includes no greater than 50 ppm oxygen, no greater than 40 ppm, 30 ppm, 20 ppm, or even 10 ppm oxygen.

[0147] In some exemplary embodiments, the substantially inert atmosphere may comprise an inert gas such as nitrogen, helium, argon, or the like. In one embodiment, the methods of the present disclosure may be carried out in an inert environment including nitrogen. In embodiments in which an inert gas is used, oxygen levels in the environment may be as low as 50 ppm, 25 ppm, or even as low as 10 ppm, and as high as 100 ppm, or even 500 ppm.

[0148] In further exemplary embodiments, the controlled environment may be operated in a vacuum or a partial vacuum. In some such embodiments in which vacuum pressures are employed, the pressures may be as low as 10^{-4} torr, 10^{-5} torr, or even as low as 10^{-6} torr; and be as high as 10^{-1} torr, 1 torr, or even 10 torr.

[0149] In further exemplary embodiments, the material comprising the layer is exposed to short wavelength polychromatic ultraviolet radiation after applying the layer to the

substrate, to at least partially cure the layer on the substrate. Short wavelength polychromatic ultraviolet light sources useful in the method of the present disclosure are those having output in the region from about 160 (+/-5) nm to about 240 (+/-5) nm, inclusive. In some exemplary embodiments of any of the foregoing, a peak intensity is at a wavelength between about 170 (+/-5) nm, 180 (+/-5) nm, or even 190 (+/-5) nm; to about 215 (+/-5) nm, 210 (+/-5) nm, 205 (+/-5) nm, or even 200 (+/-5) nm. In some particular exemplary embodiments, a peak intensity is at a wavelength of about 185 (+/-2) nm.

[0150] In certain such exemplary embodiments, the short wavelength polychromatic ultraviolet light source includes at least one low pressure mercury vapor lamp, at least one low pressure mercury amalgam lamp, at least one pulsed Xenon lamp, at least one glow discharge from a polychromatic plasma emission source, or combinations thereof.

[0151] Suitable plasma emission sources may involve excitation of a carrier gas (e.g. nitrogen) to generate electrons, ions, radicals, and photons in the form of a glow discharge. As reported in, for example, Elsner et al. [*Macromol. Mater. Eng.*, 294, 422-31 (2009)], a variety of acrylate monomers can be cured in the absence of photoinitiators using a nitrogen plasma polymerization process in which a glow discharge (i.e., UV-radiation emission) having peak intensities near 150 nm, 175 nm, and 220 nm was observed.

[0152] The intensities of incident radiation useful in the processes of the present disclosure can be from as low as about 1 mW/cm² to about 10 W/cm², preferably 5 mW/cm² to about 5 W/cm², more preferably 10 mW/cm² to 1 W/cm². When higher power levels are provided (e.g., greater than about 10 W/cm²), volatilization of low molecular weight (meth)acrylate-functional siloxane monomers and oligomers can result.

[0153] In some exemplary embodiments, it is desirable to select a short wavelength polychromatic ultraviolet source having an intensity peak at a wavelength resulting in an absorbance greater than zero but no greater than about 0.5 (+/-0.05), as determined by Beer's law for the particular silicone resin being cured and the thickness. When the absorbance goes above 0.5, a surface layer or skin may form due to the lack of penetration of the radiation through the coating thickness resulting in surface absorption and localized polymerization and cross-linking. Absorbances below 0.3 are acceptable and tend to give more uniform penetration and cure profiles but are less efficient in terms of radiation capture.

[0154] In certain exemplary embodiments, the absorbance determined by Beer's law is between 0.3 and 0.5, inclusive, e.g., between 0.4 and 0.5, inclusive, or even between 0.40 and 0.45, inclusive. As the actual absorbance and the absorbance calculated by Beer's law increase linearly with thickness, a particular silicone resin may have the desired absorbance at one thickness, e.g., 1 micrometer, while the absorbance of the same silicone resin at a greater thickness, e.g., 10 micrometers, may be too high.

[0155] The layer comprises material that is capable of undergoing at least a partial cure when exposed to short wavelength polychromatic ultraviolet radiation. In the presently disclosed embodiments, the layer comprises at least one (meth)acrylate-functional siloxane. In some such exemplary embodiments of any of the foregoing disclosed embodiments, the release liner layer consists essentially of one or more (meth)acrylate-functional siloxane monomers. In other such exemplary embodiments, the layer consists essentially of one

or more (meth)acrylate-functional siloxane oligomers. In certain other such exemplary embodiments, the layer consists essentially of one or more (meth)acrylate-functional polysiloxanes.

[0156] The curable materials are applied as a layer on at least a portion of at least one major surface of a suitable flexible or rigid substrate or surface or backing, and irradiated using the prescribed ultraviolet radiation sources. Useful flexible substrates include, but are not limited to, paper, poly-coated Kraft paper, supercalendered or glassine Kraft paper, plastic films such as poly(propylene), biaxially-oriented polypropylene, poly(ethylene), poly(vinyl chloride), polycarbonate, poly(tetrafluoroethylene), polyester [e.g., poly(ethylene terephthalate)], poly(ethylene naphthalate), polyamide film such as those commercially available under the trade designation "KAPTON" from DuPont, Wilmington, Del., cellulose acetate, and ethyl cellulose.

[0157] In addition, suitable substrates for use in the presently disclosed release liner may be formed of metal, metal foil, metallized (co)polymeric film, or ceramic sheet material. Substrates may also take the form of a cloth backing, e.g. a woven fabric formed of threads of synthetic fibers, or a non-woven web or substrate, or combinations of these. One of the advantages of the use of the short wavelength polychromatic ultraviolet light sources of the present disclosure is the ability to use such high energy, low heat sources to (co)polymerize mixtures coated on heat sensitive substrates. Commonly used longer wavelength ultraviolet lamps often generate undesirable levels of thermal radiation that can distort or damage a variety of synthetic or natural flexible substrates. Suitable rigid substrates include but are not limited to glass, wood, metals, treated metals (such as those comprising automobile and marine surfaces), (co)polymeric material and surfaces, and composite material such as fiber reinforced plastics.

[0158] In some exemplary embodiments, the substrates may be surface treated (e.g., corona or flame treatment), coated with, e.g., a primer or print receptive layer. In certain exemplary embodiments, multilayer substrates may be used. In certain exemplary embodiments, the substrate may be smooth or textured, e.g., embossed. In some exemplary embodiments, the substrate is embossed after curing the release material.

[0159] In general, (co)polymerizable (meth)acrylate-functional siloxanes are useful materials for preparing an at least partially (or in some embodiments completely) cured layer for a layer according to the present disclosure. Ethylenically unsaturated free radically (co)polymerizable siloxanes, including especially the (meth)acrylate-functional siloxane oligomers and (co)polymers containing telechelic and/or pendant acrylate or methacrylate groups, are particularly useful precursor materials for incorporation in the at least partially cured layers of the present disclosure. These (meth)acrylate-functional siloxane oligomers can be prepared by a variety of methods, generally through the reaction of chloro-, silanol-, aminoalkyl-, epoxyalkyl-, hydroxyalkyl-, vinyl-, or silicon hydride-functional polysiloxanes with a corresponding (meth)acrylate-functional capping agent. These preparations are reviewed in a chapter entitled "Photo(co)polymerizable Silicone Monomers, Oligomers, and Resins" by A. F. Jacobine and S. T. Nakos in *Radiation Curing Science and Technology*, (Plenum: New York, 1992), pp. 200-214.

[0160] Suitable (co)polymerizable (meth)acrylate-functional siloxane oligomers include those (meth)acryl-modified polysiloxane resins commercially available from, for

example, Goldschmidt Chemical Corporation (Evonik TEGO Chemie GmbH, Essen, Germany) under the TEGO™ RC designation. An example of a blend recommended for achieving premium (easy) release is a 70:30 (weight/weight, w/w) blend of TEGO RC922 and TEGO RC711.

[0161] Suitable (meth)acrylate-functional polysiloxane resins include the acrylamido-terminated monofunctional and difunctional polysiloxane resins described in U.S. Pat. No. 5,091,483 (Mazurek et al.). These (meth)acrylate-functional polysiloxane resins are pourable and may be blended for optimized properties such as level of release, adhesive compatibility, and substrate adhesion.

[0162] In some exemplary embodiments, the (co)polymerizable precursor composition making up the layer may include essentially only one or more (co)polymerizable (meth)acrylate-functional siloxane(s), and is substantially-free of other (co)polymerizable materials. Thus, in further exemplary embodiments of any of the foregoing, the layer consists essentially of one or more (meth)acrylate-functional siloxane monomers. In some such exemplary embodiments, the layer consists essentially of one or more (meth)acrylate-functional siloxane oligomers. In other such exemplary embodiments, the layer consists essentially of one or more (meth)acrylate-functional polysiloxanes.

[0163] In addition to the (meth)acrylate functional siloxane, the layer may optionally include one or more (co)polymerizable starting materials. Suitable (co)polymerizable starting materials may contain silicon or may not contain silicon.

[0164] Thus, in some exemplary embodiments, the layer further comprises a non-(meth)acrylate-functional siloxane monomer, oligomer, or (co)polymer. Such materials can be functional or non-functional. Examples of non-functional (co)polymerizable siloxanes include poly(dialkylsiloxanes), poly(dialkyl-diarylsiloxanes), poly(alkylaryl siloxanes), and poly(diarylsiloxanes), and may be linear, cyclic, or branched. Examples of functional (but non-(meth)acrylate-functional) polysiloxanes that may be used include vinyl-functional polysiloxanes, hydroxy-functional polysiloxanes, amine-functional polysiloxanes, hydride-functional polysiloxanes, epoxy-functional polysiloxanes, and combinations thereof.

[0165] In certain exemplary embodiments, the layer further comprises one or more (co)polymerizable materials selected from the group consisting of monofunctional (meth)acrylate monomers, difunctional (meth)acrylate monomers, polyfunctional (meth)acrylate monomers having functionality greater than two, vinyl ester monomers, vinyl ester oligomers, vinyl ether monomers, and vinyl ether oligomers. Suitable vinyl-functional monomers include but are not limited to acrylic acid and its esters, methacrylic acid and its esters, vinyl-substituted aromatics, vinyl-substituted heterocyclics, vinyl esters, vinyl chloride, acrylonitrile, methacrylonitrile, acrylamide and derivatives thereof, methacrylamide and derivatives thereof, and other vinyl monomers (co)polymerizable by free-radical means.

[0166] Monofunctional (meth)acrylate (co)monomers useful in the methods of the present disclosure include compositions of Formula 1:



wherein X represents $H_2C=C(R_1)C(O)O-$, in which R_1 represents $-H$ or $-CH_3$, $m=1$, and Z represents a monovalent straight chain alkyl, branched alkyl or cycloalkyl group having from about 1 to about 24 carbon atoms. A class of

particularly suitable monofunctional (co)monomers include monoethylenically unsaturated monomers having homopolymer glass transition temperatures (T_g) greater than about $0^\circ C.$, preferably greater than $15^\circ C.$

[0167] Examples of suitable monofunctional (meth)acrylate monomers include but are not limited to those selected from the group consisting of methyl(meth)acrylate, isooctyl(meth)acrylate, 4-methyl-2-pentyl(meth)acrylate, 2-methyl-butyl(meth)acrylate, isoamyl(meth)acrylate, sec-butyl(meth)acrylate, n-butyl(meth)acrylate, tert-butyl(meth)acrylate, isobornyl(meth)acrylate, butyl methacrylate, ethyl(meth)acrylate, dodecyl(meth)acrylate, octadecyl(meth)acrylate, cyclohexyl(meth)acrylate and mixtures thereof.

[0168] Particularly suitable monofunctional (meth)acrylate monomers include those selected from the group consisting of isooctyl(meth)acrylate, isononyl(meth)acrylate, isoamyl(meth)acrylate, isodecyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, isobornyl(meth)acrylate, n-butyl(meth)acrylate, sec-butyl(meth)acrylate, and mixtures thereof.

[0169] Monofunctional vinyl ester monomers useful in the methods of the present disclosure include compositions of Formula 1 wherein X represents $H_2C=CHOC(O)-$, $m=1$, and Z represents a monovalent straight chain or branched alkyl group having from about 1 to about 24 atoms. Such vinyl ester monomers include but are not limited to those selected from the group consisting of vinyl acetate, vinyl 2-ethylhexanoate, vinyl caprate, vinyl laureate, vinyl pelargonate, vinyl hexanoate, vinyl propionate, vinyl decanoate, vinyl octanoate, and other monofunctional unsaturated vinyl esters of linear or branched carboxylic acids comprising 1 to 16 carbon atoms. Preferred vinyl ester monomers include those selected from the group consisting of vinyl acetate, vinyl laureate, vinyl caprate, vinyl-2-ethylhexanoate, and mixtures thereof.

[0170] Other suitable monofunctional (co)monomers include but are not limited to those selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid, crotonic acid, maleic acid, fumaric acid, sulfoethyl methacrylate, N-vinyl pyrrolidone, N-vinyl caprolactam, acrylamide, t-butyl acrylamide, dimethyl amino ethyl acrylamide, N-octyl acrylamide, acrylonitrile, mixtures thereof, and the like. Preferred monomers include those selected from the group consisting of acrylic acid, N-vinyl pyrrolidone, and mixtures thereof.

[0171] Free radically (co)polymerizable monofunctional macromonomers or oligomers (i.e., macromers) of Formula 1, wherein X is $H_2C=CR_1COO-$, R_1 represents $-H$ or $-CH_3$, m is 1, and Z is a monovalent (co)polymeric or oligomeric radical having a degree of (co)polymerization greater than or equal to 2, and that are substantially free of aromatic, chloro- and other moieties or substituents that significantly absorb ultraviolet radiation in the range of about 160 nm to about 240 nm, may also be used in the at least partially cured layers of the present disclosure.

[0172] Examples of such monofunctional macromonomers or oligomers include those selected from the group consisting of (meth)acrylate-terminated poly(methyl methacrylate), methacrylate-terminated poly(methyl methacrylate), (meth)acrylate-terminated poly(ethylene oxide), methacrylate-terminated poly(ethylene oxide), (meth)acrylate-terminated poly(ethylene glycol), methacrylate-terminated poly(ethylene glycol), methoxy poly(ethylene glycol) methacrylate, butoxy poly(ethylene glycol) methacrylate, and mixtures thereof. These functionalized materials are preferred because

they are easily prepared using well-known ionic (co)polymerization techniques and are also highly effective in providing grafted oligomeric and (co)polymeric segments along free radically (co)polymerized (meth)acrylate (co)polymer backbones.

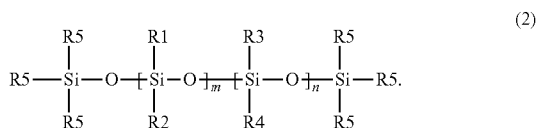
[0173] The viscosity of such monofunctional macromonomers or oligomers useful in practicing the methods of the present disclosure are generally high enough so that a thickener is not usually necessary; however, if desired, a thickener or particulate filler may be advantageously used as an adjuvant, as described further below.

[0174] Useful difunctional and other polyfunctional (meth)acrylate-functional free radically (co)polymerizable monomers include ester derivatives of alkyl diols, triols, tetrols, etc. (e.g., 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, and pentaerythritol tri(meth)acrylate). Difunctional and polyfunctional (meth)acrylate and methacrylate monomers described in U.S. Pat. No. 4,379,201 (Heilmann et al.), such as 1,2-ethanediol di(meth)acrylate, 1,12-dodecanediol di(meth)acrylate, pentaerythritol tetr(meth)acrylate can also be used in the present disclosure.

[0175] Difunctional and polyfunctional (meth)acrylates and methacrylates including (meth)acrylated epoxy oligomers, (meth)acrylated aliphatic urethane oligomers, (meth)acrylated polyether oligomers, and (meth)acrylated polyester oligomers, such as those commercially available from UCB Radcure Inc, Smyrna, Ga. under the EBECRYL tradename, and those available from Sartomer, Exton, Pa., may also be employed.

[0176] In further exemplary embodiments, the layer further includes at least one non-functional polysiloxane material. In some such further exemplary embodiments, the at least one non-functional polysiloxane material is selected from a poly(dialkylsiloxane), a poly(alkylaryl siloxane), a poly(diarylsiloxane), or a poly(dialkyldiarylsiloxane), optionally wherein the non-functional polysiloxane material comprises from 0.1 to 95 wt. %, inclusive, of the layer.

[0177] The non-functional polysiloxane material can be described generally by the following formula illustrating a siloxane backbone with a variety of substituents:



R1 through R4 represent the substituents pendant from the siloxane backbone. Each R5 may be independently selected and represent the terminal groups. Subscripts n and m are independently integers, and at least one of m or n is not zero.

[0178] As used herein, a “nonfunctional polysiloxane material” is one in which the R1, R2, R3, R4, and R5 groups are nonfunctional groups. As used herein, “nonfunctional groups” are either alkyl or aryl groups consisting of carbon, hydrogen, and in some embodiments, halogen (e.g., fluorine) atoms. In some embodiments, R1, R2, R3, and R4 are independently selected from the group consisting of an alkyl group and an aryl group, and R5 is an alkyl group. In some embodiments, one or more of the alkyl or aryl groups may

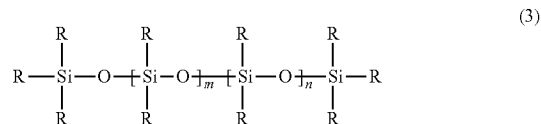
contain a halogen substituent, e.g., fluorine. For example, in some embodiments, one or more of the alkyl groups may be $-\text{CH}_2\text{CH}_2\text{C}_4\text{F}_9$.

[0179] In certain exemplary embodiments, R5 is a methyl group, i.e., the nonfunctional polysiloxane material is terminated by trimethylsiloxy groups. In some embodiments, R1 and R2 are alkyl groups and n is zero, i.e., the material is a poly(dialkylsiloxane). In certain embodiments, the alkyl group is a methyl group, i.e., poly(dimethylsiloxane) (“PDMS”). In other embodiments, R1 is an alkyl group, R2 is an aryl group, and n is zero, i.e., the material is a poly(alkylaryl siloxane). In some particular embodiments, R1 is a methyl group and R2 is a phenyl group, i.e., the material is poly(methylphenylsiloxane). In other particular embodiments, R1 and R2 are alkyl groups and R3 and R4 are aryl groups, i.e., the material is a poly(dialkyldiarylsiloxane). In certain additional embodiments, R1 and R2 are methyl groups, and R3 and R4 are phenyl groups, i.e., the material is poly(dimethyldiphenylsiloxane).

[0180] In further exemplary embodiments, the polysiloxane backbone may be linear. In some alternative exemplary embodiments, the polysiloxane backbone may be branched. For example, one or more of the R1, R2, R3, and/or R4 groups may be a linear or branched siloxane with functional or nonfunctional (e.g., alkyl or aryl, including halogenated alkyl or aryl) pendant and terminal groups. In other alternative exemplary embodiments, the polysiloxane backbone may be cyclic. For example, the silicone material may be octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, or dodecamethylcyclohexasiloxane.

[0181] In addition to the foregoing polysiloxanes, various (polyalkyl)disiloxanes may be advantageously used in the release liner layer in addition to or in place of at least a portion of the non-functional polysiloxane material. In some exemplary embodiments, hexamethyldisiloxane (i.e. $\text{O}[\text{Si}(\text{CH}_3)_3]_2$) may be used advantageously as such a non-functional (polyalkyl)disiloxane.

[0182] In some exemplary embodiments, the polysiloxane material may be functional. Generally, functional silicone systems include specific reactive groups attached to the linear, branched, or polysiloxane backbone of the starting material. For example, a linear “functional polysiloxane material” is one in which at least one of the R-groups of Formula 3 is a functional group:



[0183] In some such embodiments, a functional polysiloxane material is one in which at least 2 of the R-groups are functional groups. Generally, the R-groups of Formula 3 may be independently selected. In some embodiments, all functional groups are hydroxy groups and/or alkoxy groups. In certain such exemplary embodiments, the functional polysiloxane is a silanol terminated polysiloxane, e.g., a silanol terminated poly(dimethylsiloxane). In other such embodiments, the functional silicone is an alkoxy terminated poly(dimethylsiloxane), e.g., trimethylsiloxy terminated poly(dimethylsiloxane).

[0184] Other functional groups include those having an unsaturated carbon-carbon bond such as alkene-containing groups (e.g., vinyl groups and allyl groups) and alkyne-containing groups.

[0185] In addition to at least one functional R-group, the remaining R-groups may be nonfunctional groups, e.g., alkyl or aryl groups, including halogenated (e.g., fluorinated) alkyl and aryl groups. In some embodiments, the functionalized polysiloxane materials may be branched. For example, one or more of the R groups may be a linear or branched siloxane with functional and/or non-functional substituents. In some embodiments, the functionalized polysiloxane materials may be cyclic.

[0186] Although some embodiments of the present disclosure describe the use of functional silicone materials, the nature of the functional group is generally not critical to obtaining the desired cross-linked or cured polysiloxane materials. Although some reactions may occur through the functional groups, direct cross-linking between the polysiloxane backbones is often sufficient to obtain the desired degree of cure.

[0187] Various materials may be advantageously added to the (co)polymerizable composition used in forming the release liner layer in order to achieve advantageous effects. Some such adjuvants include, but are not limited to, the following optional additives.

[0188] In contrast to most previous methods for curing functional materials, the methods of the present disclosure do not require the use of added catalysts or initiators (e.g. photoinitiators). Thus, advantageously, in some exemplary embodiments, the methods of the present disclosure do not require the use of an added photoinitiator. In other words, exemplary methods of the present disclosure can be used to cure compositions that are "substantially free" of such catalysts or initiators (e.g., photoinitiators).

[0189] As used herein, a composition is "substantially free of added catalysts and initiators" if the composition does not include an "effective amount" of an added catalyst or initiator. As is well understood, an "effective amount" of a catalyst or initiator depends on a variety of factors including the type of catalyst or initiator, the composition of the curable material, and the curing method (e.g., thermal cure, UV-cure, and the like). In some embodiments, a particular catalyst or initiator is not present at an "effective amount" if the amount of catalyst or initiator does not reduce the cure time of the composition by at least 10% relative to the cure time for the same composition at the same curing conditions absent that catalyst or initiator.

[0190] As stated above, the use of added photoinitiators in the (co)polymerization of (meth)acrylate-functional siloxanes and oligomers introduces added costs and undesirable residuals and byproducts to the process. Articles bearing release layers prepared using the preferred initiator-free method are of particular significance in medical applications, where photoinitiator-induced contamination of release layers can lead to skin irritation and other undesirable reactions. Exclusion of this component can result in significant direct cost savings, plus elimination of any expenses involved in qualifying products containing significant amounts of a photoinitiator.

[0191] In other exemplary embodiments, an optional added photoinitiator may be advantageously included in the (co)polymerizable composition. Photoinitiators are particularly useful when higher (co)polymerization rates or very thin

release layers (or surface cures) are required. When used, photoinitiators can constitute from as low as about 0.001 to about 5 percent by weight of a (co)polymerization mixture. These photoinitiators can be organic, organometallic, or inorganic compounds, but are most commonly organic in nature. Examples of commonly used organic photoinitiators include benzoin and its derivatives, benzil ketals, acetophenone, acetophenone derivatives, benzophenone, and benzophenone derivatives.

[0192] In contrast to most previous methods for curing functional materials, the methods of the present disclosure do not require the use of organic solvents. Thus, in any of the foregoing exemplary embodiments, the layer may be (is) substantially free of an organic solvent. In any of the foregoing exemplary embodiments that are substantially free of organic solvent, the substantially inert atmosphere preferably includes no greater than 500 ppm oxygen, even more preferably no greater than 50 ppm oxygen.

[0193] In additional exemplary embodiments of any of the foregoing, the (co)polymerizable composition may further comprises a thickener. A thickener may be used in the (co)polymerizable composition of the present disclosure. A thickener may be used with monomers, but are generally not necessary with oligomers. Thickeners can increase the viscosity of the (co)polymerizable composition. The viscosity needs to be high enough to enable the (co)polymerizable composition to be coatable. In addition, the relatively high viscosity may play a role in contributing to the isolation of the free radicals, thereby improving conversion and reducing termination. A viscosity in the range of about 400-25,000 centipoise is typically desired.

[0194] Suitable thickeners are those which are soluble in the (co)polymerizable composition, and generally include oligomeric and polymeric materials. Such materials can be selected to contribute various desired properties or characteristics to resultant article. Examples of suitable polymeric thickening agents include copolymers of ethylene and vinyl esters or ethers, poly(alkyl acrylates), poly(alkyl methacrylates), polyesters such as poly(ethylene maleate), poly(propylene fumarate), poly(propylene phthalate), and the like.

[0195] Other suitable thickeners are particulate fillers which are insoluble in the (co)polymerizable composition, including but not limited to colloidal particulates having a median particle diameter of less than one micrometer. Suitable inorganic colloidal particulate fillers that may be used to good advantage as thickeners and/or adjuvants include commercially available fumed colloidal silicas such as CAB- β -SILs (Cabot Corp., Billerica, Mass.) and AER-O-SILs (Evonik North America, Parsippany, N.J.), colloidal alumina, and the like.

[0196] An exemplary apparatus for using short wavelength polychromatic ultraviolet radiation to cure a coating on a substrate is illustrated by FIG. 2. Exemplary substrates 10 each bearing a layer (e.g., 10A, 10B, 10C, 10D) of a UV-curable (co)polymerizable composition may be attached at various locations on the surface 21 of back up roll 20 located in vacuum chamber 30, as illustrated in FIG. 2. Short wavelength polychromatic ultraviolet radiation source(s) 40 (e.g., low-pressure short wavelength polychromatic mercury lamps) may be used to achieve curing of the layers on the substrates, thereby forming an at least partially cured layer (optionally a fully cured layer), such as e.g. a release layer or low adhesion backsize (LAB).

[0197] It will be understood that other apparatus, for example a continuous roll-to-roll web coater as described in U.S. Pat. No. 6,224,949, may be used in conjunction with one or more short wavelength polychromatic ultraviolet radiation sources to at least partially cure a layer of the (co)polymerizable composition on a substrate, for example, a continuous web or roll of material (e.g., a (co)polymeric film).

[0198] In further exemplary embodiments of any of the foregoing, the at least partially cured layer may be a release layer in a UV-radiation cured article, such as a liner or an adhesive tape or film. Optionally, the UV-radiation cured release layer is used as a surface release layer in a release liner, or as a low adhesion backsize (LAB) in an adhesive article.

[0199] UV-radiation cured layers prepared according to the methods of the present disclosure may be used in any of a wide variety of applications, including, e.g., as release layers, low adhesion backsize layers, and the like. Various exemplary applications are illustrated in FIG. 3. Article 100 comprises first substrate 110 and cross-linked silicone layer 120 adhered to first surface 111 of first substrate 110 forming release liner 210. In some such exemplary embodiments, the release layer has an unaged peel adhesion less than about 1.6 Newtons per decimeter. Optionally, the release layer has an aged peel adhesion less than 50 percent greater than the unaged peel adhesion.

[0200] Another particularly useful coating derived from the method of the present disclosure involves the (co)polymerization of a (meth)acrylated siloxane to form a release layer under a substantially inert (i.e. oxygen content no greater than 500 ppm) atmosphere. The use of silicone release layers has been an industry standard for many years, and is widely employed by liner suppliers and large, integrated tape manufacturers. Release layers prepared in this manner may exhibit any desired level of release, including (1) premium or easy release, (2) moderate or controlled release, or (3) tight release; premium release requires the least amount of force.

[0201] Premium release layers (i.e., those release layers having aged release forces in the range of up to about 1.0 N/dm) are typically used in release liner applications. Premium release layers are less useful, however, when coated on the back surface of pressure-sensitive adhesive tapes, because their low release force can cause tape roll instability and handling problems. Such a release layer on the back surface of a pressure-sensitive adhesive tape construction is often referred to as a "low adhesion backsize." Release layers having moderate to high levels of aged release (about 4.0 to about 35 N/dm) are especially useful when used as low adhesion backsizes.

[0202] In addition, layers containing (meth)acrylated polysiloxanes for use in the production of release layers may include, as (co)polymerizable constituents, 100% (meth)acrylated polysiloxanes or, alternatively may include free radically (co)polymerizable diluents in addition to the (meth)acrylated polysiloxanes. Such non-polysiloxane free radically (co)polymerizable diluents can be used to modify the release properties of the release layers of the present disclosure and also enhance the coating's mechanical properties and anchorage to backings or substrates used in pressure-sensitive adhesive tape or release liner constructions.

[0203] Depending on the ultimate properties desired in the (co)polymerized release layers, useful non-polysiloxane free radically (co)polymerizable diluents include monofunctional, difunctional and polyfunctional (meth)acrylate vinyl

ether, and vinyl ester monomers and oligomers. Difunctional and polyfunctional (meth)acrylate and methacrylate monomers such as 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, trimethylolpropane di(meth)acrylate, pentaerythritol tri(meth)acrylate, 1,2-ethanediol di(meth)acrylate, 1,12 dodecanediol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, pentaerythritol tetra(meth)acrylate and difunctional and polyfunctional (meth)acrylate and methacrylate oligomers including (meth)acrylated epoxy oligomers, (meth)acrylated aliphatic urethane oligomers, (meth)acrylated polyester oligomers, and (meth)acrylated polyethers such as those commercially available from Cytec Surface Specialties, Woodland Park, N.J. under the trade designation "EBECRYL", and from Sartomer, Exton, Pa., may also be advantageously employed.

[0204] The difunctional and polyfunctional (meth)acrylate monomers and oligomers employed in these release layers can be used at a concentration of from about 5 to about 95 weight percent, preferably from about 10 to 90 weight percent, based on the total weight of the release layer composition. Monofunctional monomers, such as the (meth)acrylate, vinyl ester and other free radically co(co)polymerizable monomers listed above, can also be added as non-polysiloxane free radically (co)polymerizable diluents in the release layer composition. When used, these monofunctional monomers may be employed at a concentration of up to about 25 weight percent based on the total weight of the release layer composition. Mixtures of monofunctional, difunctional and polyfunctional non-polysiloxane monomers and oligomers can also be used.

[0205] In another aspect, an adhesive article includes the foregoing release layer, and an adhesive layer adjacent to the release layer. Optionally, the adhesive layer includes one or more adhesive selected from a pressure sensitive adhesive, a hot melt adhesive, a radiation curable adhesive, a tackified adhesive, a non-tackified adhesive, a synthetic rubber adhesive, a natural rubber adhesive, a (meth)acrylic (co)polymer adhesive, and a polyolefin adhesive. In some embodiments, the adhesive may comprise a pressure sensitive adhesive, which preferably comprises a (meth)acrylic (co)polymer.

[0206] Thus, in some exemplary embodiments shown in FIG. 3, in addition to release liner 210, article 100 further comprises adhesive 140 releasably adhered to cross-linked silicone layer 120, forming transfer tape 220. In some embodiments, article 100 further comprises second substrate 150 adhered to adhesive 140, opposite cross-linked silicone layer 120.

[0207] In certain exemplary embodiments, the second substrate may be a release liner, e.g., a release liner similar to release liner 210, and article 100 may be a dual-linered transfer tape. In some embodiments, the second substrate may be permanently bonded to the adhesive and adhesive article 100 may be, for example, a tape or label.

[0208] Although not shown, in some embodiments, substrate 110 may be coated on both sides with a release material. In general, the release materials may be independently selected, and may be the same or different release materials. In some embodiments, both release materials are prepared according to the methods of the present disclosure. In some embodiments, self-wound adhesive articles may be prepared from such two-sided release liners. In some embodiments, one or more primer layers may be included. For example, in some embodiments, a primer layer may be located at surface 111 of substrate 110.

[0209] In various embodiments, the rolls of adhesive coated substrates of the present disclosure may be rolls of an adhesive tape that includes a backing layer and an adhesive coating disposed on a major surface of the backing layer. Common types of adhesive tapes include masking tape, electrical tape, duct tape, filament tape, medical tape, transfer tape, and the like.

[0210] The adhesive tape rolls may further include a release coating, or low adhesion backsize, disposed on a second major surface. Alternatively, the adhesive tape rolls may include a release liner (which may have a release coating disposed on a major surface thereof) in contact with the adhesive coated major surface of the backing layer. As another example, an adhesive tape roll may include a release liner comprising a release coating disposed on at least a portion of each of its major surfaces and an adhesive coating deposited over one of the release coatings.

[0211] Examples of suitable backing layers include, without limitation, CELLOPHANE, acetate, fiber, polyester, vinyl, polyethylene, polypropylene including, e.g., monoaxially oriented polypropylene and biaxially oriented polypropylene, polycarbonate, polytetrafluoroethylene, polyvinylfluoroethylene, polyurethane, polyimide, paper (e.g., Kraft paper), woven webs (e.g., cotton, polyester, nylon and glass), nonwoven webs, foil (e.g., aluminum, lead, copper, stainless steel and brass foil tapes) and combinations thereof.

[0212] The backing layers and release liners, can also include reinforcing agents including, without limitation, fibers, filaments (e.g., glass fiber filaments), and saturants (e.g., synthetic rubber latex saturated paper backings).

[0213] Objects and advantages of this invention are further illustrated by the following examples. The particular materials and amounts, as well as other conditions and details, recited in these examples should not be used to unduly limit this invention.

EXAMPLES

[0214] As used herein, all percentages and parts are by weight. Amounts of additives, e.g., crosslinkers, photoinitiator, tackifiers, etc. are expressed in parts per hundred resin (phr) in which 100 parts of the resin represents the weight of the monomers that form the polymer backbone, e.g., IOA, 2OA, AA.

Test Methods

Test Method 1: Shear Strength Test 1

[0215] Stainless steel (SS) plates were prepared for testing by cleaning with methyl ethyl ketone and a clean KIMWIPE tissue (Kimberly-Clark Corporation, Neenah, Wis.) three times. The adhesive films described were cut into strips (1.27 cm in width) and adhered by their adhesive to flat, rigid stainless steel plates with exactly 2.54 cm length of each adhesive film strip in contact with the plate to which it was adhered. A weight of 2 kilograms (4.4 pounds) was over the adhered portion. Each of the resulting plates with the adhered film strip was equilibrated at room temperature for 15 minutes. Afterwards, the samples were transferred to a 70° C. oven, in which a 500 g weight was hung from the free end of the adhered film strip with the panel tilted 2° from the vertical to ensure against any peeling forces. The time (in minutes) at which the weight fell, as a result of the adhesive film strip releasing from the plate, was recorded. The test was discontinued

at 10,000 minutes if there was no failure. In the Tables, this is designated as 10,000+ minutes. Two specimens of each tape (adhesive film strip) were tested and the shear strength tests were averaged to obtain the reported shear value in Tables 1-7. In some cases, the samples were prepared and hung in the same fashion but at room temperature (RT) rather than 70° C. The temperature at which the test was carried out is indicated in each table.

Test Method 2: 180° Angle Peel Adhesion Test 1

[0216] Peel adhesion was the force required to remove an adhesive-coated test specimen from a test panel measured at a specific angle and rate of removal. In the Examples, this force is expressed in ounces per inch width of coated sheet and the results are normalized to N/dm. The following procedure was used:

[0217] Peel adhesion strength was measured at a 180° peel angle using an IMASS SP-200 slip/peel tester (available from IMASS, Inc., Accord Mass.) at a peel rate of 305 mm/minute (12 inches/minute). Stainless steel (SS) test panels were prepared as described above. The cleaned panel was allowed to dry at room temperature. An adhesive coated film was cut into tapes measuring 1.27 cm×20 cm (½ in.×8 in.). A test sample was prepared by rolling the tape down onto a cleaned panel with 2 passes of a 2.0 kg (4.4 lb.) rubber roller. The prepared samples were dwelled at 23° C./50% RH for 15 minutes before testing. Four samples were tested for each example. The resulting peel adhesion was converted from ounces/0.5 inch to ounces/inch (N/dm) both values being reported in Tables 1-7.

Test Method 3: 90° Angle Peel Adhesion Test 2

[0218] For peel adhesion strength stainless steel (SS) substrates were cleaned as noted above. Two 1.0 inch (2.54 cm) by 3.0 inch (7.62 cm) strips of adhesive were laminated to a 0.005 in. (127 micrometers) aluminum foil backing for testing and were adhered to a stainless steel substrate (cleaned as described above) by rolling twice in each direction with a 6.8 kg roller onto the tape at 12 inches per minute (305 mm/min). The force required to peel the tape at an angle of 90° was measured after a 24 hour dwell at 25° C./50% humidity on an Instron (model number 4465, Instron Corporation, Norwood, Mass.). The measurements for the two tape samples were in pound-force per inch with a platen speed of 12 inches per minute (about 305 mm/min). The results were averaged and recorded in Table 8.

Test Method 4: Shear Strength Test 2

[0219] For shear strength a stainless steel (SS) backing was adhered to a stainless steel (SS) substrate (cleaned as described above) using a 1.0 inch (2.54 cm) by 0.5 inch (1.27 cm) square for 158° F. (70° C.) temperature shear testing. A weight of was 1 kg was placed on the sample for 15 minutes. A 500 g load was attached to the tape sample for testing. Each sample was suspended until failure and/or test terminated. The time to failure was recorded. Samples were run in triplicate and averaged for Table 8 below.

Test Method 5—Determination of Yellowing

[0220] Isopropyl alcohol (IPA) was dispensed onto a 2 inch (5.08 cm) by 3 inch (7.62 cm) glass microscopic slide, wiped dry with a clean KIMWIPE tissue repeated for a total of three washes with IPA and allowed to air dry. A 2 inch (5.08 cm) by

3 (7.62 cm) inch strip of adhesive tape with a release liner backing was adhered to the glass microscopic slide by rolling over the tape twice in each direction with a hand roller. Samples (with the protecting release liner removed) were then measured on a CIELAB color scale for b* using a Ultrascanpro® spectrophotometer (HunterLab, Reston, Va.). Samples were measured under four conditions and defined as follows:

- [0221] 1. Initial—adhesive measured with no UV or heat aging.
- [0222] 2. UV—adhesive exposed to 1.81 J/cm² of UV A light from a Fusion H bulb using a Model DRS-120 Fusion processor by Fusion UV Systems, Inc., Gaithersburg, Md., and measured after 24 hrs of UV exposure.
- [0223] 3. Heat—adhesive aged at 100° C. for 1 week in a Despatch LFD Series oven and measured 24 hours after removal from oven
- [0224] 4. UV and Heat—combination of UV (2) followed by Heat (3)

Samples were run in triplicate and averaged results are reported.

Test Method 6: 90° Angle Peel Adhesion Test 3 (Paper Surface)

[0225] A specimen measuring 1 in. (2.54 cm) wide and more than 3 in. (7.62 cm) long was cut in the machine direction from the test sample. The liner was removed from one side of the adhesive and it was placed on an aluminum panel measuring 2 in. by 5 in. (5.1 cm by 12.7 cm). The liner was removed from the other side of adhesive and placed on a strip of Boise copy paper (available from Packaging Corporation of America, Lake Forest, Ill., USA) under the trade designation “X-9” (92 brightness, 24 lb. (90 gsm/12M), 500 sheets, 8.5×11 (216 mm by 279 mm)) measuring 1 in. by more than 5 in. (2.54 cm by more than 12.7 cm) using light finger pressure. The construction was then rolled once in each direction with a standard FINAT test roller 4.5 lb (2 kg) at a speed of approximately 12 in./min. (305 mm/min). After applying the strips to the test panels, the panel samples were allowed to dwell at constant temperature and humidity (25° C./50% RH) for 10 minutes before testing. The test panel and strip were placed into a horizontal support. A jaw separation rate of 305 mm/min. was used. Test results were measured in grams force/in. and converted to Newtons/decimeter. The reported peel values are the average of three 90° angle peel measurements.

[0226] All the examples tested were cleanly removable from the copy paper unless specified otherwise, meaning that the paper did not tear and also did not have any staining or residue after removal of the adhesive.

Test Method 7: Shear Test 3 (Dry Wall)

Preparation of Drywall for Testing

[0227] The substrates employed were standard smooth drywall obtained from Home Depot (Woodbury, Minn.). Knock-down and orange-peel drywall was prepared by IUPAT (International Union of Painters and Allied Trades, 3205 Country Drive, Little Canada, Minn., USA). The drywall was primed using a paint roller with Sherwin-Williams Pro-Mar 200. Surfaces were dried for a minimum of 4 hours at ambient conditions before applying next coat of paint. White paint (Valspar Signature, Hi-def Advanced Color, Eggshell Inte-

rior, #221399, Ultra White/Base A) was applied to primed drywall using a new paint roller and allowed to dry at ambient conditions until tackless before applying a second coat of the same color. The final painted drywall was dried overnight at ambient conditions and then placed into a 120° C. oven for 1 week. Samples were removed from oven and cut into desired dimensions using a draw knife. Samples were dusted off using KIMWIPE tissue, paper towels, or air (no cleaning with solvents) to remove dust left over from cutting before use in testing.

[0228] A standard static shear test was performed at elevated temperature according to Pressure Sensitive Tape Council (Chicago, Ill.) PSTC-107 (procedure G). The test was performed at 70° F./50% Relative Humidity. The sample area of adhesive bonded to the prepared drywall surface was 1 in. (2.54 cm) in the vertical direction by 1 in. (2.54 cm) in the width direction (rather than 0.5 in. by 0.5 in. (1.27 cm by 1.27 cm) as called for by the method). Then a 6.8 kg weight was placed on top of the bonded sample area for 1 minute. After a dwell time of 60 seconds, the test specimen was hung in the shear stand at desired temperature and loaded immediately with a 250 g weight. The time to failure for the adhesive bond was recorded in minutes.

Test Method 8: Dynamic Mechanical Analysis

[0229] Examples 55 and 56 (0.025 in. (625 micrometers) thickness) were analyzed by Dynamic Mechanical Analysis (DMA) using a Discovery Hybrid parallel plate rheometer (TA Instruments, New Castle, Del.) to characterize the physical properties of each sample as a function of temperature. Rheology samples were prepared by punching out a section of the PSA with an 8 mm circular die, removing it from the release liners, centering it between 8 mm diameter parallel plates of the rheometer, and compressing until the edges of the sample were uniform with the edges of the top and bottom plates. The furnace doors that surround the parallel plates and shafts of the rheometer were shut and the temperature was equilibrated at 20° C. and held for 1 minute. The temperature was then ramped from 20° C. to 125 or 130° C. at 3° C./min while the parallel plates were oscillated at an angular frequency of 1 Hertz and a constant strain of 5 percent. The results are depicted in FIG. 1.

Test Method 9: 180° Angle Peel Adhesion Test 4 (Liner Release)

[0230] The 180 degree peel adhesion strength between the release liner and adhesive was measured for both sides of the liner: the “wet cast” side, also referred to herein as the “tight side release” where adhesive was directly cast onto the release liner, and the “dry laminated”, also referred to herein as the “easy side release where cured adhesive was laminated to the release liner. Liner release strengths for both sides was measured after aging for seven days at 23° C. and 50% relative humidity. A 2.54 cm wide by approximately 20 cm in long sample of the adhesive transfer tape was cut using a specimen razor cutter. For tight side testing the sample was applied with its exposed adhesive surface down and lengthwise onto the platen surface of a peel adhesion tester (Model SP2000, IMASS Incorporated, Accord, MA). The adhesive transfer tape was then rolled twice with a 2 kg rubber roller at a rate of 61 cm/minute. The tight side release liner was carefully lifted away from the adhesive layer adhered to the platen surface, doubled-back at an angle of 180 degrees, and secured

to the clamp of the peel adhesion tester. The 180 degree angle release liner peel adhesion strength was then measured as the liner was peeled from the adhesive at a rate of 230 cm/min (90 in/min). A minimum of two test specimens were evaluated with results obtained in grams/inch which were used to calculate the average release force. All release tests were carried out at 23° C. and 50% relative humidity (RH). For easy side testing two samples were applied with the first attached the platen surface and the second to the outer exposed (easy side) surface of the release liner covering the first adhesive layer. The second sample was peeled away from the easy side release liner.

Test Method 10: 180° Angle Peel Adhesion Test 5 (Adhesive Strength)

[0231] Both faceside adhesion (i.e., the adhesive strength of the adhesive surface in contact with the easy side release surface of the release liner) and backside adhesion (i.e., the adhesive strength of the adhesive surface in contact with the tight side release surface of the release liner) were evaluated.

[0232] Stainless steel (SS) plates were prepared for testing by cleaning with one rinse of acetone followed by three rinses of heptane and drying. Adhesive transfer tape was used to prepare a single coated tape having a 0.001 inch (25 micrometer) thick polyester backing. Two types of tapes were prepared. The first had the adhesive joined to the backing by the adhesive surface that had been in contact with the tight side release surface of the release liner, resulting in an exposed adhesive surface that had been in contact with the easy side release surface of the release liner. The second had the adhesive joined to the backing by the adhesive surface that had been in contact with the easy side release surface of the release liner, resulting in an exposed adhesive surface that had been in contact with the tight side release surface of the release liner. As a result, the first tape sample was evaluated for faceside adhesive strength and the second tape sample was evaluated for backside adhesive strength.

[0233] The tape samples were 2.54 cm wide by 20 cm long (1 in. by 8 in.). These were adhered to the stainless steel plates by means of the exposed adhesive, with 2.54 cm (1 in.) of length in contact with the plate, and rolled down with two passes in each direction of a 2 kg rubber roller. The samples were allowed to dwell for 15 minutes at 23° C./50% RH followed by peel adhesion testing at an angle of 180° at a rate of 30.5 cm/min (12 in./min) using an IMASS peel tester (described previously). The results were recorded in ounces/inch (oz/in) and also converted to Newtons/decimeter (N/dm).

Test Method 11: Overlap Shear Test 4

[0234] Flat, rigid, stainless steel plates were prepared for testing by cleaning with one rinse of acetone followed by three rinses of heptane and drying. The adhesives to be tested were cut into strips measuring 1.27 cm wide and 7.62 cm long, reinforced with 0.002 in (51 micrometer) aluminum foil and adhered by their exposed adhesive surface to the stainless steel plates with 2.54 cm (1 in.) of length and 1.27 cm (0.5 in.) of width of each reinforced adhesive film strip in contact with the plate. A weight of 2 kilograms (4.4 pounds) was rolled twice over the adhered portion. Each of the resulting test specimens was equilibrated at room temperature for 15 minutes. Next, the specimens were transferred to a 70° C. oven, in which a 1000 gram or 500 gram weight was hung from the

free end of the adhered film strip with the panel tilted 2° from the vertical. The time (in minutes) at which the weight fell, as a result of the adhesive film strip releasing from the plate, was recorded. The test was discontinued at 10,000 minutes if there was no failure and the result recorded as 10,000+ minutes. Two samples of each tape (adhesive film strip) were tested and the shear strength test results were averaged to obtain the reported shear values.

Materials

[0235] Material suppliers are listed with the first usage of the material. If not specified, solvents and reagents can be obtained from Aldrich. Suppliers are listed in the examples as follows:

Aldrich—Sigma Aldrich, Milwaukee, Wis.

Alfa—Alfa Aesar, Ward Hill, Mass.

BASF—BASF Corporation, Florham Park, N.J.

EMD—EMD Chemicals, Gibbstown, N.J.

Dupont—E. I du Pont de Nemours and Company, Wilmington, Del.

Mitsubishi—Mitsubishi Polyester Film Inc., Greer, S.C.

TCI—TCI, Tokyo, Japan

VWR—VWR International, LLC., Radnor, Pa.

[0236] 2-Octyl Acrylate (2OA)—Prepared according to Preparatory Example 1 of U.S. Pat. No. 7,385,020

Iso-octyl Acrylate (IOA)—Obtained from 3M Company (St. Paul, Minn., USA)

Acrylic Acid (AA)—Obtained from BASF Corporation (Florham Park, N.J., USA)

Isobornyl Acrylate (IBXA)—Obtained from San Esters Corporation (New York, N.Y., USA)

Dicyclopentenyl Acrylate (DPA)—Obtained from Monomer-Polymer Laboratories (Windham, N.H., USA)

Irgacure 651 (651)—Obtained from BASF Corporation (Florham Park, N.J., USA)

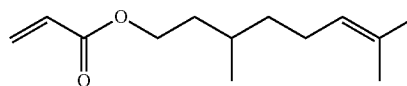
Irganox 1076 (1076)—Obtained from BASF Corporation (Florham Park, N.J., USA)

Regalrez 6108—Obtained from Eastman Chemical Corporation (Kingsport, Tenn., USA)

Preparatory Example 1

Citronellyl Acrylate (CiA)

[0237]



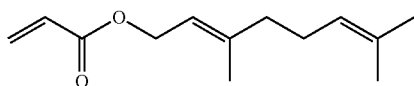
[0238] A mixture of β -citronellol (300.00 g, 1.92 mol; Aldrich), hexane (1500 mL), and triethylamine (212.49 g, 2.10 mol; Aldrich) was cooled in an ice bath. Acryloyl chloride (190.08 g, 2.10 mol; Aldrich) was added dropwise over 5 hours. The mixture was stirred for 17 hours at room tempera-

ture, and then filtered. The solution was concentrated under vacuum and washed with water. The solvent was removed under vacuum to provide a crude oil that was purified by vacuum distillation. A colorless oil (282.83 g of citronellyl acrylate) was collected at 70-75° C. at 0.30 mm Hg.

Preparatory Example 2

Geraniol Acrylate (GrA,
[(2E)-3,7-dimethylocta-2,6-dienyl]prop-2-enoate)

[0239]

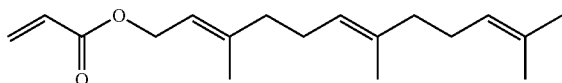


[0240] A 2-liter round bottomed flask fitted with an overhead stirrer, an addition funnel, and a condenser was charged with geraniol (195 g, 1.25 mol; Alfa), triethylamine (152 g, 1.50 mol), and methylene chloride (500 mL; EMD) and then cooled in an ice bath, and the mixture stirred. A solution of acryloyl chloride (124 g, 1.38 mol;) in methylene chloride (100 mL) was added dropwise over a 45 minute period. When addition was complete, the ice bath was removed and the reaction mixture was stirred at room temperature overnight. The reaction mixture was filtered to remove the precipitated salts and washed 2 times with 150 mL portions of a 10% solution of hydrochloric acid in water and 2 times with 150 mL portions of a saturated solution of sodium bicarbonate in water. The methylene chloride solution was dried over potassium carbonate, filtered, and the solvent was removed at reduced pressure. Phenothiazine (50 mg, 0.2 mmol; TCI) was added and the product was distilled at reduced pressure. Product was collected at a boiling range of 87 to 92° C. and a pressure range of 0.50 to 0.65 mm. NMR analysis of the distillate confirmed the structure as geraniol acrylate.

Preparatory Example 3

Farnesol Acrylate (FrA, [(2E,6E)-3,7,11-trimethyldodeca-2,6,10-trienyl]prop-2-enoate)

[0241]

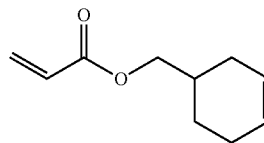


[0242] Farnesol acrylate was prepared as described in Preparatory Example 2 except the reagents were farnesol (181 g, 0.81 mol; Alfa), triethylamine (99 g, 0.98 mol), methylene chloride (350 mL), and acryloyl chloride (81 g, 0.90 mol) in methylene chloride (90 mL). The resulting product was distilled and collected at a boiling range of 112 to 118° C. and a pressure range of 0.18 to 0.25 mm. NMR analysis of the distillate confirmed the structure as farnesol acrylate.

Preparatory Example 4

3-Cyclohexene Methyl Acrylate (CMA)

[0243]

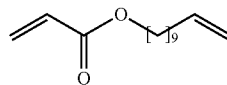


[0244] A mixture of 3-cyclohexene methanol (95.00 g, 0.85 mol; Aldrich), methylene chloride (300 mL), and triethylamine (94.11 g, 0.93 mol; EMD) was cooled in an ice bath. Acryloyl chloride (84.17 g, 0.93 mol) was added dropwise over 4 hours. The mixture was stirred for 17 hours at room temperature, then filtered. The solution was concentrated under vacuum, then diluted with ethyl acetate (500 mL; VWR). The solution was washed with saturated aqueous sodium bicarbonate and brine, then dried over magnesium sulfate. The solvent was removed under vacuum to provide a crude oil that was purified by vacuum distillation. A colorless oil (129.92 g of 3-cyclohexene methyl acrylate) was collected at 62-64° C. at 1.0 mm Hg.

Preparatory Example 5

Undecenyl Acrylate (UDA)

[0245]

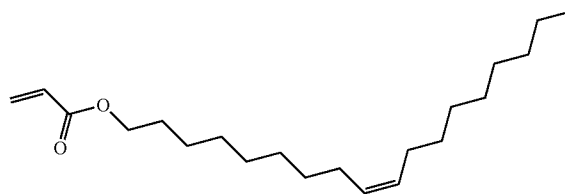


[0246] Undecenyl alcohol (69.66 g, 0.4090 mol; Alfa), toluene (300 mL), and triethylamine (45.53 g, 0.45 mol) were added to a 1000 mL 3-necked round bottomed flask. The solution was stirred and cooled to 0° C. in a nitrogen atmosphere. Acryloyl chloride (40.73 g, 0.45 mol) was added dropwise via addition funnel over a period of 4 hours. The cloudy yellow mixture was then slowly warmed to room temperature and placed on the rotary evaporator to remove the toluene. Ethyl acetate (300 mL) was added and the mixture was filtered through celite, washed with saturated sodium bicarbonate, and then the solvent was removed under vacuum. The crude yellow oil was purified by vacuum distillation. A faint yellow oil (55/75 g of 10-undecenyl acrylate) was collected at 90-96° C. @ 0.88 mm Hg.

Preparatory Example 6

Oleyl Acrylate (OA)

[0247]



[0248] A mixture of oleyl alcohol (90.00 g, 0.34 mol; Alfa), methylene chloride (300 mL), and triethylamine (38.45 g, 0.38 mol) was cooled in an ice bath. Acryloyl chloride (34.89 g, 0.38 mol) was added dropwise over 2 hours. The mixture was stirred for 17 hours at room temperature, then filtered. The solution was concentrated under vacuum. The crude oil was loaded on a column of silica gel and eluted with hexane. The eluted solution was collected and concentrated under vacuum to provide a colorless oily liquid (68.25 g of oleyl acrylate). Brij 02 Acrylate was prepared according to US2012/0154811.

Examples 1-5 and Comparative Examples C1-C4

[0249] Compositions were prepared by charging a 500 mL jar with 270 g (90 wt. %) 2-octyl acrylate (2OA), 30 g (10 wt. %) of acrylic acid (AA; BASF), 0.12 g (0.04 phr) of photoinitiator 1 (2,2-dimethoxy-2-phenylacetophenone, Irgacure 651; BASF), and the amount in phr of one of the monofunctional acrylates (from the preparatory examples) as shown in Table 1. The monomer mixture was purged with nitrogen for 10 minutes then exposed to low intensity UV A light (less than 10 mW/cm², referred to as UV A because the output is primarily between 320 and 390 nm with a peak emission at around 350 nm which is in the UV A spectral region) until a coatable syrup (Brookfield viscosity of 100-8000 cP) was formed, after which an additional 0.48 g (0.16 phr) of photoinitiator 1 was mixed into the composition.

[0250] The pre-adhesive (i.e. syrup) compositions were then coated on a release liner at a thickness of about 0.005 inches (127 micrometers) and cured under a nitrogen atmosphere by further exposure to UVA light from 350 BL light bulbs (40 watt, Osram Sylvania) as shown in Table 1 for various times to form a pressure sensitive adhesive (PSA). Total energies were measured using a PowermapTM radiometer equipped with a low intensity sensing head (available from EIT Inc., Sterling, Va.). The PSA was then laminated under hand pressure with a small silicone roller to a primed 0.002 inch (51 micrometer) thick poly(ethylene terephthalate) backing (trade designation Hostaphan 3SAB PET film; Mitsubishi Polyester Film, Incorporated, Greer, S.C.) to form a tape for adhesive testing.

[0251] Comparative Examples C1 and C2 were prepared as described above except that no crosslinker was added to the prior to the syringing step. The amounts of 1,6-hexanediol diacrylate (HDDA) was mixed into the pre-adhesive formulations before coating and curing.

[0252] Comparative Examples C3 and C4 were prepared as described in C1 and C2 except that the crosslinker was 2,4-bis(trichloromethyl)-6-(3,4-dimethoxyphenyl)-triazine (T1).

[0253] The adhesives were tested for shear adhesion at 70° C., and 180° angle peel adhesion. Results are shown in Table 1.

TABLE 1

Ex	Crosslinker			Total UV Exposure mJ/cm ²	70° C. Shear (min) (Test) Method 1)	180° Angle Peel Adhesion to SS (oz/in, N/dm) (Test) Method 2)
	Material	phr	(g)			
1	CiA	0.6	1.8	2540	10,000+	90.3, 98.6
2	CiA	0.8	2.4	2540	10,000+	92.9, 101.6

TABLE 1-continued

Ex	Crosslinker			Total UV Exposure mJ/cm ²	70° C. Shear (min) (Test) Method 1)	180° Angle Peel Adhesion to SS (oz/in, N/dm) (Test) Method 2)
	Material	phr	(g)			
3	CiA	1.0	3.0	2540	10,000+	84.9, 92.9
4	GrA	0.6	1.8	1016	10,000+	91.1, 99.7
5	FrA	0.6	1.8	1016	8264	85.1, 93.1
C1	HDDA	0.1	0.3	1016	3432	41.3, 45.2
C2	HDDA	0.2	0.6	1016	5890	17.2, 18.8
C3	T1	0.1	0.3	593	10,000+	79.1, 86.2
C4	T1	0.2	0.6	4572	10,000+	74.3, 81.3

Examples 6-10, Comparative Examples C5-C8

[0254] Adhesive compositions and tapes were prepared and tested as described in Examples 1-5 except that 270 g (90 wt. %) of isooctyl acrylate (IOA) were used instead of 2OA and the crosslinkers in the amounts shown in Table 2 were used. Test results are shown in Table 2.

[0255] Adhesives tapes for Comparative Examples C5-C6 were prepared and tested as described in Comparative Examples C1-C2. Results are shown in Table 2.

[0256] Adhesives tapes for Comparative Examples C7-C8 were prepared as described in Comparative Examples C3-C4. Results are shown in Table 2.

TABLE 2

Ex	Crosslinker			Total UV Exposure mJ/cm ²	70° C. Shear (min) (Test) Method 1)	180° Angle Peel Adhesion to SS (oz/in, N/dm) (Test) Method 2)
	Material	phr	(g)			
6	CiA	1.0	3.0	2535	10,000+	66.9, 73.2
7	GrA	0.8	2.4	2535	10,000+	65.5, 71.7
8	GrA	1.0	3.0	2535	10,000+	73.9, 80.8
9	FrA	0.8	2.4	2535	10,000+	70.3, 77.0
10	FrA	1.0	3.0	2535	10,000+	66.5, 72.8
C5	HDDA	0.1	0.3	2535	1463	68.9, 75.4
C6	HDDA	0.2	0.6	2535	3481	64.5, 70.6
C7	T1	0.1	0.3	2535	10,000+	69.5, 76.0
C8	T1	0.2	0.6	2535	10,000+	67.6, 74.0

Examples 11-25

[0257] Adhesive compositions were prepared by charging an 8 ounce jar with 45 g of IOA, 5 g of AA, 0.02 g of photoinitiator 1 and the amounts and type of monofunctional acrylates (from preparatory examples) as shown in Table 3. The monomer mixture was purged with nitrogen for 5 minutes then exposed to UV A light from a low intensity black bulb (15 watt, 365 nm peak) until the viscosity increased and a coatable syrup was prepared.

[0258] An additional 0.08 g (0.16 phr) of the photoinitiator 1 was mixed into the syrup. The compositions were then knife-coated between two clear release liners at a 0.005 inch (127 micrometers) thickness and cured by exposure to UV A light from 350 BL light bulbs (40 watt, Osram Sylvania) as shown in Table 3. Total UV exposure was measured with an Uvirad® Low Energy UV Integrating Radiometer (EIT, Inc.,

Sterling, Va.). Tapes were prepared as described in Examples 1-5, and tested for shear and peel adhesion. Results are shown in Table 3.

TABLE 3

Ex	Crosslinker			Total UV Exposure mJ/cm ²	70° C. Shear (min) (Test)	180° Angle Peel Adhesion to SS (oz/in, N/dm) (Test)
	Material	phr	(g)		Method 1)	Method 2)
11	CiA	2.0	1.0	2189	10,000+	60.3, 66.0
12	CiA	5.0	2.5	2189	10,000+	43.1, 47.2
13	CiA	10.0	5.0	2189	10,000+	27.1, 29.6
14	GrA	2.0	1.0	2189	10,000+	66.7, 73.0
15	GrA	5.0	2.5	2189	10,000+	44.2, 48.4
16	GrA	10.0	5.0	2189	10,000+	23.4, 25.6
17	FrA	2.0	1.0	2189	10,000+	51.7, 56.6
18	FrA	5.0	2.5	2189	10,000+	40.7, 44.5
19	FrA	10.0	5.0	2189	10,000+	26.7, 29.2
20	UDA	1.0	0.5	1712	10,000+	51.2, 56.0
21	UDA	5.0	2.5	1712	10,000+	21.7, 23.7
22	CMA	1.0	0.5	1712	1092	75.6, 82.7
23	CMA	5.0	2.5	1712	10,000+	68.2, 74.6
24	OA	1.0	0.5	1186	10,000+	74.6, 81.6
25	OA	5.0	2.5	1186	10,000+	60.0, 65.6
26	Brij O2 A	1.0	0.5	1500	2098	76.1, 83.2
27	Brij O2 A	5.0	2.5	1500	10,000+	61.4, 67.1

Examples 28-33

[0259] Adhesives and tapes were prepared and tested as described in Examples 11-27 except that the monofunctional acrylate crosslinker was not added to the syrup composition, but mixed in prior to coating and curing. The amounts of crosslinker and test results are shown in Table 4.

TABLE 4

Ex	Crosslinker			Total UV Exposure mJ/cm ²	70° C. Shear (min) (Test)	180° Angle Peel Adhesion to SS (oz/in, N/dm) (Test)
	Material	phr	(g)		Method 1)	Method 2)
28	CiA	1.0	0.5	1422	10,000+	62.7, 68.6
29	CiA	2.0	1.0	1422	10,000+	51.2, 56.0
30	GrA	1.0	0.5	1422	10,000+	69.1, 75.6
31	GrA	2.0	1.0	1422	10,000+	54.9, 60.1
32	FrA	1.0	0.5	1422	10,000+	66.0, 72.2
33	FrA	2.0	1.0	1422	10,000+	52.9, 57.9

Examples 34-39

[0260] Compositions for Examples 34-37 were prepared by charging a 500 mL jar with 467.5 g (93.5 wt. %) of IOA, 32.5 g (6.5 wt. %) of AA, 0.2 g (0.04 phr) of photoinitiator 2 (trade designation Irgacure 184; BASF), and the amounts of CiA shown in Table 5. The monomer mixture was purged with nitrogen for 5-10 minutes then exposed to low intensity UV A radiation until a coatable syrup was formed.

[0261] An additional 1.75 g (0.16 phr) of photoinitiator 2 and 50 g (10 phr) of tackifier (trade designation Foral 85LB, Eastman Chemical Co., Kingsport, Tenn.) were then mixed into each composition. The compositions were then coated onto a release liner at 0.004 inch (101.6 micrometer) thickness and cured under a nitrogen atmosphere by exposure to UV A light from 350 BL light bulbs (40 watt, Osram Sylva-

nia) followed by exposure to high intensity UV C light (greater than 10 mW/cm², referred to as UV C because the output of the bulbs is nearly monochromatic between 250 and 260 nm in the UV C spectral region) to form a PSA. Total UV exposure was measured as described for Examples 1-5 and is shown in Table 5. Tapes were prepared as in Examples 1-5 for adhesive testing.

[0262] Compositions and tapes for Example 38 were prepared and tested in the same manner as Example 35 except that 2OA was used instead of IOA. Test results for all tapes are shown in Table 5.

[0263] Compositions and tapes for Example 39 were prepared and tested as in Example 35 except the tackifier was trade designation Regalrez 6108 (Eastman Chemical Co., Kingsport, Tenn.) instead of trade designation Foral 85LB.

TABLE 5

Ex	Crosslinker			Total UV Exposure mJ/cm ² (UVA + UVC)	70° C. Shear (min) (Test)	180° Angle Peel Adhesion to SS (oz/in, N/dm) (Test)
	Material	phr	(g)		Method 1)	Method 2)
34	CiA	2	10	854 + 276	10,000+	59.5, 65.1
35	CiA	3	15	854 + 276	10,000+	49.6, 54.3
36	CiA	5	25	909 + 252	10,000+	25.1, 27.5
37	CiA	10	50	909 + 252	10,000+	18.0, 19.7
38	CiA	3	15	909 + 252	10,000+	43.8, 47.9
39	CiA	3	15	880 + 237	10,000+	45.1, 49.3

Examples 40-42

[0264] Compositions were prepared by charging a 500 mL jar with 420.8 g (93.5 wt. %) of IOA, 29.3 (6.5 wt. %) g of AA, 0.18 g (0.04 phr) of photoinitiator 2 (trade designation Irgacure 184), and the amounts of CiA shown in Table 6. The monomer mixture was purged with nitrogen for 5-10 minutes then exposed to low intensity ultraviolet radiation until a coatable syrup was prepared.

[0265] An additional 1.58 g (0.16 phr) of photoinitiator 2, 45 g (10 phr) of tackifier (trade designation Foral 85LB), and the amounts of triazine T2 (2,4-bis(trichloromethyl)-6-(4-methoxyphenyl)-triazine) shown in Table 6 were mixed into the composition. The pre-adhesive (syrup) formulations were then coated onto a release liner at 0.004 inch (101.6 micrometer) thickness and cured under a nitrogen atmosphere by exposure to 883 mJ/cm² of UV A light from 350 BL light bulbs (40 watt, Osram Sylvania). Total UV exposure was measured as described in Examples 1-5. The PSA was then laminated under hand pressure with a small silicone roller to a primed poly(ethylene terephthalate) (Polyester Films, Incorporated, Greer, S.C.) film backing for adhesive testing.

TABLE 6

Ex	Crosslinker (CiA/T2)			70° C. Shear (min) (Test)	180° Angle Peel Adhesion to SS (oz/in, N/dm) (Test)
	Material	phr	(g)		
40	CiA and T2	0.8/0.11	3.38/0.51	10,000+	60.9, 66.6
41	CiA and T2	1.5/0.08	6.75/0.34	10,000+	54.2, 59.3
42	CiA and T2	2.3/0.04	10.13/0.17	10,000+	48.5, 53.1

Examples 43-46

[0266] Compositions for Examples 43-45 were prepared by charging a 500 mL jar with 346.9 g (82.6 wt %) of IOA, 3.2 g (0.1 wt %) of AA, 0.14 g (0.04 phr) of photoinitiator1, and the amounts of CiA shown in Table 7. The monomer mixture was purged with nitrogen for 5-10 minutes then exposed to low intensity ultraviolet radiation to form a coatable syrup.

[0267] An additional 0.84 g (0.16 phr) of photoinitiator1, 0.26 g of antioxidant (Irganox 1076), 70 g (17 wt. %) of isobornyl acrylate (IBXA), and 100.8 g (24 phr) of tackifiers (trade designation Regalrez 6108) were added. The compositions were mixed thoroughly by rolling overnight and coated onto release liner at 5 mil (127 micrometer) thickness and cured under a nitrogen atmosphere by exposure to 827 mJ/cm² of UV A light followed by exposure to 236 mJ/cm² UV C light to form a PSA as described in Examples 34-39. Total UV exposure was measured as described in Examples 1-5. The PSA was then laminated to a primed poly(ethylene terephthalate) (Mitsubishi Polyester Films) backing for adhesive testing. Results are shown in Table 7.

[0268] Compositions and tapes for Example 46 were prepared using 2OA instead of IOA.

TABLE 7

Ex	Crosslinker			70° C. Shear (min) (Test Method 1)	180° Angle Peel Adhesion to SS (oz/in, N/dm) (Test Method 2)
	Material	phr	(g)		
43	CiA	3	10.5	19	71.6, 78.3
44	CiA	5	17.5	159	49.0, 53.6
45	CiA	10	35.0	10,000+	25.8, 28.2
46	CiA	3	10.5	63	71.8, 78.5

Examples 47-48 and Comparative Examples C9-C10

[0269] Example 47 was prepared by charging a 500 mL jar with 306.3 g (87.5 wt. %) IOA, 43.8 g (12.5 wt. %) of AA, 0.14 g (0.04 phr) of photoinitiator 1, and 2.1 g (0.6 phr) of CiA. The monomer mixture was purged with nitrogen for 10 minutes then exposed to low intensity UV A radiation until a coatable syrup was formed, after which another 0.67 g (0.16 phr) of photoinitiator1 was added. Next, 6.0 g (1.7 phr) of trade designation HDK H15 fumed silica (Wacker Silicones) were added and the syrup was mixed with a trade designation Netzsch Model 50 Dispersator. When the fumed silica was completely dispersed, 28 g (8 phr) of glass bubbles (K15, 3M Company, St. Paul Minn.) were added and the composition was mixed thoroughly by rolling overnight.

[0270] The composition was then coated between release liners at a 0.038 inch (965.2 micrometers) thickness and cured by 741 mJ/cm² of UV A light from 350 BL light bulbs (40 watt, Osram Sylvania) to form a PSA. Total UV exposure was measured as described in examples 1-5.

[0271] A composition and tape Example C9 were prepared as in Example 47 except that no CiA was added to the syrup composition, and 0.19 g (0.055 phr) HDDA was added to the syrup before coating.

[0272] A composition and tape for Example 48 were prepared as in Example 47 except the composition for the syrup was 315 g (90 wt. %) of 2OA, 35 g (10 wt %) of AA, 0.14 g (0.04 phr) of photoinitiator 1, and 3.5 g (1 phr) of CiA.

[0273] A composition and tape for Example C10 were prepared as in Example C9 except using the composition of Example 48.

[0274] Example 47-48 and C₉₋₁₀ were prepared for adhesive testing and tested as outlined in the test methods 3 and 4.

TABLE 8

Ex	Backbone Monomer	Crosslinker/phr	70° C. Shear (min) (Test Method 4)	90° Peel Adhe- sion to SS (lbf-in, kg-cm) (Test Method 3)
47	IOA	CiA/0.6	10,000+	23.5, 27.1
48	2OA	CiA/1	10,000+	19.2, 22.1
C9	IOA	HDDA/0.055	10,000+	23.1, 26.6
C10	2OA	HDDA/0.055	10,000+	22.4, 25.8

[0275] Adhesive samples from Examples 3, 35-38, 40-42, and 45, and C3 were measured for yellowing as described above. Results are shown in Table 9.

TABLE 9

Ex	Adhesive Thickness (mil)	b* Initial	b* UV	b* Heat	b* UV & Heat
3	5	0.21	0.33	0.36	0.73
35	4	0.22	0.42	0.69	1.29
36	4	0.23	0.30	0.68	1.13
37	4	0.25	0.32	0.63	0.91
38	4	0.23	0.45	0.68	1.11
40	4	0.87	1.28	1.38	2.05
41	4	0.67	0.93	0.98	1.50
42	4	0.44	0.52	0.77	1.11
45	5	0.21	0.32	0.30	0.59
C3 (T1)	5	0.76	1.33	1.14	1.98

Examples 49-52 and C11

[0276] Adhesive composition and tape 49 was made by charging a glass bottle with 54 g (90 wt. %) 2OA, 6 g (10 wt. %) of AA, 0.6 g (1 phr) CiA, 0.06 g (0.1 phr) of Vazo 52 (Dupont), and 140 g ethyl acetate. This mixture was purged with nitrogen gas for 20 minutes, and the bottle was sealed and placed in a water bath at 52° C. with shaking for 20 hours. The bottle was then removed, and sparged with air for 1 minute. 30 g of the final polymer solution was combined in a jar with 0.17 g (2 phr) of photoinitiator 1 and rolled to ensure thorough mixing. The composition was then coated at 0.005 inch (127 micrometers) thickness on a 0.002 inch (51 micrometer) thick Mitsubishi Hostaphan 3SAB PET polyester film, and dried in an oven at 70° C. for 30 minutes. The dried adhesive was covered with a release liner and exposed to 982 mJ/cm² of UVA light over 10 minutes. Adhesive testing was then carried out according to test methods 1 and 2 except the shear strength test was carried out at room temperature rather than 70° C. Results are shown in Table 10.

[0277] Adhesive composition and tape 50 was made and tested in the same manner as example 46 except that the composition was 90 g (90 wt. %) 2OA, 10 g (10 wt. %) of AA, 2 g (2 phr) CiA, 0.04 g (0.04 phr) isooctyl thioglycolate, 0.1 g (0.1 phr) of Vazo 67 (Dupont), and 233.3 g ethyl acetate, and the cure was carried out with 762 mJ/cm² of UVA light over 10 minutes.

[0278] Adhesive composition 51 was made and tested in exactly the same way as composition 49 except that no pho-

to initiator was added. Adhesive composition 52 was made in exactly the same way as composition 50 except that no photoinitiator was added.

[0279] Adhesive composition and tape C11 was made and tested in the same fashion as Example 49 except that the composition contained no CiA, and the cure was carried out with 2011 mJ/cm² of UVA light over 10 minutes.

TABLE 10

Ex	Crosslinker		Photo-initiator 1			RT Shear (min) (Modified Test	180° Angle Peel Adhesion to SS (oz/in, N/dm) (Test
	Material	phr	(g)	phr	g	Method 1)	Method 2)
49	CiA	1	0.6	2	0.17	5,246	50.3, 55.1
50	CiA	2	2	2	0.17	5,285	58.9, 64.5
51	CiA	1	0.6	0	0	135	54.6, 59.8
52	CiA	2	2	0	0	342	71.4, 78.2
C11	N/A	N/A	N/A	2	0.17	880	40.7, 44.6

Examples 53-56

[0280] Examples 53 and 54 were prepared by charging a 500 mL jar with 350 g (100 wt. %) 2OA, 0.14 g (0.04 phr) of photoinitiator 1, and a quantity of CiA according to Table 11. The monomer mixture was purged with nitrogen for 10 minutes then exposed to low intensity UVA radiation until a coatable syrup was formed, after which another 0.67 g (0.16 phr) of photoinitiator 1 was added. Next, 6.0 g (1.7 phr) of HDK H15 fumed silica (Wacker Silicones) was added and the syrup was mixed with a Netzsch Model 50 Dispersator. When the fumed silica was completely dispersed, 28 g (8 phr) of glass bubbles (K15, 3M Company, St. Paul Minn.) were added and the composition was mixed thoroughly by rolling overnight.

[0281] The composition was then coated at a 0.025 inch (635 micrometers) thickness between a release liner and a primed 0.002 inch (51 micrometer) polyethylene terephthalate (PET) and cured by a dose of UV A light (shown in Table 11) from 350 BL light bulbs (40 watt, Osram Sylvania) to form a PSA. Total UV exposure was measured as described in examples 1-5. Adhesive properties were tested according to test methods 6 and 7 and are shown in Table 11.

[0282] Examples 55 and 56 were made as described above except for the following 1) the initial composition contained 300 g (100 wt. %) 2OA, 0.12 g (0.04 phr) of photoinitiator 1, and a quantity of CiA according to Table 11, 2) 0.57 g (0.16

phr) of photoinitiator 1, 5.1 g (1.7 phr) of HDKH15 fumed silica, and 24 g (8 phr) of glass bubbles were added after the prepolymer syrup was prepared. For rheological measurements, the coatable syrup was coated at 0.025 inch (635 micrometer) thickness and cured in the same manner.

TABLE 11

Ex	Backbone Monomer	CiA (g)	CiA (phr)	UV Dose (mJ/cm ²)	70° C.	90° Angle
					Shear to Orange Peel Dry Wall (min.) (Test Method 7)	Peel Adhesion to Paper (lb-in, kg-cm) (Test Method 6)
53	2OA	1.75	0.5	1482	275	4821.3, 5554.6
54	2OA	3.5	1.0	1482	10,000+	3611.9, 4161.3
55	2OA	4.11	1.37	2664	10,000+	2677.5, 3084.7
56	2OA	5.49	1.83	2664	8790	2211.9, 2448.3

Examples 57-60

[0283] Adhesive compositions and tapes 57-60 were made and tested in exactly the same way as examples 11-25. The crosslinkers employed and adhesive properties are shown in Table 12. Dicyclopentenyl acrylate (DPA) was obtained from Monomer-Polymer Laboratories (Windham, N.H., USA). Ethylene glycol dicyclopentenyl ether acrylate (EGDA) was obtained from Aldrich.

TABLE 12

Ex	Crosslinker			Total UV Exposure mJ/cm ²	70° C. Shear (min) (Test	180° Peel Adhesion to SS (oz/in, N/dm) (Test
	Material	phr	(g)		Method 1)	Method 2)
57	EGDA	0.5	0.25	2102	1,826	92.2, 100.9
58	EGDA	1.0	0.5	2102	10,000+	82.1, 89.9
59	DPA	0.5	0.25	1934	2,246	83.3, 91.2
60	DPA	1.0	0.5	1934	10,000+	85.8, 93.9

TABLE 13

Example	Low Tg Monomer (2OA or IOA) wt-%	High Tg Monomer (AA and/or IBXA) wt-%	Crosslinking Monomer wt-%	Tackifier wt-%	Fumed Silica wt-%	Glass Bubbles wt-%
34	83.2	5.8	CiA - 1.8	8.9	0	0
35	82.5	5.7	CiA - 2.6	8.8	0	0
36	81.0	5.6	CiA - 4.3	8.7	0	0
37	77.7	5.4	CiA - 8.3	8.3	0	0
38	82.5	5.7	CiA - 2.6	8.8	0	0
39	82.5	5.7	CiA - 2.6	8.8	0	0
40	84.0	5.9	CiA/T2 - 0.7/0.1	9.0	0	0
41	83.5	5.8	CiA/T2 - 1.3/0.07	8.9	0	0
42	83.0	5.8	CiA/T2 - 2.0/0.03	8.9	0	0
43	65.2	13.7	CiA - 2.0	18.9	0	0
44	64.3	13.6	CiA - 3.2	18.7	0	0

TABLE 13-continued

Example	Low Tg Monomer (2OA or IOA) wt-%	High Tg Monomer (AA and/or IBXA) wt-%	Crosslinking Monomer wt-%	Tackifier wt-%	Fumed Silica wt-%	Glass Bubbles wt-%
45	62.3	13.1	CiA - 6.3	18.1	0	0
46	65.2	13.7	CiA - 2.0	18.9	0	0
47	79.1	11.3	CiA - 0.5	0	1.6	7.2
48	81.1	9.0	CiA - 0.9	0	1.5	7.2
53	90.5	0	CiA - 0.5	0	1.6	7.2
54	90.1	0	CiA - 0.9	0	1.5	7.2
55	89.8	0	CiA - 1.2	0	1.5	7.2
56	89.5	0	CiA - 1.6	0	1.5	7.2

Pressure Sensitive Adhesive (PSA) A

[0284] PSA A was made by charging a gallon jar with 1) 1620 g of 2OA, 2) 180 g of AA, 3) 0.72 g (0.04 phr) of 651, and 4) 36 g of citronellyl acrylate (CiA). The monomer mixture was purged with nitrogen for 10 minutes then exposed to low intensity ultraviolet radiation until a coatable syrup was obtained. An additional 2.7 g (0.15 phr) of 651 was then added. The pre-adhesive formulation were then coated onto either release liner A or B at 0.002 inches (51 micrometers) thickness and cured under nitrogen by exposure to 366 mJ/cm² of UV A light over 43 seconds and 113 mJ/cm² of UVC light over 15 seconds.

Pressure Sensitive Adhesive (PSA) B PSA B was made by charging a gallon jar with 1) 1620 g of 2OA, 2) 180 g of AA, 3) 0.72 g (0.04 phr) of 651, and 4) 36 g of dicyclopentyl acrylate (DPA). The monomer mixture was purged with nitrogen for 10 minutes then exposed to low intensity ultraviolet radiation until a coatable syrup was obtained. An additional 2.7 g (0.15 phr) of 651 was then added. The pre-adhesive formulation were then coated onto either release liner A or B at 0.002 inches (51 micrometers) thickness and cured under nitrogen by exposure to 366 mJ/cm² of UV A light over 43 seconds and 113 mJ/cm² of UVC light over 15 seconds.

Pressure Sensitive Adhesive (PSA) C

[0285] PSA C was made by charging a gallon jar with 1) 1784 g 2OA, 2) 16.2 g of AA, 3) 0.72 g of 651, and 4) 54 g of CiA. The monomer mixture was purged with nitrogen for 10 minutes then exposed to low intensity ultraviolet radiation until a coatable syrup was obtained. An additional 4.3 g (0.24 phr) of 651, 360 g of IBXA, 1.35 g of 1076, and 518.4 g of Regalrez 6108 were then added. The pre-adhesive formulations were then coated onto release liner A at 0.002 inches (51 micrometers) thickness and cured under nitrogen by exposure to 884 mJ/cm² of UV A light over 3 minutes.

Pressure Sensitive Adhesive (PSA) D

[0286] PSA D was made by charging a gallon jar with 1) 1784 g 2OA, 2) 16.2 g of AA, 3) 0.72 g of 651, and 4) 54 g of DPA. The monomer mixture was purged with nitrogen for 10 minutes then exposed to low intensity ultraviolet radiation until a coatable syrup was obtained. An additional 4.3 g (0.24 phr) of 651, 360 g of IBXA, 1.35 g of 1076, and 518.4 g of Regalrez 6108 were then added. The pre-adhesive formulations were then coated onto release liner A at 0.002 inches (51 micrometers) thickness and cured under nitrogen by exposure to 884 mJ/cm² of UV A light over 3 minutes.

Release Liner (RL) A

[0287] A 0.002 in. (51 micrometer) thick polyester film having a silicone acrylate release coating on both sides was prepared using the process described in Example 61 of US 2013059105.

Release Liner (RL) B

[0288] A 0.004 in. (51 micrometer) thick, 58 pound poly-coated Kraft paper release liner having a silicone acrylate release coating on both sides was prepared using the process described in Example 61 of US 2013059105.

Examples 61-66

[0289] The various combinations of pressure sensitive adhesives and release liners shown in Table 14 were evaluated for faceside (FS) and backside (BS) peel adhesion strengths as describe in Test Method 10: 180° Angle Peel Adhesion Test 5 (Adhesive Strength). Construction were also prepared and evaluated for release liner peel strengths as described in Test Method 9: 180° Angle Peel Adhesion Test 4 (Liner Release). The results are shown in Table 14. Release values and release ratios were also observed to remain relatively stable even after aging for 7 days at 70° C., as well as for 7 days at 90% RH and 32° C. (90° F. In addition, Examples 61-66 all exhibited overlap shear values of more than 10,000 minutes when evaluated according to Test Method 11: Overlap Shear Test 4.

TABLE 14

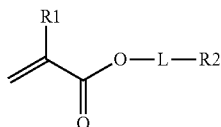
Ex.	PSA	RL	FS Peel Adhesion to SS (oz/in, N/dm)	BS Peel Adhesion to SS (oz/in, N/dm)	Easy Side Release (g/in, g/cm)	Tight Side Release (g/in, g/cm)	Release Ratio (Tight/Easy)
61	A	A	34.0, 37.2	39.1, 42.8	6.5, 2.6	28.8, 11.3	4.43
62	B	A	45.2, 49.5	41.3, 45.2	5.7, 2.2	24.1, 9.5	4.23
63	A	B	41.5, 45.4	39.5, 43.2	8.9, 3.5	58.4, 23.0	6.56
64	B	B	48.0, 52.5	40.0, 43.8	7.7, 3.0	50.9, 20.0	6.61
65	C	A	37.8, 41.4	40.2, 44.0	9.4, 3.7	32.4, 12.8	3.45
66	D	A	36.9, 40.4	48.2, 52.8	6.6, 2.6	26.4, 10.4	4.00

What is claimed is:

1. An article comprising a release liner and a pressure sensitive adhesive composition disposed on a major surface of the release liner, wherein the pressure sensitive adhesive comprises at least 50 wt-% of polymerized units derived from alkyl(meth)acrylate monomer(s); and 0.2 to 15 wt-% of at least one crosslinking monomer comprising a (meth)acrylate group and a C₆-C₂₀ olefin group, the olefin group being straight-chained or branched and optionally substituted.

2. The article of claim 1 wherein the pressure sensitive adhesive comprises at least 55, 60, 65, or 70 wt-% of polymerized units derived from one or more alkyl(meth)acrylate monomer(s).

3. The article of claim 1 wherein the crosslinking monomer has the formula:



R1 is H or CH₃,

L is an optional linking group; and

R2 is an optionally substituted C₆-C₂₀ olefin group.

4. The article of claim 3 wherein L comprises one or more alkylene oxide groups.

5. The article of claim 3 wherein the crosslinking monomer is selected from the group consisting of citronellyl(meth)acrylate, geraniol(meth)acrylate, farnesol(meth)acrylate, undecenyl(meth)acrylate, and oleyl(meth)acrylate.

6. The article of claim 1 wherein the pressure sensitive adhesive composition comprises at least 50, 55, 60, 65, or 70 wt-% of polymerized units of alkyl(meth)acrylates comprising 6 to 20 carbon atoms.

7. The article of claim 1 wherein the pressure sensitive adhesive comprises a bio-based content of at least 25% of the total carbon content.

8. The article of claim 1 wherein the pressure sensitive adhesive comprises polymerized units derived from 2-octyl(meth)acrylate.

9. The article of claim 1 wherein the pressure sensitive adhesive further comprises filler.

10. The article of claim 9 wherein the filler comprises fumed silica, glass bubbles, or a combination thereof.

11. The article of claim 1 wherein the pressure sensitive adhesive composition further comprises a tackifier.

12. The article of claim 1 wherein the pressure sensitive adhesive composition further comprises polymerized units derived from at least one monomer selected from acid-functional monomers, non-acid functional polar monomers, vinyl monomers, and combinations thereof.

13. The article of claim 1 wherein the pressure sensitive adhesive further comprises a multifunctional (meth)acrylate crosslinker, a triazine crosslinker, or a combination thereof.

14. The article of claim 1 wherein the pressure sensitive adhesive exhibits a 180° degree peel adhesion to stainless steel of at least 15 N/dm after curing.

15. The article of claim 1 wherein the pressure sensitive adhesive composition comprises 0 to 1.0 wt-% of polymerized units derived from acid-functional monomers.

16. The article of claim 1 wherein the pressure sensitive adhesive composition comprises 0 to 10 wt-% of polymerized units derived from high Tg monomers.

17. The article of claim 1 wherein the release liner is created by

applying a layer comprising a (meth)acrylate-functional siloxane to a major surface of a substrate; and

irradiating said layer, in a substantially inert atmosphere comprising no greater than 500 ppm oxygen, with a short wavelength polychromatic ultraviolet light source having at least one peak intensity at a wavelength of from about 160 nanometers to about 240 nanometers to at least partially cure the layer, optionally wherein the layer is at a curing temperature greater than 25° C.

18. The article of claim 17 wherein the at least one peak intensity is at a wavelength between about 170 nanometers to about 220 nanometers.

19. The article of claim 18 wherein the peak intensity is at a wavelength of about 185 nanometers.

20. The article of claim 17 wherein the short wavelength polychromatic ultraviolet light source comprises at least one low pressure mercury vapor lamp, at least one low pressure mercury amalgam lamp, at least one pulsed Xenon lamp, at least one glow discharge from a polychromatic plasma emission source, or combinations thereof.

21. The article of claim 17 wherein the layer consists essentially of one or more (meth)acrylate-functional siloxane monomers.

22. The article of claim 17 wherein the layer consists essentially of one or more (meth)acrylate-functional siloxane oligomers.

23. The article of claim 17 wherein the layer consists essentially of one or more (meth)acrylate-functional polysiloxanes.

24. The article of claim 17 wherein the layer further comprises one or more copolymerizable materials selected from the group consisting of monofunctional (meth)acrylate monomers, difunctional (meth)acrylate monomers, polyfunctional (meth)acrylate monomers having functionality greater than two, vinyl ester monomers, vinyl ester oligomers, vinyl ether monomers, and vinyl ether oligomers.

25. The article of claim 17 wherein the layer further comprises at least one functional polysiloxane material which does not comprise a (meth)acrylate functionality.

26. The article of claim 25 wherein the functional polysiloxane material is selected from at least one a vinyl-functional polysiloxane, a hydroxy-functional polysiloxane, an amine-functional polysiloxane, a hydride-functional polysiloxane, an epoxy-functional polysiloxane, and combinations thereof.

27. The article of claim 17 wherein the layer further comprises at least one non-functional polysiloxane material.

28. The article of claim 27 wherein the at least one non-functional polysiloxane material is selected from at least one of a poly(dialkylsiloxane), a poly(alkylarylsiloxane), a poly(diarylsiloxane), a poly(dialkylidarylsiloxane), or a combination thereof, optionally wherein the non-functional polysiloxane material comprises from 0.1 wt. % to 95 wt. %, inclusive, of the at least partially cured layer.

29. The article of claim 17 wherein the layer is substantially free of an added photoinitiator.

30. The article of claim 17 wherein the layer is substantially free of an organic solvent.

31. The article of claim 17 wherein the substantially inert atmosphere comprises no greater than 50 ppm oxygen.

32. The article of claim 17 wherein applying the layer to the surface of the substrate comprises applying a discontinuous coating.

33. The article of claim 17 wherein the layer is substantially free of metal catalyst.

34. An article comprising a release liner and a pressure sensitive adhesive composition disposed on a major surface of the release liner,

wherein the pressure sensitive adhesive is a UV curable (meth)acrylic pressure sensitive adhesive that is substantially free of halogens,

and further wherein the release liner comprises a UV curable release layer on a major surface of a substrate.

35. The article of claim 34 wherein the release layer comprises a (meth)acrylate-functional siloxane.

36. The article of claim 34 wherein the release liner is derived by applying a layer comprising a (meth)acrylate-functional siloxane to a major surface of a substrate; and irradiating said layer, in a substantially inert atmosphere comprising no greater than 500 ppm oxygen, with a short wavelength polychromatic ultraviolet light source having at least one peak intensity at a wavelength of from about 160 nanometers to about 240 nanometers to at least partially cure the layer, optionally wherein the layer is at a curing temperature greater than 25° C.

37. The article of claim 34 wherein the pressure sensitive adhesive comprises a bio-based content of at least 25% of the total carbon content.

38. An article comprising a release liner and a pressure sensitive adhesive composition disposed on a major surface of the release liner,

wherein the pressure sensitive adhesive comprises at least 50 wt-% of polymerized units derived from alkyl(meth)acrylate monomer(s); and 0.2 to 15 wt-% of at least one crosslinking monomer comprising a (meth)acrylate group and a C₆-C₂₀ olefin group, the olefin group being straight-chained or branched and optionally substituted, and further wherein the release liner is derived by applying a layer comprising a (meth)acrylate-functional siloxane to a major surface of a substrate; and irradiating said layer, in a substantially inert atmosphere comprising no greater than 500 ppm oxygen, with a short wavelength polychromatic ultraviolet light source having at least one peak intensity at a wavelength of from about 160 nanometers to about 240 nanometers to at least partially cure the layer, optionally wherein the layer is at a curing temperature greater than 25° C.

39. The article of claim 38 wherein the pressure sensitive adhesive comprises a bio-based content of at least 25% of the total carbon content.

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