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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
21 May 2015 (21.05.2015)

WIPO | PCT

(10) International Publication Number
WO 2015/074031 A1

(51) International Patent Classification:
E04D 5/14 (2006.01) ***C08G 18/71*** (2006.01)
C09J 171/02 (2006.01) ***C08G 18/28*** (2006.01)
C09J 175/04 (2006.01)

(21) International Application Number:
PCT/US2014/066101

(22) International Filing Date:
18 November 2014 (18.11.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/905,405 18 November 2013 (18.11.2013) US

(71) Applicant: FIRESTONE BUILDING PRODUCTS CO., LLC [US/US]; 250 West 96th Street, Indianapolis, Indiana 46260 (US).

(72) Inventors: TANG, Jiansheng; 13679 Cunningham Drive, Westfield, Indiana 46074 (US). **CARR, Joseph**; 8260 Lakeshore Circle, Apt. 4115, Indianapolis, Indiana 46250 (US).

(74) Agents: WOOD, Jon et al.; 10 East Firestone Boulevard, Akron, Ohio 44317 (US).

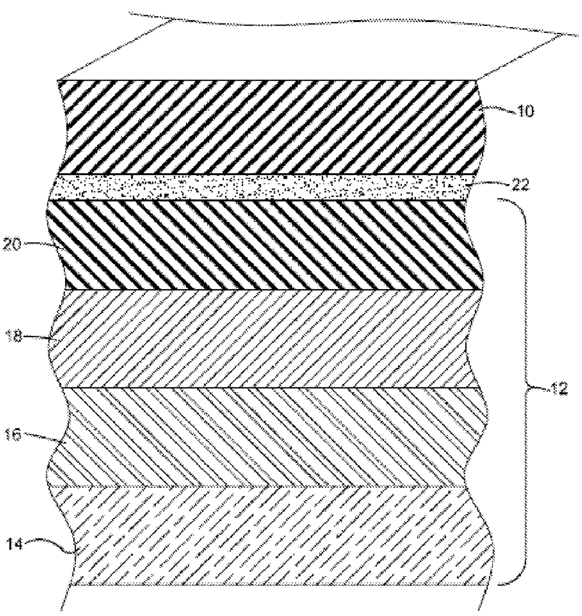
(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: BONDING ADHESIVE AND ADHERED ROOFING SYSTEMS PREPARED USING THE SAME

(57) Abstract: An adhered roofing system comprising a roof substrate, a polymeric membrane; and an adhesive disposed between the roof substrate and the polymeric membrane, where the adhesive is the cured product of an adhesive composition comprising (a) a polymer having a silicon-containing hydrolyzable terminal group, (b) a tackifier resin, and (c) a glycoxysilane moisture scavenger.



Figure

WO 2015/074031 A1

Published:

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

BONDING ADHESIVE AND ADHERED ROOFING SYSTEMS PREPARED USING THE SAME

[0001] This application claims the benefit of U.S. Provisional Application Serial No. 61/905,405, filed on November 18, 2013, which is incorporated herein by reference.

FIELD OF THE INVENTION

[0002] Embodiments in the invention are directed toward a silicon-containing bonding adhesive and adhered roofing systems prepared with the adhesive.

BACKGROUND OF THE INVENTION

[0003] Polymeric membranes, such as cured sheets of ethylene-propylene-diene copolymer rubber (EPDM) or extruded sheets of thermoplastic olefins (TPO), are often used in the construction industry to cover flat or low-sloped roofs. These membranes, which may also be referred to as panels, are typically delivered to a construction site in a bundled roll, transferred to the roof, and then unrolled and positioned. The sheets are then affixed to the building structure by employing varying techniques such as mechanical fastening, ballasting, and/or adhesively adhering the membrane to the roof. The roof substrate to which the membrane is secured may include a variety of materials depending on the situation. For example, the surface may be a concrete, metal, or wood deck, it may include insulation, cover or recover board, and/or it may include an existing membrane.

[0004] In addition to securing the membrane to the roof – which mode of attachment primary seeks to prevent wind uplift – the individual membrane panels, together with flashing and other accessories, are positioned and adjoined to achieve a waterproof barrier on the roof. Typically, the edges of adjoining panels are overlapped, and these overlapping portions are adjoined to one another through a number of methods depending upon the membrane materials and exterior conditions. One approach involves providing adhesives or adhesive tapes between the overlapping portions, thereby creating a water-resistant seal.

[0005] Thus, there are two modes of membrane attachment that are used in conjunction. The first seeks to anchor the membrane to the roof, while the second seeks to create a water-impervious barrier by attaching individual adjacent membrane panels to each other or to flashing.

[0006] Adhesive attachment is typically employed to form adhered roofing systems. The membrane may be adhered to the roof substrate substantially across the entire planar surface of the membrane to form fully-adhered systems. In other words, a majority, if not all, of the membrane panel is secured to the roof substrate as opposed to mechanical attachment methods which can only achieve direct attachment in those locations where a mechanical fastener actually affixes the membrane. Fully-adhered roofing systems are advantageously installed where maximum wind uplift prevention is desired. Also, fully-adhered systems are desirable in re-roofing situations, especially where the new membrane is placed over an existing membrane (a technique that is commonly referred to as re-skinning).

[0007] Several techniques are employed to prepare fully-adhered roofing systems. One technique includes the use of a fleece-backed EPDM membrane that is secured to the substrate by using a low-rise polyurethane foam adhesive that is sprayed over the substrate. Once the adhesive polyurethane foam is applied, the fleece-backed membrane is applied to the adhesive layer, which attaches itself to the fleece backing. Alternatively, nitrile-based bond adhesives can be applied to the substrate and the fleece-backed EPDM membrane can be secured thereto. Because these systems require fleece-backed membranes, they are expensive and suffer from manufacturing inefficiencies relating to the need to secure the fleece to the membrane.

[0008] Other techniques employ conventional EPDM membrane sheet, which is not modified with a fleece backing. In these situations, it is common to employ a contact bonding method whereby technicians coat both the membrane and the substrate that receives the membrane with an adhesive. The adhesive is then typically allowed to at least partially set to, among other things, build some wet green strength. The membrane is then mated with the substrate via the partially-set adhesive, which may include, for example, a polychloroprene-based adhesive. Because the volatile components (e.g. solvent) of the adhesives are “flashed off” prior to mating, good, early (green) bond strength can advantageously be developed. While the use of known solvent-based adhesives has proven versatile to the extent that the substrate need not be porous and cold-weather application is feasible, the technique requires application of the adhesive to both the substrate and the membrane, followed by a time delay to allow the solvent to flash off, and then a mating of the two adhesive surfaces (*i.e.,* the adhesive coated membrane is mated to the adhesive coated membrane).

[0009] Other techniques employ a water-borne bond adhesive that is applied to the substrate and then the EPDM membrane can be applied to the adhesive layer. While this attachment technique has proven useful, the use is generally limited to ambient weather conditions (e.g. greater than 40 °C) and/or in conjunction with porous substrates that absorb water thereby allowing the adhesive to dry or cure without blistering the membrane.

[0010] In yet other situations, 100% solids bond adhesives are employed. For example, U.S. Pat. No. 7,767,308 teaches a moisture-curable bond adhesive that includes a polymer or a combination of polymers having silicon-containing hydrolyzable terminal groups, a phenolic resin, and a non-polymeric silicon-containing hydrolyzable compound. These bond adhesives preferably include moisture scavengers such as vinyl-trimethoxysilanes, which are generally referred to as chemical moisture scavengers. It is believed that these moisture scavengers are included in the system to provide useful shelf life and prevent premature curing.

SUMMARY OF THE INVENTION

[0011] One or more embodiments of the present invention provide an adhered roofing system comprising a roof substrate, a polymeric membrane; and an adhesive disposed between the roof substrate and the polymeric membrane, where the adhesive is the cured product of an adhesive composition comprising (a) a polymer having a silicon-containing hydrolyzable terminal group, (b) a tackifier resin, and (c) a low VOC-generating moisture scavenger.

[0012] Still other embodiments of the present invention provide a method for forming an adhered membrane roof system, the method comprising applying a bond adhesive to a substrate on a roof to form an adhesive layer, where the bond adhesive includes (a) a polymer having a silicon-containing hydrolyzable terminal group, (b) a tackifier resin, and (c) a low VOC-generating moisture scavenger, and applying a membrane directly to the adhesive layer.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] The figure is a cross sectional view of a roofing system including EPDM membrane adhered to a substrate using an adhesive according to one or more embodiments of the present invention.

DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

[0014] Embodiments of the invention are based, at least in part, on the discovery of a bond adhesive composition that includes a polymer having a silicon-containing hydrolyzable terminal group, a tackifier resin, and a low VOC-generating moisture scavenger. In one or more embodiments, these adhesives are particularly useful as bond adhesives for adhering roofing membranes to a roof surface. These adhesives are advantageously stable due to the presence of the moisture scavenger, and yet they do not release appreciable amounts of volatile compounds, such as methanol, after application to the roof surface. While the prior art teaches the use of similar bond adhesives with conventional moisture scavengers for similar applications, it has now unexpectedly been discovered that the moisture scavengers employed in the prior art, such as vinyl-trimethoxysilanes, give rise to problems when employed to secure polymeric roofing membranes to a roof surface. Specifically, it has now been discovered that the by-products of hydrolysis (e.g. methanol) liberated from the moisture scavengers employed in the prior art bond adhesives give rise to blistering (i.e., separation between the substrate and the membrane resulting from gas pockets), which in turn deleteriously impacts the performance of the membrane. Discovery of this problem and the use of the moisture scavengers described herein provide improved roofing systems, including fully-adhered systems that advantageously meet FM 4470/4474 standards for wind uplift can be prepared.

ADHESIVE COMPOSITION

[0015] As discussed above, the adhesive compositions of this invention includes a polymer having a silicon-containing hydrolyzable terminal group, a tackifier resin, and a glycoxysilane moisture scavenger. In addition, the adhesive compositions may include an adhesion promoter, a filler, a catalyst, an antioxidant, a stabilizer, a crosslink inhibitor (a.k.a retarder), and/or a thixotropic compound. In one or more embodiments, the adhesive composition is a 100% solids composition (i.e. it is solvent free). In particular embodiments, the tackifier resin is a hydrocarbon resin, and the bond adhesive compositions employed in this invention are devoid or substantially devoid of a phenolic resin.

SILANE-TERMINATED POLYMERS

[0016] In one or more embodiments, the polymer having silicon-containing hydrolyzable terminal group may include a silane-terminate polymer, which may also be referred to as silyl-terminated polymer. The term "silicon-containing hydrolyzable terminal group" as used herein means a group wherein at least one silicon atom is combined with a hydrolyzable group, such as a methoxy group, which is subject to hydrolysis and polymerization by moisture.

[0017] The backbone of the polymer having silicon-containing hydrolyzable terminal groups may be comprised of polyethers, polyesters, polyurethanes (SPUR), or other suitable backbones.

[0018] Suitable polymers having silicon-containing hydrolyzable terminal groups are commercially available and/or can be prepared in accordance with techniques known in the art. Examples of suitable commercially available polymers having silicon-containing hydrolyzable terminal groups are Geniosil™. STP-E 35 trimethoxysilylpropyl-carbamate-terminated polyether, and Geniosil™. STP-E 30 silane-terminated polyether with dimethoxy(methyl)silylmethylcarbamate terminal groups, both of which are available from Wacker Chemical. Another commercially available polymer having silicon-containing hydrolyzable terminal groups that may be employed in the adhesive compositions of this invention is "SPUR+" silane-terminated polyurethanes, available from Momentive. Another suitable commercially available material is "MS" silyl-terminated polyether (S227H, S303, S327, S303H, SAX350), which are available from Kaneka.

[0019] While the use of a hydrocarbon resin within the adhesive compositions of the present invention provide the composition with an advantageous dynamic viscosity, further adjustments to viscosity can be advantageously accomplished, while maintaining adequate adhesion, by employing certain blends of polymers having silicon-containing hydrolyzable terminal groups. In particular embodiments, these blends include polymers having a relatively high molecular weight combined with polymers having a relatively low molecular weight. In one or more embodiments, the high molecular weight polymers having a silicon-containing hydrolyzable terminal group have a number average molecular weight greater than 12,000 g/mole, in other embodiments greater than 13,000 g/mole, in other embodiments greater than 14,000 g/mole, and in other embodiment greater than 14,000 g/mole. In one or more embodiments, the high molecular weight polymers having a silicon-containing hydrolyzable terminal group have a number average molecular weight of from about 12,000 to 30,000, in other embodiments from about 13,000 to about 25,000, and in other embodiments from about 14,000 to about 20,000 g/mole. In these or other embodiments, the high molecular weight polymers having a silicon-containing hydrolyzable terminal group are characterized by a polydispersity of from about 1.5 to about 4.0, in other embodiments from about 1.8 to about 3.5, and in other embodiments from about 2.0 to about 3.0.

TACKIFIER RESIN

[0020] In one or more embodiments, the tackifier resin is a hydrocarbon resin. In other embodiments, the tackifier resin is a phenolic resin.

HYDROCARBON RESIN

[0021] In particular embodiments, the tackifier resin is a hydrocarbon resin. In one or more embodiments, the hydrocarbon resins may include natural resins, synthetic resins, and low molecular weight polymers or oligomers. The monomer that may be polymerized to synthesize the synthetic resins or low molecular weight polymers or oligomers may include those obtained from refinery streams containing mixtures or various unsaturated materials or from pure monomer feeds. The monomer may include aliphatic monomer, cycloaliphatic monomer, aromatic monomer, or mixtures thereof. Aliphatic monomer can include C_4, C_5, and C_6 paraffins, olefins, and conjugated diolefins. Examples of aliphatic monomer or cycloaliphatic monomer include butadiene, isobutylene, 1,3-pentadiene (piperylene) along with 1,4-pentadiene, cyclopentane, 1-pentene, 2-pentene, 2-methyl-1-pentene, 2-methyl-2-butene, 2-methyl-2-pentene, isoprene, cyclohexane, 1-3-hexadiene, 1-4-hexadiene, cyclopentadiene, and dicyclopentadiene. Aromatic monomer can include C_8, C_9, and C_{10} aromatic monomer. Examples of aromatic monomer include styrene, indene, derivatives of styrene, derivatives of indene, and combinations thereof.

[0022] In one or more embodiments, examples of hydrocarbon resins include aliphatic hydrocarbon resins, at least partially hydrogenated aliphatic hydrocarbon resins, aliphatic/aromatic hydrocarbon resins, at least partially hydrogenated aliphatic aromatic hydrocarbon resins, cycloaliphatic hydrocarbon resins, at least partially hydrogenated cycloaliphatic resins, cycloaliphatic/aromatic hydrocarbon resins, at least partially hydrogenated cycloaliphatic/aromatic hydrocarbon resins, at least partially hydrogenated aromatic hydrocarbon resins, polyterpene resins, terpene-phenol resins, rosin esters, and mixtures of two or more thereof.

[0023] In certain embodiments, the synthetic aliphatic or aromatic hydrocarbon resins may be characterized by a number average molecular weight (M_n) of from about 300 g/mole to about 3,000 g/mole, and in other embodiments from about 500 g/mole to about 2,000 g/mole. These hydrocarbon resins may also be characterized by a weight average molecular weight (M_w) of from about 500 g/mole to about 6,000 g/mole, and in other embodiments from about 700 g/mole to about 5,000 g/mole. Molecular weight may be determined by size exclusion chromatography (SEC) by using a Waters 150 gel permeation chromatograph equipped with the differential refractive index detector and calibrated using polystyrene standards.

[0024] In certain embodiments, the hydrocarbon resins include those produced by thermal polymerization of dicyclopentadiene (DCPD) or substituted DCPD, which may further include aliphatic or aromatic monomers. In one embodiment, the DCPD or substituted DCPD is copolymerized with aromatic monomer, and the final product includes less than 10% aromatic content. In another embodiment, the hydrocarbon resin derives from the copolymerization of both aliphatic monomer and aromatic monomer. In particular embodiments, the dicyclopentadiene tackifier resin is hydrogenated. Hydrogenated dicyclopentadiene tackifier resins are commercially available from Neville.

[0025] In one or more embodiments, synthetic oligomers may include dimers, trimers, tetramers, pentamers, hexamers, septamers, and octamers of petroleum distillate monomer. In one or more embodiments, this petroleum distillate monomer may have a boiling point of from about 30° to about 210°C. The oligomers may include byproducts of resin polymerization including thermal and catalytic polymerization. For example, oligomers may derive from processes where DCPD, aliphatic monomer, and/or aromatic monomer are oligomerized.

[0026] The hydrocarbon resins may be characterized by an aromatic content of from about 1 to about 60, in other embodiments from about 2 to about 40, and in other embodiments from about 5 to about 10. In one or more embodiments, the tackifier resins are hydrogenated or partially hydrogenated; useful resins include those that are at least 50 percent, in other embodiments at least 80 percent, in other embodiments at least 95 percent, and in other embodiments at least 99 percent or fully hydrogenated. For example, the hydrocarbon resin prior to grafting may contain less than 90, in other embodiments less than 50, in other embodiments less than 25, in other embodiments less than 10, in other embodiments less than 2, in other embodiments less than 1, in other embodiments less than 0.5, and in other embodiments less than 0.05 olefinic protons. Aromatic content and olefin content may be measured by ^{1}H-NMR as measured directly from the ^{1}H NMR spectrum from a spectrometer with a field strength greater than 300 MHz, and in other embodiments 400 MHz (frequency equivalent). Aromatic content includes the integration of aromatic protons versus the total number of protons. Olefin proton or olefinic proton content includes the integration of olefinic protons versus the total number of protons.

[0027] In one or more embodiments, the hydrocarbon resin may be characterized by a softening point of from about 5 °C to about 210 °C, in other embodiments from about 65 °C to about 170 °C, and in other embodiments from about 90°C to about 140 °C. Softening point can be determined according to ASTM E-28 (Revision 1996).

[0028] In these or other embodiments, the hydrocarbon resin may be characterized by a glass transition temperature of less than 120 °C, in other embodiments less than 110 °C, and in other embodiment from about -40 °C to about 80 °C. Glass transition temperature may be determined according to ASTM D 341-88 by using differential scanning calorimetry.

[0029] In these or other embodiments, the hydrocarbon resin may be characterized by a Saponification number (mg KOH/g resin material) of greater than 10, in other embodiments greater than 15, and in other embodiments greater than 19.

[0030] In these or other embodiments, the hydrocarbon resin may be characterized by an acid number greater than 10, in other embodiments greater than 15, and in other embodiments greater than 20, and in other embodiments greater than 25.

PHENOLIC RESIN

[0031] In particular embodiments, the tackifier resin is a phenolic resin. In one or more embodiments, the phenolic resins that may be employed in the compositions of this invention include resol-type and/or novolac-type phenolic resins obtained by condensation reaction of phenolic compounds, e.g., phenol, cresol, xylenol, resorcinol, an alkylphenol, and a modified phenol such as cashew nut shell oil modified phenol or tall oil modified phenol, with aldehyde compounds, e.g., formaldehyde and paraformaldehyde; and nitrogen-containing phenol resins obtained by condensation reaction of the above-mentioned phenolic compounds and aldehyde compounds in the presence of a catalyst such as ammonia or an amine compound. The phenol resins may be employed alone or in admixture. In one or more embodiments, the term phenolic resin refers to a phenol-formaldehyde resin. For example, the term phenolic resin may include a novolac resin, which is a phenol-formaldehyde resin where the molar ratio of the formaldehyde to phenol is less than one. These resins are typically synthesized by using an acid catalyst. The term phenolic resin also refers resol resins wherein the molar ratio of the formaldehyde to phenol is greater than one. These resins are typically synthesized by using a base catalyst.

ADHESION PROMOTER

[0032] In one or more embodiments, the adhesion promoter includes a non-polymeric silicon-containing hydrocarbon compound that has a lower molecular weight than the polymer having a silicon-containing hydrolysable group (i.e. the silane-terminate polymer). Also, the adhesion promoter includes at least one hydrolyzable group capable of reacting with a hydrolyzed functional group on the polymer having silicon-containing hydrolyzable terminal groups, and includes at least one moiety capable of interacting (i.e., promoting adhesion) with materials that are to be bonded with one another (such as a rubber membrane material). The expression non-polymeric, as used to modify the silicon-containing hydrocarbon compound is meant to exclude polymers and copolymers having at least 10 repeat units or monomeric units, such as urethane prepolymers having silicon-containing hydrolyzable terminal groups, but is meant to encompass oligomeric silicon-containing hydrolyzable compounds having fewer than 10 repeat units or monomers, and which are useful for promoting adhesion between a substrate and a cured adhesive composition. Examples of suitable aminosilane adhesion promoters that may function as the non-polymeric silicon-containing hydrolyzable compound include, but are not limited to gamma-aminopropyltrimethoxysilane, gamma-aminopropyltriethoxysilane,gamma-(aminoethyl)-aminopropyltrimethoxy- silane, methylaminopropyldimethoxysilane, methyl-gamma-(aminoethyl)-aminopropyldimethoxysilane, gamma-dimethylaminopropyltrimethoxysilane, and the like.

PLASTICIZERS

[0033] In one or more embodiments, examples of a plasticizer include phthalic acid esters (such as dioctyl phthalate, diisooctyl phthalate, dibutyl phthalate, diundecyl phthalate, diisononyl phthalate, diisodecyl phthalate, diisodocecyl phthalate and butylbenzyl phthalate); aliphatic dibasic acid esters (such as dioctyl adipate, isodecyl succinate, and dibutyl sebacate); glycol esters (such as diethylene glycol dibenzoate and pentaerythritol ester); aliphatic esters (such as butyl oleate and methyl acetylricinoleate); phosphoric acid esters (such as tricresyl phosphate, trioctyl phosphate, and octyldiphenyl phosphate); epoxy plasticizers (such as epoxidated soybean oil, epoxidated linseed oil, and benzyl epoxystearate); polyester plasticizers (such as polyesters of dibasic acid and a divalent alcohol); polyethers (such as polypropylene glycol and its derivatives); polystyrenes (such as poly-α-methylstyrene and polystyrene); polybutadiene butadiene-acrylonitrile copolymer; polychloroprene; polyisoprene; polybutene; chlorinated paraffins; benzoic esters; glycol esters; phosphoric esters; sulfonic esters; and mixtures thereof, wherein any given compound is different than an ingredient otherwise included in the composition of the invention.

[0034] In addition, high-molecular weight plasticizers can also be used. Specific examples of such high-molecular weight plasticizer include, but are not limited to, vinyl polymers obtainable by polymerizing a vinyl monomer by various methods; polyalkylene glycol esters such as diethyl ene glycol dibenzoate, triethylene glycol dibenzoate and pentaerythritol esters; polyester plasticizers obtainable from a dibasic acid, such as sebacic acid, adipic acid, azelaic acid or phthalic acid, and a dihydric alcohol, such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol or dipropylene glycol; polyethers such as polyether polyols, e.g. polyethylene glycol, polypropylene glycol and polytetramethylene glycol that have a molecular weight of 500 or more, and even further 1,000 or more, and derivatives of these as obtainable by converting the hydroxyl groups of these polyether polyols to an ester, ether or the like groups; polystyrenes such as polystyrene and poly-α-methylstyrene; polybutadiene, polybutene, polyisobutylene, butadiene-acrylonitrile, polychloroprene and the like. In one or more specific embodiments, plasticizers include propylene glycol dibenzoate, diisononyl phthalate, and soy methyl esters, Mesamol II, HB-40, butylbenzylphthalate. In other specific embodiments, the plasticizers employed are phthalic acid esters. In one or more embodiments, the plasticizers may include high boiling solvents that promote tackification, lowering of viscosity, and sprayability.

MOISTURE SCAVENGER

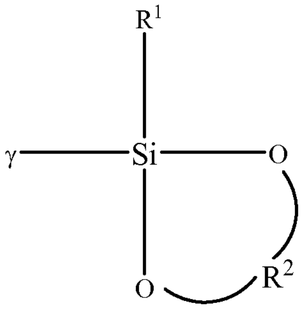
[0035] As suggested above, a low VOC-generating moisture scavenger is employed within the adhesive compositions of the present invention. In one or more embodiments, these moisture scavengers are silanes including at least one organo functional group and at least one hydrolyzable group that, upon hydrolysis, generates a non-volatile organic compound or low vapor volatile organic compound (e.g., a glycol or other polyhydric alcohol of relatively high boiling point and/or low vapor pressure). Useful moisture scavenger compounds are described in U.S. Patent No. 8,088,940, which is incorporated herein by reference.

[0036] In one or more embodiments, the moisture scavengers can be defined by the formula

$$(X^1{}_aX^2{}_bX^3{}_cSiR^1)_dZ$$

where each occurrence of R^1 is independently a chemical bond between a silicon atom and a carbon atom of the Z group; a hydrocarbyl group of 1 to 10 carbon atoms; or a heterocarbyl of 1 to 10 carbon atoms and at least one heteroatom of nitrogen or oxygen; each occurrence of X^1 is a monovalent alkyl or aryl group of from 1 to 6 carbon atoms or a monovalent heterocarbyl group of from 2 to 8 carbon atoms and at least two heteroatom selected from the group consisting of oxygen and nitrogen, with the proviso that one heteroatom is bonded to a carbon atom of the heterocarbyl group and to the silicon atom; each occurrence of X^2 is a divalent heterocarbyl group of from 2 to 8 carbon atoms and at least two heteroatoms selected from the group consisting of oxygen and nitrogen, with the proviso that two heteroatoms are bonded to two different carbon atoms of the heterocarbyl group and to the same silicon atom; each occurrence of X^3 is a trivalent heterocarbyl group of from about 3 to 8 carbons and at least three heteroatoms selected from the group consisting of oxygen and nitrogen, with the proviso that three heteroatoms are bonded to three different carbon atoms of the heterocarbyl group and to the same silicon atom; each Z is a monovalent or polyvalent organofunctional group of valence d selected from the group consisting of hydrogen, amino, carbamato, epoxy, ureido and alkenyl groups, provided, where Z does not possess a carbon atom, R^1 cannot be a chemical bond; and, each occurrence of a, b, c and d are integers, wherein a is 0 to 3; b is 0 or 1; c is 0 or 1; and d is 1 to 4; with the proviso that when c is 0, then $a+2b=3$ and when b is 1, then $a=1$ and $c=0$.

[0037] In one or more embodiments, the moisture scavenger is a glycoxysilane moisture scavenger. In particular embodiments, the glycoxysilane moisture scavenger may be defined by the formula:



where R^1 is a monovalent organic group, R^2 is a divalent organic group, and γ is an electron donating group. In particular embodiments, R^1 is a hydrocarbyl group. In other embodiments, R^1 is a hydrocarbyloxy group. In one or more embodiments, γ is a vinyl group.

[0038] In one or more embodiments, the monovalent organic groups of the glycoxysilane may be hydrocarbyl groups, which include, but not limited to, alkyl, cycloalkyl, alkenyl, cycloalkenyl, aryl, allyl, aralkyl, alkaryl, or alkynyl groups. Hydrocarbyl groups also include substituted hydrocarbyl groups, which refer to hydrocarbyl groups in which one or more hydrogen atoms have been replaced by a substituent such as a hydrocarbyl group. In one or more embodiments, these groups may include from one, or the appropriate minimum number of carbon atoms to form the group, to about 20 carbon atoms. These groups may or may not contain heteroatoms. Suitable heteroatoms include, but not limited to, nitrogen, boron, oxygen, silicon, sulfur, tin, and phosphorus atoms. In one or more embodiments, the cycloalkyl, cycloalkenyl, and aryl groups are non-heterocyclic groups. In these or other embodiments, the substituents forming substituted hydrocarbyl groups are non-heterocyclic groups.

[0039] In one or more embodiments, the monovalent organic groups of the glycoxysilane may be hydrocarbyloxy groups which include, but are not limited to, alkoxy, cycloalkoxy, substituted cycloalkoxy, alkenyloxy, cycloalkenyloxy, substituted cycloalkenyloxy, aryloxy, allyloxy, substituted aryloxy, aralkyloxy, alkaryloxy, or alkynyloxy groups. Substituted hydrocarbyloxy groups include hydrocarbyloxy groups in which one or more hydrogen atoms attached to a carbon atom have been replaced by a substituent such as an alkyl group. In one or more embodiments, the hydrocarbyloxy groups may include from one, or the appropriate minimum number of carbon atoms to form the group, to 20 carbon atoms. The hydrocarbyloxy groups may contain heteroatoms such as, but not limited to nitrogen, boron, oxygen, silicon, sulfur, and phosphorus atoms.

[0040] In one or more embodiments, the divalent organic groups of the glycoxysilane may include hydrocarbylene groups such as, but not limited to, alkylene, cycloalkylene, alkenylene, cycloalkenylene, alkynylene, cycloalkynylene, or arylene groups. Hydrocarbylene groups include substituted hydrocarbylene groups, which refer to hydrocarbylene groups in which one or more hydrogen atoms have been replaced by a substituent such as a hydrocarbyl group. In one or more embodiments, these groups may include from one, or the appropriate minimum number of carbon atoms to form the group, to about 20 carbon atoms. These groups may or may not contain heteroatoms. Suitable heteroatoms include, but not limited to, nitrogen, boron, oxygen, silicon, sulfur, tin, and phosphorus atoms. In one or more embodiments, the cycloalkylene, cycloalkenylene, and arylene groups are non-heterocyclic groups. In these or other embodiments, the substituents forming substituted hydrocarbylene groups are non-heterocyclic groups.

[0041] Specific examples of glycoxysilane compounds include vinyl, methyl, 2-methyl-1,3-propanedioxy silane, which may also be referred to as 2,5-dimethyl-2-vinyl[1,2,3]dioxasilinane. These moisture scavengers are available under the tradename Y-15866 (Momentive).

THIXATROPE

In one or more embodiments, suitable thixotropic agents may include, but are not limited to, polyvinylpyrrolidone, titanate coupling agents, metal soaps (such as calcium stearate, aluminum stearate, and barium stearate, aluminum distearate, and aluminum tristearate), copolymers with acidic groups, compounds having ionic groups, fumed silica, colloidal silica, asbestine, organic derivatives of castor oil (such as hydrogenated castor oil derivatives), treated clays, organic bentonite, modified polyester polyols (such as polyoxyethylene-polyoxypropylene block copolymers), aliphatic amides, and polyamides (such as polyamide waxes). Specific examples include polyamide waxes, such as "Crayvallac SLX" available from Arkema, or polymerized castor oils such as Flowtone R from Crayvalley.

ANTIOXIDANTS

[0042] Antioxidants that may be employed if desired. Examples of useful antioxidants include hindered phenols and phosphate esters.

FILLERS

[0043] Generally, any compatible filler, such as calcium carbonate may be employed if desired for a particular application. As the skilled person will appreciate, fillers will generally be omitted when the adhesive composition is intended to be sprayed onto one surface that is subsequently applied to a second surface on which the adhesive is or is not deposited.

CATALYST

[0044] As mentioned above, the adhesive composition may include one or more catalysts for the purpose of promoting the crosslinking the silane-terminated polymer. Without wishing to be bound by any particular theory, it is believed that these catalysts promote the hydrolysis and condensation of organosilicon compounds (i.e., reactions between the terminal groups of the polymer having silicon-containing hydrolyzable terminal groups, and reactions between the optional adhesion promoter when present and the polymer having silicon-containing hydrolyzable terminal groups). In one or more embodiments, hydrolysis of organosilicon compounds may be catalyzed by either acids or bases. Useful basic catalysts that may be employed in the compositions of this invention include alkali metal hydroxides such as potassium hydroxide, silanolates such as lithium silanolate, organic amines, and Lewis bases such as alkali metal carbonates and bicarbonates. Suitable acid catalysts include mineral acids such as sulfuric and phosphoric acids, organic acids such as acetic, propanoic and methane sulfonic acids. Other suitable acid catalysts include Lewis acids such as aluminum chloride, organotin compounds such as dibutyl tin dilaurate and titanium compounds such as the alkyl ortho esters, including tetrabutyl titanate.

SOLVENT

[0045] As mentioned above, the adhesive composition is devoid or substantially devoid of a solvent. As used herein, the term solvent refers to a volatile liquid that is either a VOC or VOC exemption liquid. Examples of solvents that are excluded include toluene and acetone.

[0046]

AMOUNTS

SILANE-TERMINATED POLYMER

[0047] In one or more embodiments, the adhesive compositions of the invention include at least 25 wt%, in other embodiments at least 30%, and in other embodiments at least 35 wt. % silane-terminated polymer. In these or other embodiments, the adhesive compositions of the invention include at most 80%, in other embodiments at most 75%, and in other embodiments at most 70% wt. % silane-terminated polymer. In one or more embodiments, the adhesive compositions of the invention include from about 25% to about 80%, in other embodiments from about 30% to about 75%, and in other embodiments from about 35% to about 70% wt. % silane-terminate polymer.

[0048] In one or more embodiments, the silane-terminated polymer component of the adhesive compositions of the present invention may, in one or more embodiments, include a blend of high and low molecular weight polymer. In one or more embodiments, the silane-terminated polymer component includes at least 40 wt %, in other embodiments at least 50 wt %, and in other embodiments at least 60 wt % high-molecular weight silane-terminated polymer (e.g., a molecular weight of greater than

12,000 g/mole), based upon the entire weight of the silane-terminated polymer component. In these or other embodiments, the silane-terminated polymer component includes at most 100 wt %, in other embodiments at most 80 wt %, and in other embodiments at most 70 wt % high-molecular weight silane-terminated polymer, based upon the entire weight of the silane-terminated polymer component. In one or more embodiments, the silane-terminated polymer component of the adhesive compositions includes from about 40 to about 100, in other embodiments from about 50 to about 80, and in other embodiments from about 60 to about 70 weight percent high-molecular weight silane-terminated polymer, based upon the entire weight of the silane-terminated polymer component.

[0049] In one or more embodiments, the silane-terminated polymer component includes at least 0 wt %, in other embodiments at least 20 wt %, and in other embodiments at least 30 wt % low-molecular weight silane-terminated polymer (a molecular weight of less than 12,000 g/mole), based upon the entire weight of the silane-terminated polymer component. In these or other embodiments, the silane-terminated polymer component includes at most 60 wt %, in other embodiments at most 50 wt %, and in other embodiments at most 40 wt % low-molecular weight silane-terminated polymer, based upon the entire weight of the silane-terminated polymer component. In one or more embodiments, the silane-terminated polymer component of the adhesive compositions includes from about 0 to about 60, in other embodiments from about 20 to about 50, and in other embodiments from about 30 to about 40 weight percent low-molecular weight silane-terminated polymer, based upon the entire weight of the silane-terminated polymer component.

TACKIFIER RESIN

[0050] In one or more embodiments, the adhesive compositions of the invention include at least 1%, in other embodiments at least 3%, and in other embodiments at least 5% wt. % tackifier resin (e.g., hydrocarbon resin or phenolic resin). In these or other embodiments, the adhesive compositions of the invention include at most 30%, in other embodiments at most 25%, and in other embodiments at most 20% wt. % tackifier resin. In one or more embodiments, the adhesive compositions of the invention include from about 1% to about 30%, in other embodiments from about 3% to about 25%, and in other embodiments from about 5% to about 20% wt. % tackifier resin.

ADHESION PROMOTERS

[0051] In one or more embodiments, the adhesive compositions of the invention include at least 1%, in other embodiments at least 1.5%, and in other embodiments at least 2% wt. % adhesion promoter. In these or other embodiments, the adhesive compositions of the invention include at most 10%, in other embodiments at most 9%, and in other embodiments at most 8% wt. % adhesion promoter. In one or more embodiments, the adhesive compositions of the invention include from about 1% to about 10%, in other embodiments from about 1.5% to about 9%, and in other embodiments from about 2% to about 8% wt. % adhesion promoter.

CATALYST

[0052] In one or more embodiments, the adhesive compositions of the invention include at least 0.05%, in other embodiments at least 0.1%, and in other embodiments at least 0.15 wt. % catalyst. In these or other embodiments, the adhesive compositions of the invention include at most 3%, in other embodiments at most 2.5%, and in other embodiments at most 2% wt. % catalyst. In one or more embodiments, the adhesive compositions of the invention include from about 0.05% to about 3%, in other embodiments from about 0.1% to about 2.5%, and in other embodiments from about 0.15% to about 2% wt. % catalyst.

THIXATROPE

[0053] In one or more embodiments, the adhesive compositions of the invention include at least 0%, in other embodiments at least 0%, and in other embodiments at least 0% wt. % thixatrope. In these or other embodiments, the adhesive compositions of the invention include at most 6%, in other embodiments at most 5%, and in other embodiments at most 4% wt. % thixatrope. In one or more embodiments, the adhesive compositions of the invention include from about 0% to about 6%, in other embodiments from about 0% to about 5%, and in other embodiments from about 0% to about 4% wt. % thixatrope.

MOISTURE SCAVENGER

[0054] In one or more embodiments, the adhesive compositions of the invention include at least 0.25%, in other embodiments at least 0.5%, and in other embodiments at least 0.75% wt. % moisture scavenger, based on the entire weight of the composition. In these or other embodiments, the adhesive compositions of the invention include at most 5%, in other embodiments at most 4%, and in other embodiments at most 3% wt. % moisture scavenger, based on the entire weight of the composition. In one or more embodiments, the adhesive compositions of the invention include from about 0.25% to about 5%, in other embodiments from about 0.5% to about 4%, and in other embodiments from about 0.75% to about 3% wt. % moisture scavenger, based on the entire weight of the composition.

FILLERS

[0055] In one or more embodiments, the adhesive compositions of the invention include at least 0%, in other embodiments at least 0%, and in other embodiments at least 0% wt. % filler. In these or other embodiments, the adhesive compositions of the invention include at most 65%, in other embodiments at most 60%, and in other embodiments at most 55% wt. % filler. In one or more embodiments, the adhesive compositions of the invention include from about 0% to about 65%, in other embodiments from about 0% to about 60%, and in other embodiments from about 0% to about 55% wt. % filler.

ANTIOXIDANTS

[0056] In one or more embodiments, the adhesive compositions of the invention include at least 0.1%, in other embodiments at least 0.15%, and in other embodiments at least 0.2% wt. % antioxidant. In these or other embodiments, the adhesive compositions of the invention include at most 3%, in other embodiments at most 2.5%, and in other embodiments at most 2% wt. % antioxidant. In one or more embodiments, the adhesive compositions of the invention include from about 0.1% to about 3%, in other embodiments from about 0.15% to about 2.5%, and in other embodiments from about 0.15% to about 2% wt. % antioxidant.

PLASTICIZER

[0057] In one or more embodiments, the adhesive compositions of the invention include at least 5%, in other embodiments at least 10%, and in other embodiments at least 15% wt. % plasticizer. In these or other embodiments, the adhesive compositions of the invention include at most 65%, in other embodiments at most 60%, and in other embodiments at most 55% wt. % plasticizer. In one or more embodiments, the adhesive compositions of the invention include from about 5% to about 65%, in other embodiments from about 10% to about 60%, and in other embodiments from about 15% to about 55% wt. % plasticizer.

SOLVENT

[0058] As discussed above, the adhesive compositions of the invention may advantageously be 100% solids compositions. In one or more embodiments, the compositions may be devoid of solvent. In these or other embodiments, the adhesive compositions are substantially devoid of solvents, which refers to that amount of solvent or less that will not have an appreciable impact on the composition. In one or more embodiments, the compositions of this invention include less than 10%, in other embodiments less than 8%, and in other embodiments less than 5% wt.% solvent.

PHENOLIC RESIN

[0059] As discussed above, the adhesive compositions of particular embodiments are devoid or substantially devoid of phenolic resin. In one or more embodiments, the compositions may be devoid of phenolic resin. In these or other embodiments, the adhesive compositions are substantially devoid of phenolic resin, which refers to that amount of solvent or less that will not have an appreciable impact on the composition. In one or more embodiments, the compositions of this invention include less than 3%, in other embodiments less than 2%, and in other embodiments less than 1% wt.% phenolic resin.

PREPARATION OF ADHESIVE

[0060] The adhesive compositions of the present invention may be prepared by batch mixing using conventional batch mixing equipment. In one or more embodiments, the mixer may be equipped with an emulsifier. The mixing can take place under atmospheric pressure and at room temperature. The ingredients can conveniently be introduced to the mixer by first introducing the silane-terminate polymer followed by introduction of the other ingredients. Mixing may continue until desired viscosity or level of dispersion/solubility is achieved. In particular embodiments, mixing is conducted for at least 100 minutes, in other embodiments at least 150 minutes, in other embodiments at least 180 minutes, and in other embodiments at least 190 minutes.

[0061] The adhesive compositions of this invention may be formulated as either one-part or two-part compositions. In the case of one-part compositions, the composition may be free of water, and contains the moisture scavenger as discussed above. In the case of a two part composition that is combined at the point of use, one part may contain a small amount of water to initiate moisture curing and components that are not sensitive to moisture, whereas the other part may contain components that are sensitive to moisture such as adhesion promoters and more reactive polymers having silicon-containing hydrolyzable terminal groups.

CHARACTERISTICS OF ADHESIVE COMPOSITION

[0062] In one more embodiments, the adhesive composition is formulated to offer various characteristics that are advantageous in practicing the present invention.

[0063] In one or more embodiments, the adhesive composition is characterized by an advantageous dynamic viscosity. While the skilled person will appreciate that the static viscosity of the adhesive can be increased through the use of thixotropic agents, the dynamic viscosity is generally equivalent to the baseline viscosity of the adhesive composition. In other words, the thixotropic agents do not serve to drop the dynamic viscosity below that of the baseline viscosity. In one or more embodiments, the dynamic viscosity of the adhesive compositions of this invention, as measured by using a Brookfield viscometer equipped with a #6 spindle operating at room temperature and 10 rpm, is less than 20,000 cPs, in other embodiments less than 18,000 cPs, in other embodiments less than 17,000 cPs, in other embodiments less than 16,000 cPs, in other embodiments less than 15,000 cPs, in other embodiments less than 14,000 cPs, in other embodiments less than 13,000 cPs, and in other embodiments less than 11000 cPs. In one or more embodiments, the dynamic viscosity of the adhesive compositions of this invention is from about 3,000 to 20,000 cPs, in other embodiments from about 3,300 to 18,000 cPs, in other embodiments from about 4,000 to 16,000 cPs, in other embodiments from about 4,500 to 15,000 cPs, and in other embodiments from about 4,500 to about 11,000 cPs.

[0064] In one or more embodiments, the adhesive compositions of the present invention are characterized by an advantageous static viscosity, which may be measured by a Brookfield viscometer equipped with a #6 spindle operating at room temperature and 2 rpm. In one or more embodiments, the static viscosity of the adhesive composition is at least 24,000 cPs, in other embodiments at least 22,000 cPs, and in other embodiments, at least 20,000 cPs. In one or more embodiments, the static viscosity of the adhesive composition is from about 3600 to about 24,000 cPs, in other embodiments from about 4000 to about 22,000 cPs, and in other embodiments, from about 4600 to about 20,000 cPs.

[0065] Applicants have advantageously discovered that the relatively high static viscosity of the adhesive compositions of this invention give rise to several advantages including higher coverage rates while maintaining useful adhesion. These higher coverage rates stem from the low absorption of the adhesive composition into the substrate. In one or more embodiments, where the substrate includes a polyisocyanurate insulation board having a glass-reinforced paper facer, the absorption of the adhesive material into the facer and/or foam insulation board is, on a weight basis, less than 60%, in other embodiments less than 55%, in other embodiments less than 50%, and in other embodiments less than 45%.

[0066] In one or more embodiments, the adhesive compositions of this invention when used to bond EPDM rubber sheet material to a high density particleboard have generally exhibited a peel strength of at least 2.5-4 pounds per linear inch (pli) after 30 day ambient cure. However, the thermosetting reactions in these compositions substantially improve with time and temperature. In one or more embodiments, after 30 days curing at 150 degrees Fahrenheit (normal rooftop conditions) peel strengths as high as 7.8 pli were obtained.

INDUSTRIAL APPLICABILITY

[0067] In one or more embodiments, the adhesive composition of the present invention may be employed as a adhesive in roofing applications. In particular embodiments, the adhesive may be employed to fully secure a membrane panel to a substrate on a roof deck. In particular embodiments, the adhesive may be employed in preparing a fully-adhered roofing membrane system. In other embodiments, the adhesive may be used for securing membrane panel or flashing to vertical surfaces within a roofing system.

[0068] Practice of the present invention is not necessarily limited by the selection of a particular roofing membrane that is secured to a substrate on a roof surface. As is known in the art, numerous roofing membranes have been proposed in the art and several are used commercially including thermoset and thermoplastic roofing membranes. Commercially available thermoplastic roofing membranes may include polyvinyl chloride, or polyolefin copolymers. For example, thermoplastic olefin (TPO) membranes are available under the trade names UltraPly™, and ReflexEON™ (Firestone Building Products). Commercially available thermoset roofing membranes may include elastomeric copolymers such as ethylene-propylene-diene copolymer (EPDM) rubber and functionalized olefins such as chlorosulfonated polyethylene (CSPE). For example, EPDM membranes are available under the trade name RubberGard™, RubberGard Platinum™, RubberGard EcoWhite™, and RubberGard MAX™ (Firestone Building Products). Useful EPDM membrane is disclosed in, for example, U.S. Patent Nos 7,175,732, 6,502,360, 6,120,869, 5,849,133, 5,389,715, 4,810,565, 4,778,852, 4,732,925, and 4,657,958, which are incorporated herein by reference. EPDM membranes are commercially available from a number of sources; examples include those available under the tradenames RubberGard (Firestone Building Products) and SURE-SEAL (Carlisle SynTec).

[0069] In particular embodiments, EPDM membranes are employed. As is known in the art, EPDM membrane panels include vulcanized or cured rubber compositions. These compositions may include, in addition to the rubber that is ultimately vulcanized, fillers, processing oils, and other desired ingredients such as plasticizers, antidegradants, adhesive-enhancing promoters, etc., as well as vulcanizing agents such as sulfur or sulfur-donating compounds.

[0070] In one or more embodiments, the EPDM roofing panels have a thickness in accordance with ASTM D-4637-04. In one or more embodiments, the EPDM roofing panels have a thickness of at least 45 mil ± 10%, in other embodiments at least 60 mil ± 10%, and in other embodiments at least 90 mil ± 10%. In these or other embodiments, the EPDM roofing panels may have a thickness of less than 65 mil ± 10%, in other embodiments less than 80 mil ± 10%, and in other embodiments less than 110 mil ± 10%.

[0071] In one or more embodiments, the bonding adhesive may be applied to at least a portion of a membrane panel or flashing to form a wet film of the composition on at least a portion of the membrane. In preparing a fully-adhered system, substantially one side of the membrane panel is coated with the composition to form a wet film over a substantial portion of the membrane.

[0072] In other embodiments, the substrate to which the membrane panel or flashing is ultimately attached is provided with a film of the adhesive composition. In other words, the adhesive composition is applied to at least a portion of the substrate. Thus, the adhesive can be applied to one of the two mating surfaces. While it can be applied to both surfaces, it is not necessary in order to practice the present invention.

[0073] In other embodiments, the bond adhesive composition of the present invention is applied exclusively to the substrate (e.g. the roof or materials on the roof such as insulation board), and the membrane is subsequently positioned over the adhesive layer without application of the adhesive directly to the membrane.

APPLICATION METHOD

[0074] In one or more embodiments of this invention, an adhered roofing system is constructed by applying the adhesive composition to a roof substrate to form a layer of adhesive and then subsequently contacting a surface of an EPDM panel to the layer of adhesive disposed on the substrate. Advantageously, the process can be used to construct a roofing system meeting the standards of UL and Factory Mutual for wind uplift without the need for applying an adhesive directly to the EPDM panel being installed. Moreover, these standards can be met in the absence of a fleece or other backing material applied to the membrane.

[0075] The substrate to which the adhesive composition is applied may include a roof deck, which may include steel, concrete, and/or wood. In other embodiments, the adhesive composition may be applied to insulation materials, such as insulation boards and cover boards. As those skilled in the art appreciate, insulation boards and cover boards may carry a variety of facer materials including, but not limited to, paper facers, fiberglass-reinforced paper facers, fiberglass facers, coated fiberglass facers, metal facers such as aluminum facers, and solid facers such as wood, OSB and plywood, as well as gypsum. In yet other embodiments, the adhesive composition may be applied to existing membranes. These existing membranes may include cured rubber systems such as EPDM membranes or chlorosulfonated polyethylene, thermoplastic polymers systems such as TPO membranes or PVC membranes, or asphalt-based systems such as modified asphalt membranes and/or built roof systems. Advantageously, practice of the present invention provides adhesion to asphalt-based substrates by offering sufficient oil resistance, which is required to maintain sufficient adhesion to asphalt systems.

[0076] In one or more embodiments, the adhesive composition is applied to the substrate by dip and roll techniques, which are conventional in the art of applying adhesives to substrates and/or membrane panels. In other embodiments, the adhesive composition is applied to the substrate by spraying. In one or more embodiments, the spraying may be accomplished by using airless spray equipment or air-assisted spray equipment. In one or more embodiments, the adhesive composition is atomized during the spraying operation. Useful spraying equipment is known in the art, such as the spray equipment available from Graco and Garlock. In other embodiments, the adhesive can be applied by a power roller, where the adhesive is pumped to the roller head. Examples include power rollers as supplied by Garlock. In yet other embodiments, the adhesive can be applied by using a drop spreader, which generally includes gravity feeding of the adhesive from a mobile platform such as that sold under the tradename BetterSpreader (Roofmaster). In one or more embodiments, the adhesive can also be applied with a squeezer.

[0077] In one or more embodiments, time is permitted between the application of the adhesive composition and application of the EPDM panel. In one or more embodiments, this time provided is less than 1 hour, in other embodiments less than 30 minutes, in other embodiments less than 10 minutes, and in other embodiments less than 3 minutes. In one or more embodiments, the time provided is from 1 minute to 1 hour.

[0078] In one or more embodiments, the wet film applied to the membrane and/or the substrate can be at least 7 mils, in other embodiments at least 10 mils, in other embodiments at least 13 mils, and in other embodiments at least 15 mils thick (wet film thickness). In these or other embodiments, the wet film thickness on each of the respective layers may be less than 30 mils, in other embodiments less than 25 mils, in other embodiments less than 18 mils, and in other embodiments less than 15 mils thick (wet film thickness).

[0079] It has advantageously been discovered that practice of the present invention allows for application of a thinner wet film than has been previously employed using conventional bond adhesives while achieving technologically useful bond adhesion. As a result, during use of the bond adhesive, the application rate can be reduced (*i.e.,* less bond adhesive is needed per square foot, which translates into an increased application rate). For example, in one or more embodiments, technologically useful adhesion can be achieved at application rates of at least 50 square foot per gallon, in other embodiments at least 60 square foot per gallon, in other embodiments at least 70 square foot per gallon, in other embodiments at least 80 square foot per gallon, in other embodiments at least 90 square foot per gallon, and in other embodiments at least 100 square foot per gallon. In other embodiments at least 150 square foot per gallon, in other embodiments at least 200 square foot per gallon.

[0080] In one or more embodiments, the application of the adhesive composition is applied to the substrate in an amount sufficient to form a dried layer having a dry-film thickness of from about 3 to about 35 mils, in other embodiments from about 3 to about 20 mils, in other embodiments from about 5 to about 30 mils, in other embodiments from about 5 to about 15 mils, in other embodiments from about 7 to about 20, and in other embodiments from about 7 to about 12 mils.

[0081] In one or more embodiments, the EPDM panel may be applied to the adhesive layer using several known techniques. For example, the EPDM panel may be unrolled on to the adhesive layer.

ROOF CONSTRUCTION

[0082] Aspects of the invention may be understood with reference to the figure, which shows membrane 10 adhered to substrate 12. The substrate may include one or more of a roof deck 14, an insulation layer 16, a coverboard 18, and an existing membrane 20. In other words, membrane 10 may be adhered to roof deck 14, insulation layer 16, coverboard 18, or existing membrane 20. Disposed between an adhering membrane 10 to substrate 12 is a layer 22 of adhesive, which layer may be continuous or substantially continuous between membrane 10 and substrate 12 (i.e. a fully-adhered system). In one or more embodiments, the adhesive layer covers at least 20%, in other embodiments at least 30%, in other embodiments at least 40%, in other embodiments at least 50%, and in other embodiments at least 60% of the surface of the substrate. In these or other embodiments, the adhesive layer covers less than 90%, in other embodiments less than 75%, and in other embodiments less than 60% of the surface of the substrate. Notably absent from the construction of one or more embodiments is a fleece layer between membrane 10 and substrate 12. In other words, adhesive layer 22 is adhesively bonded directly to membrane 10.

[0083] In one or more embodiments, the bond between substrate 12 and membrane 10, which is formed by adhesive layer 22, can be quantified based upon standardized peel adhesion tests pursuant to ASTM D1876. In one or more embodiments, the bond between membrane 10 and substrate 12 exceeds at least 1 pli, in other embodiments at least 2 pli, and in other embodiments at least 2.5 pli. Advantageously, in one or more embodiments, the bond formed between membrane 10 and substrate 12 exceeds the pull strength limitations and/or tensile limitations of the substrate. In other words, the substrate fails under pull force (for example the facer pulls from the insulation or substrate boards) prior to the failure of adhesive layer 22.

[0084] In order to demonstrate the practice of the present invention, the following examples have been prepared and tested. The examples should not, however, be viewed as limiting the scope of the invention. The claims will serve to define the invention.

EXAMPLES

[0085] Two adhesive formulations were prepared by using the recipes provided in Table I.

Table I

Sample	**1**	**2**
Ingredient		
Silicon-terminated polyether Blend	52.98 wt%	52.98 wt%
Plasticizer	30.52 wt%	30.52 wt%
Hydrocarbon Tackifier Resin	10 wt%	10 wt%
Antioxidant	0.5 wt%	0.5 wt%
Vinyl Trimethoxy Silane Moisture Scavenger	1.3 wt%	--
Vinyl, theyl, 2-methyl-1,3-propanedioxy silane	--	1.3 wt%
Adhesion Promoter	4.3 wt%	4.3 wt%
Catalyst	0.4 wt%	0.4 wt%
Analytical		
Blistered Area (%)	13.12%	8.69%

[0086] Generally, the silicon-terminated polyether, plasticizer, hydrocarbon resin, and antioxidant were initially charged to a mixer where they were mixed and heated to about 248 °F (120 °C) under about 12 mm mercury vacuum. The composition was then cooled below 80 °F (27 °C) and the vacuum was withdrawn. The moisture scavenger was then added and mixing was continued. The adhesion promoter was then added and mixed. Finally, the catalyst was added and mixing was continued while the vacuum was again applied. The composition was then sealed in a container and stored until use.

[0087] The two adhesive compositions were used in the following test. Test samples were prepared by employing an EPDM membrane that had been used in the field. The membrane was cleaned with cleaning solvents and cut into sample substrates that were slightly larger than one square foot. A virgin EPDM membrane was cut into sample specimens of exactly one square foot. About 38 grams of the adhesive compositions were applied to the cleaned EPDM substrates, respectively, in an area matching the exact dimensions of the virgin EPDM cut specimens. The virgin EPDM specimen was mated to the cleaned EPDM in the area covered by the adhesive, and the edges were sealed with a butyl-based taped, and the edges of the tape were caulked with a butyl-based caulk to ensure a gas tight seal around the periphery of the virgin EDPM specimen.

[0088] Following preparation of the test assemblies, the assemblies were placed into an over preheated to 200 °F (93 °C) for one week. The assemblies were examined daily for the formation of blisters, and the surface area of the blisters was recorded. Table I provides the average total surface area that blistered after one week for three samples tested on each adhesive formulation.

[0089] The results of this test clearly show that the use of conventional moisture scavengers, such as vinyl, trimethoxy silanes, contribute to membrane blistering. And, where a low VOC-generating moisture scavenger is employed, blistering can be markedly reduced.

[0090] Various modifications and alterations that do not depart from the scope and spirit of this invention will become apparent to those skilled in the art. This invention is not to be duly limited to the illustrative embodiments set forth herein.

CLAIMS

What is claimed is:

1. An adhered roofing system comprising:
   - i. a roof substrate;
   - ii. a polymeric membrane; and
   - iii. an adhesive disposed between the roof substrate and the polymeric membrane, where the adhesive is the cured product of an adhesive composition comprising (a) a polymer having a silicon-containing hydrolyzable terminal group, (b) a tackifier resin, and (c) a low VOC-generating moisture scavenger.

2. The adhered roofing system of claim 1, where the adhesive composition further includes an adhesion promoter.

3. The adhered roofing system of any of the preceding claims, where the adhesive composition further includes a catalyst.

4. The adhered roofing system of any of the preceding claims, where the low VOC-generating moisture scavenger is a silane including at least one organo functional group and at least one hydrolyzable group that, upon hydrolysis, generates a non-volatile organic compound or a low vapor volatile organic compound.

5. The composition of any of the preceding claims, where the moisture scavenger is defined by the formula:

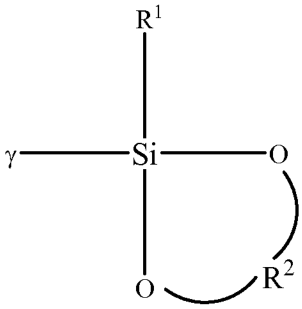
$$(X^1{}_aX^2{}_bX^3{}_cSiR^1)_dZ$$

wherein each occurrence of R^1 is independently a chemical bond between a silicon atom and a carbon atom of the Z group; a hydrocarbyl group of 1 to

10 carbon atoms; or a heterocarbyl of 1 to 10 carbon atoms and at least one heteroatom of nitrogen or oxygen; each occurrence of X^1 is a monovalent alkyl or aryl group of from 1 to 6 carbon atoms or a monovalent heterocarbyl group of from 2 to 8 carbon atoms and at least two heteroatom selected from the group consisting of oxygen and nitrogen, with the proviso that one heteroatom is bonded to a carbon atom of the heterocarbyl group and to the silicon atom; each occurrence of X^2 is a divalent heterocarbyl group of from 2 to 8 carbon atoms and at least two heteroatoms selected from the group consisting of oxygen and nitrogen, with the proviso that two heteroatoms are bonded to two different carbon atoms of the heterocarbyl group and to the same silicon atom; each occurrence of X^3 is a trivalent heterocarbyl group of from about 3 to 8 carbons and at least three heteroatoms selected from the group consisting of oxygen and nitrogen, with the proviso that three heteroatoms are bonded to three different carbon atoms of the heterocarbyl group and to the same silicon atom; each Z is a monovalent or polyvalent organofunctional group of valence d selected from the group consisting of hydrogen, amino, carbamato, epoxy, ureido and alkenyl groups, provided, where Z does not possess a carbon atom, R^1 cannot be a chemical bond; and, each occurrence of a, b, c and d are integers, wherein a is 0 to 3; b is 0 or 1; c is 0 or 1; and d is 1 to 4; with the proviso that when c is 0, then $a+2b=3$ and when b is 1, then $a=1$ and $c=0$.

6. The adhered roofing system of any of the preceding claims, where the moisture scavenger is a glycoxysilane.

7. The adhered roofing system of claim 1, where the glycoxysilane moisture scavenger may be defined by the formula:



where R^1 is a monovalent organic group, R^2 is a divalent organic group, and γ is an electron donating group.

8. The composition of any of the preceding claims, where R^1 is a hydrocarbyl group, R^2 is a hydrocarbylene group, and α is a vinyl group.

9. The composition of any of the preceding claims, where the polymer having a silicon-containing hydrolyzable terminal group is a silane-terminated polyether.

10. The adhered roofing system of any of the preceding claims, where the substrate includes an insulation board.

11. The adhered roofing system of any of the preceding claims, where the substrate includes an existing membrane.

12. The adhered roofing system of any of the preceding claims, where the existing membrane includes an asphalt-based roofing membrane.

13. The adhered roofing system of any of the preceding claims, where said step of applying a membrane includes applying an EPDM membrane.
14. The method of any of the preceding claims, where the membrane is a rubber-based membrane.

15. The adhered roofing system of any of the preceding claims, where the membrane is a thermoplastic-based membrane.

16. A method for forming an adhered membrane roof system, the method comprising:

    i. applying a bond adhesive to a substrate on a roof to form an adhesive layer, where the bond adhesive includes (a) a polymer having a silicon-containing hydrolyzable terminal group, (b) a tackifier resin, and (c) a low VOC-generating moisture scavenger; and
    ii. applying a membrane directly to the adhesive layer.

17. The method of any of the preceding claims, where the low VOC-generating moisture scavenger is a silane including at least one organo functional group and at least one hydrolyzable group that, upon hydrolysis, generates a non-volatile organic compound or a low vapor volatile organic compound.

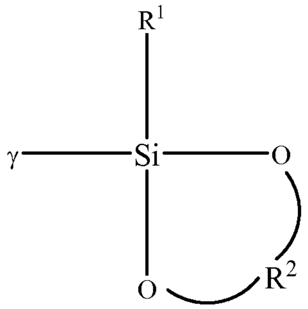
18. The method of any of the preceding claims, where the moisture scavenger is defined by the formula:

$$(X^1{}_aX^2{}_bX^3{}_cSiR^1)_dZ$$

wherein: each occurrence of R^1 is independently a chemical bond between a silicon atom and a carbon atom of the Z group; a hydrocarbyl group of 1 to 10 carbon atoms; or a heterocarbyl of 1 to 10 carbon atoms and at least one heteroatom of nitrogen or oxygen; each occurrence of X^1 is a monovalent alkyl or aryl group of from 1 to 6 carbon atoms or a monovalent heterocarbyl group of from 2 to 8 carbon atoms and at least two heteroatom selected from the group consisting of oxygen and nitrogen, with the proviso that one heteroatom is bonded to a carbon atom of the heterocarbyl group and to the silicon atom; each occurrence of X^2 is a divalent heterocarbyl group of from 2 to 8 carbon atoms and at least two heteroatoms selected from the group consisting of oxygen and nitrogen, with the proviso that two heteroatoms are bonded to two different carbon atoms of the heterocarbyl group and to the same silicon atom; each occurrence of X^3 is a trivalent heterocarbyl group of from about 3 to 8 carbons and at least three heteroatoms selected from the group consisting of oxygen and nitrogen, with the proviso that three heteroatoms are bonded to three different carbon atoms of the heterocarbyl group and to the same silicon atom; each Z is a monovalent or polyvalent organofunctional group of valence d selected from the group consisting of hydrogen, amino, carbamato, epoxy, ureido and alkenyl groups, provided, where Z does not possess a carbon atom, R^1 cannot be a chemical bond; and, each occurrence of a, b, c and d are integers, wherein a is 0 to 3; b is 0 or 1; c is 0 or 1; and d is 1 to 4; with the proviso that when c is 0, then a+2b=3 and when b is 1, then a=1 and c=0.

19. The method of any of the preceding claims, where the moisture scavenger is a glycoxysilane.

20. The method of claim 1, where the glycoxysilane moisture scavenger may be defined by the formula:



where R^1 is a monovalent organic group, R^2 is a divalent organic group, and γ is an electron donating group.

21. The method of any of the preceding claims, where R^1 is a hydrocarbyl group, R^2 is a hydrocarbylene group, and α is a vinyl group.

22. The method of any of the preceding claims, where the adhesive forms a substantially continuous layer between the substrate and the membrane over at least 40% of the entire roof surface.

23. The method of any of the preceding claims, where the method is devoid of any step of applying the adhesive directly to the rubber membrane.

24. The method of any of the preceding claims, where said step of applying the adhesive includes dip and roll techniques.

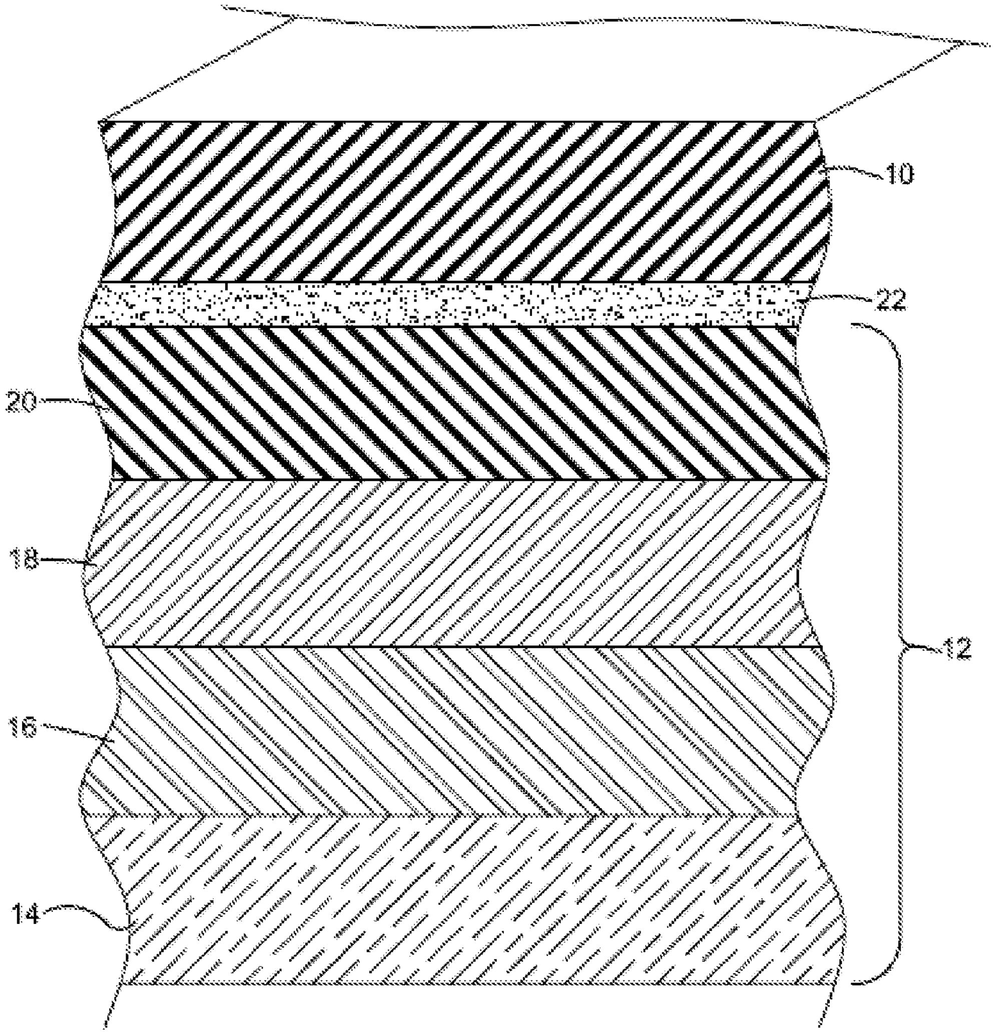
25. The method of any of the preceding claims, where said step of applying the adhesive includes spraying the adhesive on the substrate.

26. The method of any of the preceding claims, where the substrate includes a coverboard.

27. The method of any of the preceding claims, where the existing membrane is a roofing membrane.

28. The method of any of the preceding claims, where the bond adhesive further includes an adhesion promoter.

29. The method of any of the preceding claims, where the polymer having a silicon-containing hydrolyzable terminal group is a silane-terminated polyether.



Figure

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/066101

A. CLASSIFICATION OF SUBJECT MATTER
INV. E04D5/14 C09J171/02 C09J175/04 C08G18/71 C08G18/28
C08G65/336
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
E04D C09J C08G

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 544 254 A1 (CHEM LINK INC [US]) 22 June 2005 (2005-06-22)	1-5, 9-18, 22-29
A	paragraph [0009] - paragraph [0042] paragraph [0045] - paragraph [0047] examples 1,2 -----	6-8, 19-21
X	US 7 767 308 B2 (GEORGEAU PHILLIP C [US] ET AL) 3 August 2010 (2010-08-03) cited in the application	1-5, 9-18, 22-29
A	column 2, line 41 - column 7, line 17 column 8, line 27 - line 34 -----	6-8, 19-21
X	WO 00/37534 A1 (ADCO PRODUCTS INC [US]) 29 June 2000 (2000-06-29)	1-5, 9-18, 22-29
A	page 2, line 6 - page 7, line 2 examples 1,2 -----	6-8, 19-21

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 27 January 2015	Date of mailing of the international search report 03/02/2015
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Stinchcombe, John

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2014/066101

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1544254 A1	22-06-2005	AU 2004224892 A1	02-06-2005
		CA 2487188 A1	14-05-2005
		EP 1544254 A1	22-06-2005
		US 2005107499 A1	19-05-2005
US 7767308 B2	03-08-2010	CA 2564452 A1	14-04-2007
		US 2007088137 A1	19-04-2007
WO 0037534 A1	29-06-2000	AU 2388900 A	12-07-2000
		WO 0037534 A1	29-06-2000