



(51) International Patent Classification:

C08G 75/045 (2016.01) B64C 1/14 (2006.01)

(21) International Application Number:

PCT/IB2020/053166

(22) International Filing Date:

02 April 2020 (02.04.2020)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/829,263 04 April 2019 (04.04.2019) US

(71) Applicant: 3M INNOVATIVE PROPERTIES COMPANY [US/US]; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

(72) Inventors: ZOOK, Jonathan D.; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US). HEBERT, Larry S.; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US). DEMOSS, Susan E.; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US). TOWNSEND, Erik M.; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US). COOK, Clinton J.; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US). MOSER, William H.; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US). SWAN, Michael D.; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US). BOYD, Scott A.; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

(74) Agent: GROSS, Kathleen B., et al.; 3M Center, Office of Intellectual Property Counsel, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (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, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

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

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

Published:

- with international search report (Art. 21(3))
- in black and white; the international application as filed contained color or greyscale and is available for download from PATENTSCOPE

(54) Title: METHOD OF IRRADIATING A COMPOSITION THROUGH A SUBSTRATE

(57) Abstract: The method includes providing a composition that includes a polythiol, a second component, and at least one of a photoinitiator or photosensitizer that absorbs light having a wavelength greater than 400 nanometers; positioning the composition adjacent to the substrate; and irradiating the composition through the substrate with light having a wavelength greater than 400 nanometers, wherein irradiating causes the polythiol to react with the second component. The substrate can have an average percent transmittance of less than 50 percent over a wavelength range of 350 nanometers to 390 nanometers. The method may be a method of making a window assembly, for example, for an aircraft.



METHOD OF IRRADIATING A COMPOSITION THROUGH A SUBSTRATE

Cross-Reference to Related Application

5 This application claims priority to U.S. Provisional Application No. 62/829,263, filed April 4, 2019, the disclosure of which is incorporated by reference in its entirety herein.

Background

10 Sulfur-containing polymers are known to be well-suited for use in aerospace sealants due to their fuel-resistant nature upon crosslinking. Such crosslinking can be carried out, for example, by reaction of a thiol-terminated, sulfur-containing compound with an epoxy resin, generally in the presence of an amine accelerator as described in U.S. Pat. No. 5,912,319 (Zook et al.). Desirable properties for aerospace sealants, which are difficult to obtain, are the combination of long application time (i.e., the time during which the sealant remains usable) and short curing time (the time required to reach a predetermined strength).

15 Other crosslinked sulfur-containing polymers have been made, for example, by reaction of a thiol-terminated sulfur-containing compound with a polyene in the presence of a photoinitiator as described in U.S. Pat. Appl. Nos. 2012/0040103 (Keledjian et al.) and U.S. Pat. No. 8,932,685 (Keledjian et al.). The reactions are effected by irradiating the materials with UV light, and specifically UV light with a wavelength of 180 nm to 400 nm.

20 Methods and compositions for making UV-curable sealants are also disclosed in Int. Pat. App. Pub. No. WO2014/066039 (Vimelson), which describes materials that are at least partially transmissive to ultraviolet radiation with a wavelength of 180 nm to 400 nm.

25 Sealants have been used in combination with a seal cap, for example, over rivets, bolts, or other types of fasteners. The seal cap and the curable sealant are sometimes made from the same material. In some cases, the sealant is cured by exposure to radiation through the seal cap. For more details regarding seal caps, see, for example, Int. Pat. App. Pub. No. WO2014/172305 (Zook et al.).

Summary

30 In one aspect, the present disclosure provides a method of irradiating a composition through a substrate. The method includes providing a composition that includes a polythiol, a second component, and at least one of a photoinitiator or photosensitizer that absorbs light having a wavelength greater than 400 nanometers; positioning the composition adjacent to the substrate; and irradiating the composition through the substrate with light having a wavelength greater than 400 nanometers. Irradiating causes the polythiol to react with the second component. Over a wavelength range of 350 nanometers to 390 nanometers, the substrate has an average percent transmittance of less than 50 percent.

In another aspect, the present disclosure provides a method of making a window assembly. The method includes providing a composition that includes a polythiol, a second component, and at least one of a photoinitiator or photosensitizer that absorbs light having a wavelength greater than 400 nanometers; positioning the composition adjacent to a window; and irradiating the composition through the window with light having a wavelength greater than 400 nanometers. Irradiating causes the polythiol to react with the second component. Over a wavelength range of 350 nm to 390 nm, the window may have an average percent transmittance of less than 50 percent. The window assembly may be useful, for example, in an aircraft, automobile, marine vessel, or building.

The methods described above may be useful, for example, in a method of making an aircraft.

In this application:

Terms such as "a", "an" and "the" are not intended to refer to only a singular entity but include the general class of which a specific example may be used for illustration. The terms "a", "an", and "the" are used interchangeably with the term "at least one".

The phrase "comprises at least one of" followed by a list refers to comprising any one of the items in the list and any combination of two or more items in the list. The phrase "at least one of" followed by a list refers to any one of the items in the list or any combination of two or more items in the list.

The term "adjacent to" refers to near or next to. In the method disclosed herein, the composition may not need to be in direct contact with the substrate, in some embodiments, the window.

The average percent transmittance is measured at a representative position on the substrate.

Transmittances measured at the wavelengths in the range of 350 nm to 390 nm in no greater than 2-nm increments are averaged to provide the average percent transmittance.

The terms "cure" and "curable" refer to joining polymer chains together by covalent chemical bonds, usually via crosslinking molecules or groups, to form a network polymer. Therefore, in this disclosure the terms "cured" and "crosslinked" may be used interchangeably. A cured or crosslinked polymer is generally characterized by insolubility but may be swellable in the presence of an appropriate solvent.

The term "polymer or polymeric" will be understood to include polymers, copolymers (e.g., polymers formed using two or more different monomers), oligomers or monomers that can form polymers, and combinations thereof, as well as polymers, oligomers, monomers, or copolymers that can be blended.

The term "ceramic" refers to glasses, crystalline ceramics, glass-ceramics, and combinations thereof.

"Alkyl group" and the prefix "alk-" are inclusive of both straight chain and branched chain groups and of cyclic groups. In some embodiments, alkyl groups have up to 30 carbons (in some embodiments, up to 20, 15, 12, 10, 8, 7, 6, or 5 carbons) unless otherwise specified. Cyclic groups can be monocyclic or

polycyclic and, in some embodiments, have from 3 to 10 ring carbon atoms. Terminal "alkenyl" groups have at least 3 carbon atoms.

"Alkylene" is the multivalent (e.g., divalent or trivalent) form of the "alkyl" groups defined above.

"Arylalkylene" refers to an "alkylene" moiety to which an aryl group is attached. "Alkylarylene" refers to an "arylene" moiety to which an alkyl group is attached.

The terms "aryl" and "arylene" as used herein include carbocyclic aromatic rings or ring systems, for example, having 1, 2, or 3 rings and optionally containing at least one heteroatom (e.g., O, S, or N) in the ring optionally substituted by up to five substituents including one or more alkyl groups having up to 4 carbon atoms (e.g., methyl or ethyl), alkoxy having up to 4 carbon atoms, halo (i.e., fluoro, chloro, bromo or iodo), hydroxy, cyano, or nitro groups. Examples of aryl groups include phenyl, naphthyl, biphenyl, fluorenyl as well as furyl, thienyl, pyridyl, quinoliny, isoquinoliny, indolyl, isoindolyl, triazolyl, pyrrolyl, tetrazolyl, imidazolyl, pyrazolyl, oxazolyl, and thiazolyl.

The phrase "interrupted by arylene", for example, with regard to an alkylene group refers to having part of the alkylene on both sides of the arylene group. For example, $-\text{CH}_2\text{CH}_2-\text{C}_6\text{H}_5-\text{CH}_2-\text{CH}_2-$ is an alkylene group interrupted by a phenylene group. Similarly, $-\text{CH}_2\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-$ is an alkylene group interrupted by an -NH- group.

"Ambient conditions" means at a temperature of 25 degrees Celsius and a pressure of 1 atmosphere (approximately 100 kilopascals).

"Ambient or room temperature" means at a temperature of 25 degrees Celsius.

The term "(meth)acrylate" refers to at least one of an acrylate or methacrylate.

All numerical ranges are inclusive of their endpoints and non-integral values between the endpoints unless otherwise stated (e.g., 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.80, 4, 5, etc.).

Brief Description of the Drawings

FIG. 1 is a top view of an embodiment of a window frame assembly made by the method of the present disclosure; and

FIG. 2 is a cross-sectional view of a portion of the window frame assembly of FIG. 1.

Detailed Description

The method of the present disclosure includes irradiating the composition through a substrate. In some embodiments, over a wavelength range of 350 nanometers (nm) to 390 nm, the substrate has an average percent transmittance of less than 50 percent. In some embodiments, over a wavelength range of 350 nm to 390 nm, the substrate has an average percent transmittance of less than 45, 40, 35, 30, 25, 20, 15, or 10 percent.

It is understood from Beer's law that absorbance increases with both the molar absorptivity constant and the thickness of the material. Thus, a thicker substrate having a molar absorptivity constant at a particular wavelength will have a higher absorbance and lower percent transmittance at that wavelength than a thinner substrate. The substrate in the method of the present disclosure can have a variety of useful thicknesses, depending on the desired application of the substrate. In some embodiments, including embodiments in which the substrate is a window, the thickness of the substrate is at least 2 millimeters (mm), in some embodiments, at least 4 mm, 5 mm, 6 mm, 8 mm, or 10 mm. In some embodiments, the thickness of the substrate is up to 100 centimeters (cm), 50 cm, 25 cm, 10 cm, or 5 cm. For a substrate having a length, width, and thickness, the thickness is the smallest dimension of the substrate. In some embodiments, the thickness of the substrate is at least 0.2 mm, in some embodiments, at least 0.4 mm, 0.5 mm, 0.6 mm, 0.8 mm, or 1.0 mm.

The substrate useful for practicing the present disclosure is generally able to transmit some portion of visible light, in other words, the substrate is translucent. In some embodiments, over a wavelength range of 400 nm to 750 nm, the substrate has an average percent transmittance of at least 50 percent. In some embodiments, over a wavelength range of 400 nm to 750 nm, the substrate has an average percent transmittance of at least 55, 60, 65, 70, 75, 80, 85, or 90 percent. In some embodiments, over a wavelength range of 400 nm to 500 nm, the substrate has an average percent transmittance of at least 50 percent. In some embodiments, over a wavelength range of 400 nm to 500 nm, the substrate has an average percent transmittance of at least 55, 60, 65, 70, 75, 80, 85, or 90 percent. In some embodiments, the substrate useful for practicing the present disclosure is optically transparent, meaning transparent to the extent that the article does not prevent a viewer from resolving an image, e.g., reading text. In some embodiments, the percent transmittance of the substrate is generally uniform over the area of the substrate. In some embodiments, for an area defined by the length and width of the substrate, at least 90%, 95%, 96%, 97%, 98%, 99% of the area of the substrate has an average percent transmittance over a wavelength range of 400 nm to 750 nm of at least 50, 55, 60, 65, 70, 75, 80, 85, or 90 percent. In some embodiments, for an area defined by the length and width of the substrate, at least 90%, 95%, 96%, 97%, 98%, 99% of the area of the substrate has an average percent transmittance over a wavelength range of 400 nm to 500 nm of at least 50, 55, 60, 65, 70, 75, 80, 85, or 90 percent. In some embodiments, for an area defined by the length and width of the substrate, the entire area has an average percent transmittance over a wavelength range of 400 nm to 750 nm or 400 nm to 500 nm of at least 50, 55, 60, 65, 70, 75, 80, 85, or 90 percent.

Substrates useful for practicing the present disclosure include those comprising organic polymers. The substrate can be a thermoplastic or a thermoset. In some embodiments, the substrate comprises at least one of a poly(meth)acrylate, a polyester, a polycarbonate, an epoxy, or a polyurethane. In some embodiments, the substrate comprises poly(methyl methacrylate) (PMMA). Methyl methacrylate and other acrylates can be used in combination and/or other poly(meth)acrylates can be blended with

poly(methyl methacrylate) if desired. Poly(methyl methacrylate) (PMMA) exhibits high transparency to visible light, but optical transmission diminishes rapidly at wavelengths below approximately 400 nm. The optical transmission diminishes more quickly at wavelengths below approximately 400 nm with increased thickness. A similar trend is observed for polycarbonate although, at a given thickness, polycarbonate tends to have a larger average percent transmittance in a range from 350 nm to 390 nm than PMMA. There are a number of commercially available optically transparent epoxy resins that block light with a wavelength in a range from 350 nm to 390 nm., for example, “MASTERBOND EP30-2LB” optically clear epoxy available from MasterBond, Hackensack, N.J. Polyurethanes exhibit high transparency (> 80% transmission) to visible light at wavelengths above 500 nm. Optical transmission diminishes at wavelengths below approximately 450 nm. Suitable polyesters include polyethylene terephthalates (PET) or polyethylene naphthalates (PEN). The absorption of UV-light by polyethylene terephthalates, for example, starts at around 360 nm, increases markedly below 320 nm, and is very pronounced at below 300 nm. Polyethylene naphthalates strongly absorb UV-light in the 310-370 nm range, with an absorption tail extending to about 410 nm, and with absorption maxima occurring at 352 nm and 337 nm.

In some embodiments, the substrate comprises an organic polymer as described above in any of its embodiments and a nanoparticulate filler. The average particle size of the filler can be selected so that it is not more than 400 nm, in some embodiments, not more than 300 nm, 200 nm, 100 nm, 50 nm, 10 nm, 5 nm, and, in some embodiments, not greater than 1 nm. Suitable fillers include silica (e.g., fumed silica), titanium dioxide, zirconium dioxide, calcium carbonate, aluminum oxide, and aluminum trihydrate.

Silica can include nanosilica and amorphous fumed silica, for example. Silica nanoparticles can have a particle size from 1 nm to 100 nm, 5 nm to 75 nm, or 10 nm to 50 nm. Examples of commercially available nanosilicas include those available from Nalco Chemical Co. (Naperville, Ill.) under the trade designation “NALCO COLLOIDAL SILICAS”. For example, silicas include NALCO products 1040, 1042, 1050, 1060, 2327 and 2329. Suitable fumed silicas include, for example, products available from DeGussa AG, (Hanau, Germany) under the trade designation “AEROSIL”, for example, series OX-50, -130, -150, and -200, and from Cabot Corp. (Tuscola, Ill.) under the trade designations “CAB-O-SPERSE 2095”, “CAB-O-SPERSE A10 5”, and “CAB-O-SIL M5”.

In some embodiments, the nanoparticulate filler comprises zirconia nanoparticles. Zirconia nanoparticles can have a particle size from 5 nm to 50 nm, 5 nm to 15 nm, or about 10 nm. Zirconias are commercially available, for example, from Nalco Chemical Co. under the trade designation “NALCO OOSOO8”. Other useful nanoparticulate fillers include titania, antimony oxides, alumina, tin oxides, and/or mixed metal oxide fillers comprise nanoparticles having a particle size or associated particle size from 5 nm to 50 nm, or 5 nm to 15 nm, or about 10 nm. Mixed metal oxides are commercially available, for example, from Catalysts & Chemical Industries Corp., (Kawasaki, Japan) under the product designation “OPTOLAKE 3”. Further suitable fillers include fibers (e.g., ceramic fibers, in some

embodiments, glass fibers). Examples of suitable fibers include “3M NEXTEL” Ceramic Fibers from 3M Company, St. Paul, Minn. In some embodiments, suitable fibers have at least one dimension having a size of not more than 400 nm, in some embodiments, not more than 300 nm, 200 nm, or not more than 100 nm.

5 In some embodiments, the substrate useful in the method of the present disclosure is a window, for example, of a building or a vehicle (e.g., an automobile, aircraft, or marine vessel). The composition useful in the method may be at least one of an adhesive for adhering a window to a window frame or a window sealant. In addition to the organic polymers and composites described above, when the substrate is a window, the substrate can also comprise glass. In some embodiments, the substrate is a window of an
10 aircraft. The window sealant may be useful for preventing the ingress of weather and may provide a smooth transition between the outer surfaces of a vehicle to achieve desired aerodynamic properties. The method according to the present disclosure may likewise be carried out to allow the interior of the aircraft (e.g., the passenger cabin) to maintain pressurization at higher altitudes. Compositions including the polythiol in the method according to the present disclosure can be cured into, for example, aviation fuel-
15 resistant sealants.

FIG. 1 is a top view of an embodiment of a window frame assembly 10 that can be made by the method of the present disclosure. The window frame assembly 10 may be for a commercial aircraft. In FIG. 1, outer windowpane 12 is mounted in an aperture in the outer mold line 16 of the aircraft. Composition 18 can be useful for at least one of adhering outer windowpane 12 in the window frame or
20 sealing the aperture.

FIG. 2 is a cross-sectional view of a portion of the window frame assembly 10 of FIG. 1. Pressurized outer windowpane 12 and non-pressurized inner windowpane 14 are separated from one another by air gap 13. The air gap 13 may be useful, for example, for preventing fogging. The panes are sealed to a window frame 15 with composition 18 and assembled as a joint window set. The window set
25 is affixed to the window frame 15 from the inside of the aircraft by a retainer 17 that both covers the window seal and blends with the aircraft interior design.

When light is used to cure composition 18, it can be shone from the direction of light source 21 illustrated in FIG. 2. Some of composition 18 may be exposed to light 23. In the illustrated embodiment, most of the composition 18 is covered by outer windowpane 12. The windowpanes 12, 14 themselves are
30 most often formed from a transparent thermoplastic material. For aesthetic and safety reasons, the windows of passenger airplanes are typically optically clear and allow the passage of visible light. PMMA is desirable as a material for the windowpanes because of its transparency, shatter-resistance, and lower density in comparison to standard silicon-based glass. PMMA exhibits superior transparency to visible light, but its optical transmission diminishes rapidly at wavelengths below approximately 400 nm, especially at typical thicknesses of windowpanes, which are about 9 mm to 10 mm thick. The window
35 frame 15, outer mold line 16, and retainer 17 may include metals such as titanium, stainless steel, and

aluminum, and/or composites, any of which may be anodized, primed, organic-coated (e.g., polymer-coated), or chromate-coated.

The method of the present disclosure includes irradiating the composition through the substrate with light having a wavelength greater than 400 nanometers. The at least one of the photoinitiator or
5 photosensitizer absorbs the light at the selected wavelength. Irradiating causes the polythiol to react with the second component to form an at least partially crosslinked network. In some of these embodiments, useful photoinitiators and photosensitizers absorb light in a wavelength range from 400 nm to 750 nm or 400 nm to 650 nm. In some embodiments, the light having the wavelength greater than 400 nanometers comprises blue light. Blue light can be considered to have a wavelength range of 400 nm to 495 nm or, in
10 some embodiments, 450 nm to 495 nm or 450 nm to 485 nm.

In some embodiments, the composition includes at least one photosensitizer. A photosensitizer can be useful, for example, if the photoinitiator does not have a strong absorbance in a wavelength range that is desired for curing the composition. As used herein, a photosensitizer may be understood to be, for example, a compound having an absorption spectrum that overlaps or closely matches the emission
15 spectrum of the radiation source to be used and that can improve the overall quantum yield by means of, for example, energy transfer or electron transfer to other component(s) of the curable sealant or solution (e.g., the photoinitiator).

The light source and exposure time can be selected, for example, based on the nature and amount of the composition. Suitable light includes light from artificial sources, including both point sources and
20 flat radiators. In some embodiments, the light source is a blue light source. Examples of useful light sources include carbon arc lamps; xenon arc lamps; medium-pressure, high-pressure, and low-pressure mercury lamps, doped if desired with metal halides (metal halogen lamps); microwave-stimulated metal vapor lamps; excimer lamps; superactinic fluorescent tubes; fluorescent lamps; incandescent filament lamps, incandescent argon lamps; electronic flashlights; xenon flashlights; photographic flood lamps;
25 light-emitting diodes; laser light sources (for example, excimer lasers); and combinations thereof. The distance between the light source and the substrate can vary depending upon thickness of the substrate.

In some embodiments, the surface of the substrate may be cleaned before applying the composition. It is typically desirable to remove foreign materials such as dust, oil, grease, and other contamination. Cleaning may be carried out, for example, with an organic solvent (e.g., a ketone such as
30 acetone or an alcohol such as isopropanol), with water, with a solution of sodium hydroxide (e.g., 2, 5, or 10 percent by weight aqueous sodium hydroxide), or with a combination thereof. The cleaning may be carried out at room temperature or at an elevated temperature (e.g., in a range from about 50 °C to about 100 °C). Techniques for cleaning a substrate surface include wiping, rinsing, and sonicating. After cleaning, the substrate may be dried, for example, under a stream of air or nitrogen or at an elevated
35 temperature. The substrate can also be primed with an adhesion promoter, such as those described below in connection with the composition.

Sulfur-containing polymers are known to be well-suited for use in aerospace sealants due to their fuel-resistant nature upon crosslinking. Accordingly, in some embodiments, the composition useful for practicing the present disclosure includes a polythiol having more than one thiol group. In some embodiments, the polythiol includes at least two thiol groups. Generally, in order to achieve chemical crosslinking between polymer chains, greater than two thiol groups and/or greater than two crosslinking groups are present in at least some of the polythiol and curing agent molecules, respectively. In some embodiments, mixtures of curing agents and/or polythiols having at least 5 percent functional equivalents of thiol groups contributed by polythiols having at least three thiol groups may be useful.

A variety of polythiols having more than one thiol group are useful in the method according to the present disclosure. In some embodiments, the polythiol is monomeric. In these embodiments, the polythiol may be an alkylene, arylene, alkylarylene, arylalkylene, or alkylenearylalkylene having at least two mercaptan groups, wherein any of the alkylene, alkylarylene, arylalkylene, or alkylenearylalkylene are optionally interrupted by one or more ether (i.e., -O-), thioether (i.e., -S-), or amine (i.e., -NR¹-) groups and optionally substituted by alkoxy or hydroxyl. Useful monomeric polythiols may be dithiols or polythiols with more than 2 (in some embodiments, at least 3 or 4) mercaptan groups. In some embodiments, the polythiol is an alkylene dithiol in which the alkylene is optionally interrupted by one or more ether (i.e., -O-) or thioether (i.e., -S-) groups. Examples of useful dithiols include 1,2-ethanedithiol, 1,2-propanedithiol, 1,3-propanedithiol, 1,3-butanedithiol, 1,4-butanedithiol, 2,3-butanedithiol, 1,3-pentanedithiol, 1,5-pentanedithiol, 1,6-hexanedithiol, 1,3-dimercapto-3-methylbutane, dipentenedimercaptan, ethylcyclohexyldithiol (ECHDT), dimercaptodiethylsulfide, methyl-substituted dimercaptodiethylsulfide, dimethyl-substituted dimercaptodiethylsulfide, dimercaptodioxaoctane, 1,5-dimercapto-3-oxapentane and mixtures thereof. Examples of polythiols having more than two mercaptan groups include propane-1,2,3-trithiol; 1,2-bis[(2-mercaptoethyl)thio]-3-mercaptopropane; tetrakis(7-mercapto-2,5-dithiaheptyl)methane; and trithiocyanuric acid. Combination of any of these or with any of the dithiols mentioned above may be useful.

In some embodiments, the polythiol in the method according to the present disclosure is oligomeric or polymeric. Examples of useful oligomeric or polymeric polythiols include polythioethers and polysulfides. Polythioethers include thioether linkages (i.e., -S-) in their backbone structures. Polysulfides include disulfide linkages (i.e., -S-S-) in their backbone structures.

Polythioethers can be prepared, for example, by reacting dithiols with dienes, diynes, divinyl ethers, diallyl ethers, ene-ynes, or combinations of these under free-radical conditions. Useful dithiols include any of the dithiols listed above. Examples of suitable divinyl ethers include divinyl ether, ethylene glycol divinyl ether, butanediol divinyl ether, hexanediol divinyl ether, diethylene glycol divinyl ether, triethylene glycol divinyl ether, tetraethylene glycol divinyl ether, cyclohexanedimethanol divinyl ether, polytetrahydrofuryl divinyl ether, and combinations of any of these. Useful divinyl ethers of formula $\text{CH}_2=\text{CH}-\text{O}-(\text{R}^{2'}-\text{O})_{m'}-\text{CH}=\text{CH}_2$, in which m' is a number from 0 to 10, $\text{R}^{2'}$ is C_2 to C_6 branched

alkylene can be prepared by reacting a polyhydroxy compound with acetylene. Examples of compounds of this type include compounds in which $R^{2'}$ is an alkyl-substituted methylene group such as $-\text{CH}(\text{CH}_3)-$ (e.g., those obtained from BASF, Florham Park, N.J., under the trade designation "PLURIOL", for which R^2 is ethylene and m is 3.8) or an alkyl-substituted ethylene (e.g., $-\text{CH}_2\text{CH}(\text{CH}_3)-$ such as those obtained from International Specialty Products of Wayne, N.J., under the trade designation "DPE" (e.g., "DPE-2" and "DPE-3"). Examples of other suitable dienes, diynes, and diallyl ethers include 4-vinyl-1-cyclohexene, 1,5-cyclooctadiene, 1,6-heptadiyne, 1,7-octadiyne, and diallyl phthalate. Small amounts of trifunctional compounds (e.g., triallyl-1,3,5-triazine-2,4,6-trione, 2,4,6-triallyloxy-1,3,5-triazine) may also be useful in the preparation of oligomers.

Examples of oligomeric or polymeric polythioethers useful for practicing the present disclosure are described, for example, in U.S. Pat. Nos. 4,366,307 (Singh et al.), 4,609,762 (Morris et al.), 5,225,472 (Cameron et al.), 5,912,319 (Zook et al.), 5,959,071 (DeMoss et al.), 6,172,179 (Zook et al.), and 6,509,418 (Zook et al.). In some embodiments, the polythioether is represented by formula $\text{HS}-\text{R}^{3'}-[\text{S}-(\text{CH}_2)_2-\text{O}-[\text{R}^{4'}-\text{O}]_m-(\text{CH}_2)_2-\text{S}-\text{R}^{3'}]_n-\text{SH}$, wherein each $\text{R}^{3'}$ and $\text{R}^{4'}$ is independently a C_{2-6} alkylene, wherein alkylene may be straight-chain or branched, C_{6-8} cycloalkylene, C_{6-10} alkylcycloalkylene, $-(\text{CH}_2)_{p'}-\text{X}-[\text{CH}_2]_{q'}-(\text{CH}_2)_r$, in which at least one $-\text{CH}_2-$ is optionally substituted with a methyl group, X is selected from the group consisting of O , S and $-\text{NR}^{5'}$, $\text{R}^{5'}$ denotes hydrogen or methyl, m' is a number from 0 to 10, n' is a number from 1 to 60, p' is an integer from 2 to 6, q is an integer from 1 to 5, and r is an integer from 2 to 10. Polythioethers with more than two mercaptan groups may also be useful.

In some embodiments, a free-radical initiator is combined with the dithiols with dienes, diynes, divinyl ethers, diallyl ethers, ene-ynes, or combinations of these, and the resulting mixture is heated to provide the polythioethers. Examples of suitable free-radical initiators include azo compounds (e.g., 2,2'-azobisisobutyronitrile (AIBN), 2,2'-azobis(2-methylbutyronitrile), or azo-2-cyanovaleric acid). In some embodiments, the free-radical initiator is an organic peroxide. Examples of useful organic peroxides include hydroperoxides (e.g., cumene, *tert*-butyl or *tert*-amyl hydroperoxide), dialkyl peroxides (e.g., di-*tert*-butylperoxide, dicumylperoxide, or cyclohexyl peroxide), peroxyesters (e.g., *tert*-butyl perbenzoate, *tert*-butyl peroxy-2-ethylhexanoate, *tert*-butyl peroxy-3,3,5,5-trimethylhexanoate, *tert*-butyl monoperoxymaleate, or di-*tert*-butyl peroxyphthalate), peroxycarbonates (e.g., *tert*-butylperoxy 2-ethylhexylcarbonate, *tert*-butylperoxy isopropyl carbonate, or di(4-*tert*-butylcyclohexyl) peroxydicarbonate), ketone peroxides (e.g., methyl ethyl ketone peroxide, 1,1-di(*tert*-butylperoxy)cyclohexane, 1,1-di(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane, and cyclohexanone peroxide), and diacylperoxides (e.g., benzoyl peroxide or lauryl peroxide). The organic peroxide may be selected, for example, based on the temperature desired for use of the organic peroxide and compatibility with the monomers. Combinations of two or more organic peroxides may also be useful.

The free-radical initiator useful for making a polythioether may also be a photoinitiator. Examples of useful photoinitiators include benzoin ethers (e.g., benzoin methyl ether or benzoin butyl ether); acetophenone derivatives (e.g., 2,2-dimethoxy-2-phenylacetophenone or 2,2-diethoxyacetophenone); 1-hydroxycyclohexyl phenyl ketone; and acylphosphine oxide derivatives and acylphosphonate derivatives (e.g., bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide, diphenyl-2,4,6-trimethylbenzoylphosphine oxide, isopropoxyphenyl-2,4,6-trimethylbenzoylphosphine oxide, or dimethyl pivaloylphosphonate). Many photoinitiators are available, for example, from IGM Resins under the trade designation "OMNIRAD". The photoinitiator may be selected, for example, based on the desired wavelength for curing and compatibility with the monomers. When using a photoinitiator, the polythioether is typically prepared using an actinic light source (e.g., at least one of a blue light source or a UV light source).

Polythioethers can also be prepared, for example, by reacting dithiols with diepoxides, which may be carried out by stirring at room temperature, optionally in the presence of a tertiary amine catalyst (e.g., 1,4-diazabicyclo[2.2.2]octane (DABCO)). Useful dithiols include any of those described above. Useful epoxides can be any of those having two epoxide groups. In some embodiments, the diepoxide is a bisphenol diglycidyl ether, wherein the bisphenol (i.e., $-O-C_6H_5-CH_2-C_6H_5-O-$) may be unsubstituted (e.g., bisphenol F), or either of the phenyl rings or the methylene group may be substituted by halogen (e.g., fluoro, chloro, bromo, iodo), methyl, trifluoromethyl, or hydroxymethyl. Polythioethers prepared from dithiols and diepoxides have pendent hydroxyl groups and can have structural repeating units represented by formula $-S-R^{3'}-S-CH_2-CH(OH)-CH_2-O-C_6H_5-CH_2-C_6H_5-O-CH_2-CH(OH)-CH_2-S-R^{3'}-S-$, wherein $R^{3'}$ is as defined above, and the bisphenol (i.e., $-O-C_6H_5-CH_2-C_6H_5-O-$) may be unsubstituted (e.g., bisphenol F), or either of the phenyl rings or the methylene group may be substituted by halogen (e.g., fluoro, chloro, bromo, iodo), methyl, trifluoromethyl, or hydroxymethyl. Mercaptan-terminated polythioethers of this type can also be reacted with any of the dienes, diynes, divinyl ethers, diallyl ethers, and ene-yne listed above under free radical conditions. Any of the free-radical initiators and methods described above may be useful for preparing the polythioethers. In some embodiments, the mixture includes a thermal initiator and is heated to provide the polythioethers.

Other useful polythiols can be formed from the addition of hydrogen sulfide (H_2S) (or its equivalent) across carbon-carbon double bonds. For example, dipentene and triglycerides which have been reacted with H_2S (or its equivalent). Specific examples include dipentene dimercaptan and those polythiols available as POLYMERCAPTAN 358 (mercaptanized soybean oil) and POLYMERCAPTAN 805C (mercaptanized castor oil) from Chevron Phillips Chemical Co. LLP. At least for some applications, the polythiols are POLYMERCAPTAN 358 and 805C since they are produced from largely renewable materials, i.e., the triglycerides, soybean oil and castor oil, and have relatively low odor in comparison to many thiols. Useful triglycerides have at least 2 sites of unsaturation, i.e., carbon-carbon double bonds, per molecule on average, and sufficient sites are converted to result in at least 2 thiols per

molecule on average. In the case of soybean oil, this requires a conversion of approximately 42 percent or greater of the carbon-carbon double bonds, and in the case of castor oil this requires a conversion of approximately 66 percent or greater of the carbon-carbon double bonds. Typically, POLYMERCAPTAN 358 and 805C can be obtained with conversions greater than approximately 60 percent and 95 percent, respectively. Useful polythiols of this type also include those derived from the reaction of H₂S (or its equivalent) with the glycidyl ethers of bisphenol A epoxy resins, bisphenol F epoxy resins, and novolak epoxy resins. A useful polythiol of this type is QX11, derived from bisphenol A epoxy resin, from Japan Epoxy Resins (JER) as EPOMATE. Other polythiols suitable include those available as EPOMATE QX10 and EPOMATE QX20 from JER.

Polysulfides are typically prepared by the condensation of sodium polysulfide with bis-(2-chloroethyl) formal, which provides linear polysulfides having two terminal mercaptan groups. Branched polysulfides having three or more mercaptan groups can be prepared using trichloropropane in the reaction mixture. Examples of useful polysulfides are described, for example, in U.S. Pat. Nos. 2,466,963 (Patrick et al); 2,789,958 (Fettes et al); 4,165,425 (Bertozzi); and 5,610,243 (Vietti et al.). Polysulfides are commercially available under the trademarks "THIOKOL" and "LP" from Toray Fine Chemicals Co., Ltd., Urayasu, Japan and are exemplified by grades "LP-2", "LP-2C" (branched), "LP-3", "LP-33", and "LP-541".

Polythioethers and polysulfides can have a variety of useful molecular weights. In some embodiments, the polythioethers and polysulfides have number average molecular weights in a range from 500 grams per mole to 20,000 grams per mole, 1,000 grams per mole to 10,000 grams per mole, or 2,000 grams per mole to 5,000 grams per mole.

In some embodiments, the composition comprises at least one unsaturated compound comprising more than one carbon-carbon double bond, at least one carbon-carbon triple bond, or a combination thereof as a second component. These unsaturated compounds are useful, for example, as curing agents for polythiols. In some embodiments, the unsaturated compound includes at least two carbon-carbon double bonds, at least one carbon-carbon triple bond, or combinations thereof. Generally, in order to achieve chemical crosslinking between polymer chains, greater than two thiol groups and/or greater than two carbon-carbon double bonds, carbon-carbon triple bonds, or a combination thereof are present in at least some of the polythiol and unsaturated compounds, respectively. It should be understood that the unsaturated compound has carbon-carbon double bonds and/or carbon-carbon triple bonds that are reactive and generally not part of an aromatic ring. In some of these embodiments, the carbon-carbon double and triple bonds are terminal groups in a linear aliphatic compound. However, styryl groups and allyl-substituted aromatic rings may be useful. The unsaturated compound may also include one or more ether (i.e., -O-), thioether (i.e., -S-), amine (i.e., -NR¹-), or ester (e.g., so that the compound is an acrylate or methacrylate) groups and one or more alkoxy or hydroxyl substituents. In some embodiments, the unsaturated compound does not include ester groups or carbonate groups. In these embodiments, the

unsaturated compound is not an acrylate, methacrylate, vinyl ester, or vinyl carbonate. Unsaturated compounds without ester and carbonate groups may be more chemically stable than unsaturated compounds that contain these groups. Suitable unsaturated compounds include dienes, diynes, divinyl ethers, diallyl ethers, ene-ynes, and trifunctional versions of any of these. Combinations of any of these groups may also be useful. Examples of useful unsaturated compounds having more than one carbon-carbon double bond and/or carbon-carbon triple bond include any of those described above in connection with the preparation of polythioethers. When curing polythiols having two thiol groups, a mixture of unsaturated compounds may be useful in which at least one unsaturated compound has two carbon-carbon double or triple bonds, and at least one unsaturated compound has at least three carbon-carbon double or triple bonds. Mixtures of unsaturated compounds having at least 5 percent functional equivalents of carbon-carbon double or triple bonds contributed by polyenes having at least three carbon-carbon double or triple bonds may be useful.

Further examples of unsaturated compounds suitable for curing polythiols include unsaturated hydrocarbon compounds having from 5 to 30 carbon atoms or 5 to 18 carbon atoms (e.g., 1,4-pentadiene, 1,5-hexadiene, 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, 1,10-undecadiene, 1,11-dodecadiene, 1,13-tetradecadiene, 1,15-hexadecadiene, 1,17-octadecadiene, 1,19-icosadiene, 1,21-docosadiene, divinylbenzene, dicyclopentadiene, limonene, diallylbenzene, triallylbenzene); vinyl or allyl ethers having from 4 to 30 carbon atoms or 4 to 18 carbon atoms (e.g., divinyl ether, ethylene glycol divinyl ether, 1,4-butanediol divinyl ether, 1,6-hexanediol divinyl ether, diethylene glycol divinyl ether, triethylene glycol divinyl ether, tetraethylene glycol divinyl ether, cyclohexanedimethanol divinyl ether, trimethylolpropane trivinyl ether, pentaerythritol tetravinyl ether, bisphenol A divinyl ether, bisphenol F divinyl ether, bisphenol A diallyl ether, and bisphenol F diallyl ether); diynes having from 5 to 30 carbon atoms or 5 to 15 carbon atoms (e.g., 1,6-heptadiyne); isocyanurates having from 9 to 30 carbon atoms or 9 to 15 carbon atoms (e.g., diallyl isocyanurate and triallyl isocyanurate); cyanurates having from 9 to 30 carbon atoms or 9 to 15 carbon atoms (e.g., diallyl cyanurate and triallyl cyanurate); and certain ethenyl and/or ethynyl-substituted polymers such as, for example, polytetrahydrofuryl divinyl ether, polyethylene oxide divinyl ether, polyethylene oxide diallyl ether, polypropylene oxide divinyl ether, polypropylene oxide diallyl ether, and mixtures thereof. Ethenyl and/or ethynyl-substituted polymers may have two, three, four, or more ethenyl (e.g., vinyl) and/or ethynyl (e.g., acetylenyl) pendant group and/or end groups. Compounds having both ethenyl and ethynyl groups may also be useful. Combinations of the foregoing may be useful.

Typically, the amounts of the polythiol(s) and unsaturated compound(s) are selected for the composition so that there is a stoichiometric equivalence of thiol groups and carbon-carbon double bonds, carbon-carbon triple bonds, or a combination thereof. In some embodiments, the number of the thiol groups is within 10, 5, 3, 2, or 1 percent of the number of the carbon-carbon double bonds. The

stoichiometry expressed as a ratio of thiol groups to carbon-carbon double bonds can be in the range of 0.8 to 1.2, 0.9 to 1.1, or 0.95 to 1.05, although this is not a requirement.

In some embodiments, compositions useful for practicing the present disclosure include a Michael acceptor comprising more than one Michael acceptor group as the second component. A "Michael acceptor" refers to an unsaturated compound useful, for example, for curing polythiols, that is an activated alkene, such as an alkenyl group proximate to an electron-withdrawing group such as a ketone, halo, nitrile, carbonyl, or nitro group. Michael acceptors are well known in the art. A "Michael acceptor group" refers to an activated alkenyl group and an electron-withdrawing group. In some embodiments, a Michael acceptor comprises at least one of a vinyl ketone, a vinyl sulfone, a quinone, an enamine, a ketimine, oxazolidine, an acrylate, acrylonitrile, acrylamides, maleimides, alkyl methacrylates, cyanoacrylate, alpha, beta-unsaturated aldehydes, vinyl phosphonates, vinyl pyridines, beta-keto acetylenes, and acetylene esters. In some embodiments, the composition is substantially free of a Michael acceptor. "Substantially free" refers to having up to 5, 4, 3, 2, or 1 percent by weight of a Michael acceptor, based on the total weight of the composition. "Substantially free" of a Michael acceptor also includes being free of a Michael acceptor.

In some of these embodiments, including any of the embodiments described above in which the composition includes a polythiol and an unsaturated compound, the curable sealant includes a free-radical photoinitiator suitable for curing a polythiol with a second component comprising an unsaturated compound having at least one carbon-carbon double bond and/or carbon-carbon triple bond. In some embodiments, the free radical photoinitiator is a cleavage-type photoinitiator. Cleavage-type photoinitiators include acetophenones, alpha-aminoalkylphenones, benzoin ethers, benzoyl oximes, acylphosphine oxides and bisacylphosphine oxides and mixtures thereof. Examples of useful photoinitiators include benzoin ethers (e.g., benzoin methyl ether or benzoin butyl ether); substituted acetophenone (e.g., 2,2-dimethoxy-2-phenylacetophenone or 2,2-diethoxyacetophenone); 1-hydroxycyclohexyl phenyl ketone; and acylphosphonate derivatives (e.g., bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide, diphenyl-2,4,6-trimethylbenzoylphosphine oxide, isopropoxyphenyl-2,4,6-trimethylbenzoylphosphine oxide, or dimethyl pivaloylphosphonate). Other useful photoinitiators include those described above in connection with the preparation of polythioethers. Many photoinitiators are available, for example, from IGM Resins under the trade designation "OMNIRAD". The photoinitiator may be selected, for example, such that it absorbs light having a wavelength greater than 400 nanometers and is compatible in the composition. Two or more of any of these photoinitiators may also be used together in any combination.

A composition including a free-radical photoinitiator can be packaged as a one-part product including the photoinitiator, or a two-part product in which at least one of the parts includes the photoinitiator and can be mixed just before it is applied to the substrate. The photoinitiator can be added to the composition in any amount suitable to initiate curing. In some embodiments, the photoinitiator is

present in an amount in a range from 0.05 weight percent to about 5 weight percent (in some embodiments, 0.1 weight percent to 2.5 weight percent, or 0.1 weight percent to 2 weight percent), based on the total weight of the composition.

In some embodiments, the composition further includes an organic peroxide. Examples of useful organic peroxides include hydroperoxides (e.g., cumene, *tert*-butyl or *tert*-amyl hydroperoxide), dialkyl peroxides (e.g., di-*tert*-butylperoxide, dicumylperoxide, or cyclohexyl peroxide), peroxyesters (e.g., *tert*-butyl perbenzoate, *tert*-butyl peroxy-2-ethylhexanoate, *tert*-butyl peroxy-3,5,5-trimethylhexanoate, *tert*-butyl monoperoxymaleate, or di-*tert*-butyl peroxyphthalate), peroxycarbonates (e.g., *tert*-butylperoxy 2-ethylhexylcarbonate, *tert*-butylperoxy isopropyl carbonate, or di(4-*tert*-butylcyclohexyl) peroxydicarbonate), ketone peroxides (e.g., methyl ethyl ketone peroxide, 1,1-di(*tert*-butylperoxy)cyclohexane, 1,1-di(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane, and cyclohexanone peroxide), and diacylperoxides (e.g., benzoyl peroxide or lauryl peroxide). In some embodiments, the peroxide is selected from the group consisting of di-*tert*-butyl peroxide, methyl ethyl ketone peroxide, and benzoyl peroxide. The organic peroxide may be selected, for example, based on the temperature desired for use of the organic peroxide and compatibility with the polythiol and the unsaturated compound. Combinations of two or more organic peroxides may also be useful.

Organic peroxides can be useful, for example, as a free-radical initiator for curing the composition in combination with the photoinitiator described above. A peroxide initiator can be useful, for example, when at least a portion of the composition is in shadow (e.g., between opaque substrates not able to transmit some portion of visible light) and/or if the composition is highly filled with an opaque filler. The organic peroxide can cause typically cause the polythiol to react with the second component before light exposure, for example. Organic peroxides can also be useful, for example, when the composition includes a polysulfide oligomer or polymer. In these cases, the organic peroxide can serve as an oxidizing agent that can minimize the degradation or interchanging of disulfide bonds in the sealant network.

In some embodiments, the organic peroxide is an organic hydroperoxide. Organic hydroperoxides have the general structure $R'-OOH$, wherein R' is an alkyl group, aryl group, arylalkylene group, alkylarylene group, alkylarylenealkylene group, or a combination thereof. Examples of useful organic hydroperoxides include cumene hydroperoxide, *tert*-butyl hydroperoxide, *tert*-amyl hydroperoxide, 1,1,3,3-tetramethylbutyl hydroperoxide, isopropylcumyl hydroperoxide, p-menthane hydroperoxide (i.e., 1-methyl-1-(4-methylcyclohexyl)ethyl hydroperoxide), diisopropylbenzene hydroperoxide (e.g., 3,5-diisopropylhydroperoxide). In some embodiments, the organic hydroperoxide includes a ketone peroxide (e.g., methyl ethyl ketone peroxide, acetone peroxide, and cyclohexanone peroxide).

When used as an initiator to cure the composition, the organic peroxide can be used in combination with an amine, wherein the peroxide and the amine together provide a peroxide-amine redox

initiator. In some embodiments, the amine is a tertiary amine. In some embodiments, the amine is selected from the group consisting of dihydroxyethyl-p-toluidine, N,N-diisopropylethylamine, and N, N, N', N'', N'''-pentamethyl-diethylenetriamine.

While organic hydroperoxides tend to be some of the more stable peroxides and require some of the highest temperatures for thermal initiation, we have found that in the presence of a polythiol and unsaturated compound in the composition of the present disclosure, the organic hydroperoxide can initiate curing at room temperature. In some embodiments, compositions that comprise an organic hydroperoxide further comprise a nitrogen-containing base. In some embodiments, a combination of a nitrogen-containing base and an organic hydroperoxide can be considered a redox initiator. The nitrogen atom(s) in the nitrogen-containing base can be bonded to alkyl groups, aryl groups, arylalkylene groups, alkylarylene, alkylarylenealkylene groups, or a combination thereof. The nitrogen-containing base can also be a cyclic compound, which can include one or more rings and can be aromatic or non-aromatic (e.g., saturated or unsaturated). Cyclic nitrogen-containing bases can include a nitrogen as at least one of the atoms in a 5- or 6-membered ring. In some embodiments, the nitrogen-containing base includes only carbon-nitrogen, nitrogen-hydrogen, carbon-carbon, and carbon-hydrogen bonds. In some embodiments, the nitrogen-containing base can be substituted with at least one of alkoxy, aryl, arylalkylenyl, haloalkyl, haloalkoxy, halogen, nitro, hydroxy, hydroxyalkyl, mercapto, cyano, aryloxy, arylalkyleneoxy, heterocyclyl, or hydroxyalkyleneoxyalkylenyl. In some embodiments, the nitrogen-containing base is a tertiary amine. Examples of useful tertiary amines include triethylamine, dimethylethanolamine, benzyl dimethylamine, dimethylaniline, tribenzylamine, triphenylamine, N,N-dimethyl-para-toluidine, N,N-dimethyl-ortho-toluidine, tetramethylguanidine (TMG), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), 1,4-diazabicyclo[2.2.2]octane (DABCO), quinuclidine, dimethylaminomethyl phenol, tris(dimethylaminomethyl)phenol, N,N-dihydroxyethyl-p-toluidine, N,N-diisopropylethylamine, and N, N, N', N'', N'''-pentamethyl-diethylenetriamine. Useful nitrogen-containing bases also include guanidines such as diphenylguanidine (DPG). In some embodiments, the nitrogen-containing base comprises a substituted or unsubstituted nitrogen-containing ring. In some embodiments, the substituted or unsubstituted nitrogen-containing ring has 5 or 6 atoms in the ring. The substituted or unsubstituted nitrogen-containing ring can be aromatic or nonaromatic and can have up to 4 nitrogen atoms in the ring. The ring can optionally include other heteroatoms (e.g., S and O). Substituted aromatic or nonaromatic rings can be substituted by one or more substituents independently selected from the group consisting of alkyl, aryl, arylalkylenyl, alkoxy, haloalkyl, haloalkoxy, halogen, nitro, hydroxy, hydroxyalkyl, mercapto, cyano, aryloxy, arylalkyleneoxy, heterocyclyl, hydroxyalkyleneoxyalkylenyl, amino, alkylamino, dialkylamino, (dialkylamino)alkyleneoxy, and oxo. The alkyl substituent can be unsubstituted or substituted by at least one of alkoxy having up to 4 carbon atoms, halo, hydroxy, or nitro. In some embodiments, the aryl or arylalkylenyl is unsubstituted or substituted by at least one of alkyl having up to 4 carbon atoms, alkoxy having up to 4 carbon atoms, halo, hydroxy, or nitro. In some

embodiments, the nitrogen-containing base is a substituted or unsubstituted pyridine, pyrazine, imidazole, pyrazole, tetrazole, triazole, oxazole, thiazole, pyrimidine, pyridazine, triazine, tetrazine, or pyrrole. Any of these may be substituted with halogen (e.g., iodo, bromo, chloro, fluoro), alkyl (e.g., having from 1 to 4, 1 to 3, or 1 to 2 carbon atoms), arylalkylenyl (e.g., benzyl), or aryl (phenyl). In some embodiments, the nitrogen-containing base, is a substituted or unsubstituted imidazole or pyrazole. The imidazole or pyrazole may be substituted with halogen (e.g., iodo, bromo, chloro, fluoro), alkyl (e.g., having from 1 to 4, 1 to 3, or 1 to 2 carbon atoms), arylalkylenyl (e.g., benzyl), or aryl (phenyl). Examples of useful nitrogen-containing rings include 1-benzylimidazole, 1,2-dimethylimidazole, 4-iodopyrazole, 1-methylbenzimidazole, 1-methylpyrazole, 3-methylpyrazole, 4-phenylimidazole, and pyrazole.

Organic peroxides, in some embodiments, organic hydroperoxides, can be added in any amount suitable to initiate curing of the composition. In some embodiments, the organic peroxide is present in an amount in a range from 0.05 weight percent to about 10 weight percent (in some embodiments, 0.1 weight percent to 5 weight percent, or 0.5 weight percent to 5 weight percent), based on the total weight of the composition. The organic peroxide and its amount may be selected to provide the composition with a desirable open time. In some embodiments, the composition has an open time of at least 10 minutes, at least 30 minutes, at least one hour, or at least two hours.

The nitrogen-containing base, which in some embodiments, provides a redox curing system in the presence of an organic peroxide, and its amount may be selected to provide the composition with a desirable open time. In some embodiments, the composition has an open time of at least 10 minutes, at least 30 minutes, at least one hour, or at least two hours. The amount of the nitrogen-containing base and its conjugate acid pKa can both affect the open time. A composition with a smaller amount of a nitrogen-containing base having a higher pKa may have the same open time as a composition having a larger amount of a nitrogen-containing base having a lower pKa. In some embodiments, the nitrogen-containing base is present in an amount in a range from 0.05 weight percent to about 10 weight percent (in some embodiments, 0.1 weight percent to 5 weight percent, or 0.5 weight percent to 5 weight percent), based on the total weight of the composition.

In some embodiments, when used as an initiator to cure the composition, the organic peroxide, including any of those described above, can be used in combination with an organoborane-amine complex. The organoborane-amine complex is a latent form of an organoborane which is liberated upon decomplexing the base with a compound that reacts with the base, such as an acid or its equivalent. The free organoborane is an initiator capable of initiating free-radical polymerization of the composition, for example.

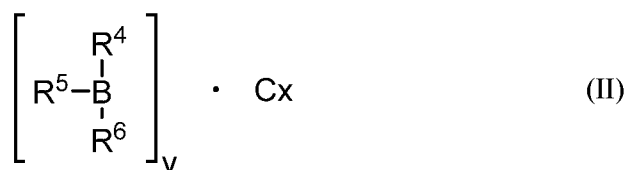
The organoborane portion of the organoborane-amine complex is shown in Formula I (below):



wherein R^4 , R^5 , and R^6 are organic groups (typically having 30 atoms or less, or 20 atoms or less, or 10 atoms or less). In some embodiments of Formula I, R^4 represents an alkyl group having from 1 to 10 carbon atoms, or from 1 to 6 carbon atoms, or from 1 to 5 carbon atoms, or from 1 to 4 carbon atoms, or from 2 to 4 carbon atoms, or from 3 to 4 carbon atoms.

In some embodiments of Formula I, R^5 and R^6 independently represent (i.e., they may be the same or different): alkyl groups having 1 to 10 carbon atoms (or from 1 to 6 carbon atoms, or from 1 to 5 carbon atoms, or from 1 to 4 carbon atoms, or from 2 to 4 carbon atoms, or from 3 to 4 carbon atoms); cycloalkyl groups having 3 to 10 carbon atoms; aryl groups having from 6 to 12 carbon atoms (e.g., phenyl); or aryl groups having from 6 to 12 carbon atoms (e.g., phenyl) substituted with alkyl groups having 1 to 10 carbon atoms (or from 1 to 6 carbon atoms, or from 1 to 5 carbon atoms, or from 1 to 4 carbon atoms, or from 2 to 4 carbon atoms, or from 3 to 4 carbon atoms), or cycloalkyl groups having 3 to 10 carbon atoms. Any two of R^4 , R^5 , and R^6 groups may optionally be part of a ring (e.g., two groups can combine to form a ring).

The organoborane initiator is complexed with a basic complexing agent (i.e., a base that complexes with the organoborane) to form a stable organoborane-amine complex. The organoborane-amine complex may be represented by Formula II (below):



wherein R^4 , R^5 , and R^6 are as previously defined, and Cx represents a complexing agent selected from a compound having one or more amine groups and optionally one or more alkoxyl groups; and v is a positive number. The value of v is selected so as to render the organoborane-amine complex stable under ambient conditions. For example, when the organoborane-amine complex is stored in a capped vessel at about 20 °C to 22 °C and under otherwise ambient conditions (i.e., the vessel is capped in an ambient air environment and not under vacuum or an inert atmosphere), the complex remains useful as an initiator for at least two weeks. In some cases, the complexes may be readily stored under these conditions for many months, and up to a year or more. In some embodiments, the value of v is typically at least 0.1, or at least 0.3, or at least 0.5, or at least 0.8, or at least 0.9 and, up to 2, or up to 1.5, or up to 1.2. In some embodiments, v is in a range of 0.1 to 2, or in a range of 0.5 to 1.5, or in a range of 0.8 to 1.2, or in a range of 0.9 to 1.1, or 1.

In Formulas I and II, an alkyl group may be straight chain or branched. In some embodiments, a ring formed by two groups of R^4 , R^5 , and R^6 may be bridged by the boron atom in Formula I or Formula II. The organoborane-amine complex typically does not include a thiol group.

Examples of useful organoboranes of the organoborane-amine complexes are trimethylborane, triethylborane, tri-*n*-propylborane, triisopropylborane, tri-*n*-butylborane, triisobutylborane, and tri-*sec*-butylborane.

Useful basic complexing agents (Cx) include, for example, amines, aminoalcohols, aminoethers and compounds that contain a combination of such functionality (e.g., an amino group and an alkoxy group). A sufficient amount of complexing agent is provided to ensure stability of the organoborane-amine complex under ambient conditions. An insufficient amount of complexing agent could leave free organoborane, a material that tends to be pyrophoric. In practice, to ensure stability of the complex at ambient conditions, the compound that serves as the complexing agent is often in excess, i.e., some of the compound is free or not complexed in the composition. The amount of excess basic complexing agent is chosen to ensure stability of the complex under ambient conditions while still achieving desired performance such as cure rate of the polymerizable composition and mechanical properties of the cured composition. For example, there may be up to 100 percent molar excess, or up to 50 percent molar excess, or up to 30 percent molar excess of the basic complexing agent relative to the organoborane. Often, there is 10 to 30% molar excess of the basic complexing agent relative to the organoborane.

Useful basic complexing agents include, for example, amines and aminoethers. The amine compounds may have primary and/or secondary amino group(s), for example.

Amine complexing agents (Cx) may be provided by a wide variety of materials having one or more primary or secondary amine groups, including blends of different amines. Amine complexing agents may be a compound with a single amine group or may be a polyamine (i.e., a material having multiple amine groups such as two or more primary, secondary, or tertiary amine groups). Suitable polyamines can have at least one amine group that is a primary and/or secondary amine group.

The organoborane-amine complex may be readily prepared using known techniques, as described, for example, in U. S. Pat. Nos. 5,616,796 (Pocius et al.), 5,621,143 (Pocius), 6,252,023 (Moren), 6,410,667 (Moren), and 6,486,090 (Moren).

Suitable organoborane-amine complexes are available from suppliers such as BASF and AkzoNobel. TEB-DAP (triethylborane-1,3-diaminopropane (or 1,3-propanediamine) complex), TnBB-MOPA (tri-*n*-butylborane-3-methoxypropylamine complex), TEB-DETA (triethylborane-diethylenetriamine complex), TnBB-DAP (tri-*n*-butylborane-1,3-diaminopropane complex), and TsBB-DAP (tri-*sec*-butylborane-1,3-diaminopropane complex) are all available from BASF (Ludwigshafen, Germany). TEB-HMDA (triethylborane-hexamethylenediamine (also 1,6-hexanediamine or 1,6-diaminohexane) complex) is available from AkzoNobel, Amsterdam, The Netherlands.

The organoborane-amine complex is generally employed in an effective amount, which is an amount large enough to permit reaction (i.e., curing by polymerizing and/or crosslinking) to readily occur to obtain a polymer of sufficiently high molecular weight for the desired end use. If the amount of organoborane produced is too low, then the reaction may be incomplete. On the other hand, if the amount

is too high, then the reaction may proceed too rapidly to allow for effective mixing and use of the resulting composition. Useful rates of reaction will typically depend at least in part on the method of applying the composition to a substrate. Thus, a faster rate of reaction may be accommodated by using a high-speed automated industrial applicator rather than by applying the composition with a hand applicator or by manually mixing the composition.

Within these parameters, an effective amount of the organoborane-amine complex is typically an amount that provides at least 0.003 percent by weight of boron, or at least 0.008 percent by weight of boron, or at least 0.01 percent by weight of boron. An effective amount of the organoborane-amine complex is typically an amount that provides up to 1.5 percent by weight of boron, or up to 0.5 percent by weight of boron, or up to 0.3 percent by weight of boron. The percent by weight of boron in a composition is based on the total weight of the polymerizable material in the composition (that is, the polythiol and the second component).

Alternatively stated, an effective amount of the organoborane-amine complex is at least 0.1 percent by weight, or at least 0.5 percent by weight. An effective amount of the organoborane-amine complex is up to 10 percent by weight, or up to 5 percent by weight, or up to 3 percent by weight. The percent by weight of the organoborane-amine complex in a composition is based on the total weight of the polymerizable material in the composition (that is, the polythiol and the second component).

A decomplexing agent (e.g., mineral acids, Lewis acids, carboxylic acids, acid anhydrides, acid chlorides, sulfonyl chlorides, phosphonic acids, isocyanates, aldehydes, 1,3-dicarbonyl compounds, acrylates, and epoxies) may be included to activate the organoborane-amine complex, however, it is presently discovered that it is generally not needed; for example, the composition may contain less than 1, less than 0.1, or less than 0.01 weight percent of the decomplexing agent, or even be free of the decomplexing agent. As used herein, the term "decomplexing agent" refers to a compound capable of liberating the organoborane from its complexing agent, thereby enabling initiation of the reaction (curing by polymerizing and/or crosslinking) of the polymerizable material of the composition. Decomplexing agents may also be referred to as "activators" or "liberators" and these terms may be used synonymously herein.

In some embodiments, the composition includes a polyepoxide having more than one epoxide group as the second component. Epoxides are useful, for example, as curing agents for polythiols. In some embodiments, the polyepoxide includes at least two epoxide groups. Generally, in order to achieve chemical crosslinking between polymer chains, greater than two thiol groups and/or greater than two epoxide groups are present in at least some of the polythiol and polyepoxide molecules, respectively. When using a polythiol having two thiol groups, for example, a mixture of polyepoxides may be useful in which at least one polyepoxide has two epoxide groups, and at least one polyepoxide has at least three epoxide groups. Mixtures of polyepoxides and/or polythiols having at least 5 percent functional equivalents of epoxide groups contributed by polyepoxides having at least three epoxide groups or at least

5 percent functional equivalents of thiol groups contributed by polythiols having at least three thiol groups may be useful. A variety of polyepoxides having more than one epoxide group are useful in the method according to the present disclosure. In some embodiments, the polyepoxide is monomeric. In some embodiments, the polyepoxide is oligomeric or polymeric (that is, an epoxy resin). A monomeric polyepoxide may be an alkylene, arylene, alkylarylene, arylalkylene, or alkylenearylalkylene having at least two epoxide groups, wherein any of the alkylene, alkylarylene, arylalkylene, or alkylenearylalkylene are optionally interrupted by one or more ether (i.e., -O-), thioether (i.e., -S-), or amine (i.e., -NR¹-) groups and optionally substituted by alkoxy, hydroxyl, or halogen (e.g., fluoro, chloro, bromo, iodo). Useful monomeric polyepoxides may be diepoxides or polyepoxides with more than 2 (in some embodiments, 3 or 4) epoxide groups. An epoxy resin may be prepared by chain-extending any of such polyepoxides.

Some useful polyepoxides are aromatic. Useful aromatic polyepoxides and epoxy resins typically contain at least one (in some embodiments, at least 2, in some embodiments, in a range from 1 to 4) aromatic ring (e.g., phenyl group) that is optionally substituted by a halogen (e.g., fluoro, chloro, bromo, iodo), alkyl having 1 to 4 carbon atoms (e.g., methyl or ethyl), or hydroxyalkyl having 1 to 4 carbon atoms (e.g., hydroxymethyl). For polyepoxides and epoxy resin repeating units containing two or more aromatic rings, the rings may be connected, for example, by a branched or straight chain alkylene group having 1 to 4 carbon atoms that may optionally be substituted by halogen (e.g., fluoro, chloro, bromo, iodo). In some embodiments, the aromatic polyepoxide or epoxy resin is a novolac. In these embodiments, the novolac epoxy may be a phenol novolac, an ortho-, meta-, or para-cresol novolac, or a combination thereof. In some embodiments, the aromatic polyepoxide or epoxy resin is a bisphenol diglycidyl ether, wherein the bisphenol (i.e., -O-C₆H₅-CH₂-C₆H₅-O-) may be unsubstituted (e.g., bisphenol F), or either of the phenyl rings or the methylene group may be substituted by halogen (e.g., fluoro, chloro, bromo, iodo), methyl, trifluoromethyl, or hydroxymethyl. In some embodiments, the polyepoxide is a novolac epoxy resin (e.g., phenol novolacs, ortho-, meta-, or para-cresol novolacs or combinations thereof), a bisphenol epoxy resin (e.g., bisphenol A, bisphenol F, halogenated bisphenol epoxies, and combinations thereof), a resorcinol epoxy resin, and combinations of any of these. Examples of useful aromatic monomeric polyepoxides include the diglycidyl ethers of bisphenol A and bisphenol F and tetrakisglycidyl-4-phenylolethane and mixtures thereof.

Some useful polyepoxides are non-aromatic. The non-aromatic epoxy can include a branched or straight-chain alkylene group having 1 to 20 carbon atoms optionally interrupted with at least one -O- and optionally substituted by hydroxyl. In some embodiments, the non-aromatic epoxy can include a poly(oxyalkylene) group having a plurality (x) of oxyalkylene groups, OR^{1'}, wherein each R^{1'} is independently C₂ to C₅ alkylene, in some embodiments, C₂ to C₃ alkylene, x is 2 to about 6, 2 to 5, 2 to 4, or 2 to 3. Examples of useful non-aromatic monomeric polyepoxides include ethylene glycol diglycidyl ether, propylene glycol diglycidyl ether, diethylene glycol diglycidyl ether, dipropylene glycol diglycidyl

ether, polyethylene glycol diglycidyl ether, polypropylene glycol diglycidyl ether, glycerol diglycidyl ether, propanediol diglycidyl ether, butanediol diglycidyl ether, and hexanediol diglycidyl ether.

Examples of useful polyepoxides having more than two epoxide groups include glycerol triglycidyl ether, and polyglycidyl ethers of 1,1,1-trimethylolpropane, pentaerythritol, and sorbitol. Other examples of useful polyepoxides include glycidyl ethers of cycloaliphatic alcohols (e.g., 1,4-cyclohexanedimethanol, bis(4-hydroxycyclohexyl)methane or 2,2-bis(4-hydroxycyclohexyl)propane), cycloaliphatic epoxy resins (e.g., bis(2,3-epoxycyclopentyl) ether, 2,3-epoxycyclopentyl glycidyl ether, 1,2-bis(2,3-epoxycyclopentyloxy)ethane and 3,4-epoxycyclohexylmethyl 3',4'-epoxycyclohexanecarboxylate), and hydantoin diepoxide. Examples of polyepoxides having amine groups include poly(N-glycidyl) compounds obtainable by dehydrochlorinating the reaction products of epichlorohydrin with amines containing at least two amine hydrogen atoms. These amines are, for example, aniline, n-butylamine, bis(4-aminophenyl)methane, m-xylylenediamine or bis(4-methylaminophenyl)methane. Examples of polyepoxides having thioether groups include di-S-glycidyl derivatives of dithiols (e.g., ethane-1,2-dithiol or bis(4-mercaptomethylphenyl) ether).

In some embodiments of compositions useful in the methods according to the present disclosure, the polyepoxide is an oligomeric or polymeric diepoxide. In some embodiments, epoxides may be chain extended to have any desirable epoxy equivalent weight. Chain extending epoxy resins can be carried out by reacting a monomeric diepoxide, for example, with a diol in the presence of a catalyst to make a linear polymer. In some embodiments, the resulting epoxy resin (e.g., either an aromatic or non-aromatic epoxy resin) may have an epoxy equivalent weight of at least 150, 170, 200, or 225 grams per equivalent. In some embodiments, the aromatic epoxy resin may have an epoxy equivalent weight of up to 2000, 1500, or 1000 grams per equivalent. In some embodiments, the aromatic epoxy resin may have an epoxy equivalent weight in a range from 150 to 2000, 150 to 1000, or 170 to 900 grams per equivalent. Epoxy equivalent weights may be selected, for example, so that the epoxy resin may be used as a liquid.

Mixtures of polythiols and mixtures of polyepoxides, including any of those described above, may also be useful. Typically, the amounts of the polythiol(s) and polyepoxide(s) are selected for the composition so that there is a stoichiometric equivalence of mercaptan groups and epoxide groups. The stoichiometry expressed as a ratio of -SH groups / epoxide groups can be in the range of 0.8 to 1.2, 0.9 to 1.1, or 0.95 to 1.05, although this is not a requirement.

Photoinitiators suitable for curing a polythiol with a curing agent comprising polyepoxide having more than one epoxide group include a photolabile base. A photolabile base photochemically generates a base that can catalyze the reaction between the polythiol and the polyepoxide. In some embodiments of the method disclosed herein, the base is a first amine. Photolabile bases are also useful, for example, for curing a polythiol with a curing agent comprising a Michael acceptor.

A variety of photolabile bases can be useful in the methods of the present disclosure. Many useful photolabile bases, any of which may be useful for practicing the present disclosure, have been

reviewed in Suyama, K. and Shirai, M., "Photobase Generators: Recent Progress and Application Trend in Polymer Systems" *Progress in Polymer Science* 34 (2009) 194-209. Photolabile bases useful for practicing the present disclosure include photocleavable carbamates (e.g., 9-xanthenylmethyl, fluorenylmethyl, 4-methoxyphenacyl, 2,5-dimethylphenacyl, benzyl, and others), which have been shown to generate primary or secondary amines after photochemical cleavage and liberation of carbon dioxide. Other photolabile bases described in the review as useful for generating primary or secondary amines include certain O-acyloximes, sulfonamides, and formamides. Acetophenones, benzophenones, and acetophenones bearing quaternary ammonium substituents are reported to undergo photocleavage to generate tertiary amines in the presence of a variety of counter cations (borates, dithiocarbamates, and thiocyanates). Examples of these photolabile ammonium salts are N-(benzophenonemethyl)tri-N-alkyl ammonium triphenylborates. Certain sterically hindered α -aminoketones are also reported to generate tertiary amines.

Recently, quaternary ammonium salts made from a variety of amines and phenylglyoxylic acid have been shown to generate amines that catalyze a thiol/epoxy reaction after exposure to UV light. (See Salmi, H., et al. "Quaternary Ammonium Salts of Phenylglyoxylic acid as Photobase Generators for Thiol-Promoted Epoxide Photopolymerization" *Polymer Chemistry* 5 (2014) 6577-6583.) Such salts are also suitable as photolabile bases useful for practicing the present disclosure.

In some embodiments, the photolabile base useful for practicing the present disclosure is a 1,3-diamine compound represented by the formula $N(R_{7a})(R_{6a})-CH(R_{5a})-N(R_{4a})-C(R_{1a})(R_{2a})(R_{3a})$ such as those described in U.S. Pat. No. 7,538,104 (Baudin et al.). Such compounds can be considered arylalkenyl substituted reduced amidines or guanidines. In formula $N(R_{7a})(R_{6a})-CH(R_{5a})-N(R_{4a})-C(R_{1a})(R_{2a})(R_{3a})$, R_{1a} is selected from aromatic radicals, heteroaromatic radicals, and combinations thereof that absorb light in the wavelength range from 200 nm to 650 nm and that are unsubstituted or substituted one or more times by at least one monovalent group selected from alkyl, alkenyl, alkynyl, haloalkyl, $-NO_2$, $-NR_{10a}R_{11a}$, $-CN$, $-OR_{12a}$, $-SR_{12a}$, $-C(O)R_{13a}$, $-C(O)OR_{14a}$, halogen, groups of the formula $N(R_{7a})(R_{6a})-CH(R_{5a})-N(R_{4a})-C(R_{2a})(R_{3a})-$ where R_{2a} - R_{7a} are as defined below, and combinations thereof, and that upon absorption of light in the wavelength range from 200 nm to 650 nm bring about a photoelimination that generates an amidine or guanidine. R_{2a} and R_{3a} are each independently selected from hydrogen, alkyl, phenyl, substituted phenyl (that is, substituted one or more times by at least one monovalent group selected from alkyl, $-CN$, $-OR_{12a}$, $-SR_{12a}$, halogen, haloalkyl, and combinations thereof), and combinations thereof; R_{5a} is selected from alkyl, $-NR_{8a}R_{9a}$, and combinations thereof; R_{4a} , R_{6a} , R_{7a} , R_{8a} , R_{9a} , R_{10a} and R_{11a} are each independently selected from hydrogen, alkyl, and combinations thereof; or R_{4a} and R_{6a} together form a C_2 - C_{12} alkylene bridge that is unsubstituted or is substituted by one or more monovalent groups selected from C_1 - C_4 alkyl radicals and combinations thereof; or R_{5a} and R_{7a} , independently of R_{4a} and R_{6a} , together form a C_2 - C_{12} alkylene bridge that is unsubstituted or is substituted by one or more monovalent groups selected from C_1 - C_4 alkyl radicals and combinations thereof; or, if R_{5a}

is $-NR_{8a}R_{9a}$, then R_{7a} and R_{9a} together form a C_2-C_{12} alkylene bridge that is unsubstituted or is substituted by one or more monovalent groups selected from C_1-C_4 alkyl radicals and combinations thereof; and R_{12a} , R_{13a} , and R_{14a} are each independently selected from hydrogen, alkyl, and combinations thereof. Any of the alkyl and haloalkyl groups above can be linear or branched and, in some embodiments, contain 1 to about 19 carbon atoms (in some embodiments, 1 to about 18, 1 to about 12, or 1 to about 6 carbon atoms). In some embodiments, halogen atoms are chlorine, fluorine, and/or bromine (in some embodiments, chlorine and/or fluorine). The alkenyl groups can be linear or branched and, in some embodiments, contain 2 to about 18 carbon atoms (in some embodiments, 2 to about 12 or 2 to about 6 carbon atoms). The alkynyl groups can be linear or branched and, in some embodiments, contain 2 to about 18 carbon atoms (in some embodiments, 2 to about 12 or 2 to about 6 carbon atoms).

In some embodiments of formula $N(R_{7a})(R_{6a})-CH(R_{5a})-N(R_{4a})-C(R_{1a})(R_{2a})(R_{3a})$, R_{1a} is selected from substituted and unsubstituted phenyl, naphthyl, phenanthryl, anthryl, pyrenyl, 5,6,7,8-tetrahydro-2-naphthyl, 5,6,7,8-tetrahydro-1-naphthyl, thienyl, benzo[b]thienyl, naphtho[2,3-b]thienyl, thianthrenyl, anthraquinonyl, dibenzofuryl, chromenyl, xanthenyl, thioxanthenyl, pyrrolyl, imidazolyl, pyrazolyl, pyrazinyl, pyrimidinyl, pyridazinyl, indoliziny, isoindolyl, indolyl, indazolyl, purinyl, quinoliziny, isoquinolyl, quinolyl, phthalazinyl, naphthyridinyl, quinoxaliny, quinazolinyl, cinnolinyl, pteridinyl, carbazolyl, β -carbolinyl, phenanthridinyl, acridinyl, perimidinyl, phenanthrolinyl, phenazinyl, isothiazolyl, phenothiazinyl, isoxazolyl, furazanyl, terphenyl, stilbenyl, fluorenyl, phenoxazinyl, and combinations thereof, any of these being unsubstituted or substituted one or more times by C_1-C_{18} alkyl, C_2-C_{18} alkenyl, C_2-C_{18} alkynyl, C_1-C_{18} haloalkyl, $-NO_2$, $-NR_{10a}R_{11a}$, $-CN$, $-OR_{12a}$, $-SR_{12a}$, $-C(O)R_{13a}$, $-C(O)OR_{14a}$, halogen, a radical of the formula $N(R_{7a})(R_{6a})-CH(R_{5a})-N(R_{4a})-C(R_{2a})(R_{3a})-$, or a combination thereof, where $R_{2a}-R_{7a}$ and $R_{10a}-R_{14a}$ are as defined above. In some embodiments of formula $N(R_{7a})(R_{6a})-CH(R_{5a})-N(R_{4a})-C(R_{1a})(R_{2a})(R_{3a})$, R_{1a} is a substituted or unsubstituted biphenyl radical, wherein each phenyl group is independently substituted with from zero to three (in some embodiments, zero or one) substituents selected from C_1-C_{18} alkyl, C_2-C_{18} alkenyl, $-OH$, $-CN$, $-OR_{10a}$, $-SR_{10a}$, halogen, radicals of the formula $N(R_{7a})(R_{6a})-CH(R_{5a})-N(R_{4a})-C(R_{2a})(R_{3a})-$, and combinations thereof, where $R_{2a}-R_{7a}$ and $R_{10a}-R_{14a}$ are as defined above. In some embodiments of formula $N(R_{7a})(R_{6a})-CH(R_{5a})-N(R_{4a})-C(R_{1a})(R_{2a})(R_{3a})$, R_{1a} is selected from phenyl, 3-methoxyphenyl, 4-methoxyphenyl, 2,4,6-trimethoxyphenyl, 2,4-dimethoxyphenyl, and combinations thereof.

In some embodiments of formula $N(R_{7a})(R_{6a})-CH(R_{5a})-N(R_{4a})-C(R_{1a})(R_{2a})(R_{3a})$, R_{2a} and R_{3a} each are independently selected from hydrogen, C_1-C_6 alkyl, and combinations thereof (in some embodiments, both are hydrogen); R_{4a} and R_{6a} together form a C_2-C_6 alkylene (in some embodiments, C_3 alkylene) bridge that is unsubstituted or is substituted by one or more groups selected from C_1-C_4 alkyl radicals and combinations thereof; and/or R_{5a} and R_{7a} together form a C_2-C_6 alkylene (in some embodiments, C_3 or C_5 alkylene) bridge that is unsubstituted or is substituted by one or more groups selected from C_1-C_4 alkyl radicals and combinations thereof, or, if R_{5a} is $-NR_{8a}R_{9a}$, R_{9a} and R_{7a} together form a C_2-C_6 alkylene

bridge that is unsubstituted or substituted by one or more groups selected from C₁-C₄ alkyl radicals and combinations thereof.

Examples of suitable photolabile bases useful for practicing the present disclosure include 5-benzyl-1,5-diazabicyclo[4.3.0]nonane, 5-(anthracen-9-yl-methyl)-1,5-diaza[4.3.0]nonane, 5-(2'-nitrobenzyl)-1,5-diazabicyclo[4.3.0]nonane, 5-(4'-cyanobenzyl)-1,5-diazabicyclo[4.3.0]nonane, 5-(3'-cyanobenzyl)-1,5-diazabicyclo[4.3.0]nonane, 5-(anthraquinon-2-yl-methyl)-1,5-diaza[4.3.0]nonane, 5-(2'-chlorobenzyl)-1,5-diazabicyclo[4.3.0]nonane, 5-(4'-methylbenzyl)-1,5-diazabicyclo[4.3.0]nonane, 5-(2',4',6'-trimethylbenzyl)-1,5-diazabicyclo[4.3.0]nonane, 5-(4'-ethenylbenzyl)-1,5-diazabicyclo[4.3.0]nonane, 5-(3'-trimethylbenzyl)-1,5-diazabicyclo[4.3.0]nonane, 5-(2',3'-dichlorobenzyl)-1,5-diazabicyclo[4.3.0]nonane, 5-(naphth-2-yl-methyl)-1,5-diazabicyclo[4.3.0]nonane, 1,4-bis(1,5-diazabicyclo[4.3.0]nonanylmethyl)benzene, 8-benzyl-1,8-diazabicyclo[5.4.0]undecane, 8-benzyl-6-methyl-1,8-diazabicyclo[5.4.0]undecane, 9-benzyl-1,9-diazabicyclo[6.4.0]dodecane, 10-benzyl-8-methyl-1,10-diazabicyclo[7.4.0]tridecane, 11-benzyl-1,11-diazabicyclo[8.4.0]tetradecane, 8-(2'-chlorobenzyl)-1,8-diazabicyclo[5.4.0]undecane, 8-(2',6'-dichlorobenzyl)-1,8-diazabicyclo[5.4.0]undecane, 4-(diazabicyclo[4.3.0]nonanylmethyl)-1,1'-biphenyl, 4,4'-bis(diazabicyclo[4.3.0]nonanylmethyl)-1,1'-biphenyl, 5-benzyl-2-methyl-1,5-diazabicyclo[4.3.0]nonane, 5-benzyl-7-methyl-1,5,7-triazabicyclo[4.4.0]decane, and combinations thereof. Such compounds can be made, for example, using the methods described in U.S. Pat. No. 7,538,104 (Baudin et al.), assigned to BASF, Ludwigshafen, Germany. An example of a photolabile base is available from BASF under the trade designation "CGI 90", which is reported to generate 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) upon exposure to actinic radiation (see, e.g., US2013/0345389 (Cai et al.)).

Other suitable photolabile bases useful for practicing the present disclosure and/or for practicing the methods disclosed herein include those described in U.S. Pat. Nos. 6,410,628 (Hall-Goulle et al.), 6,087,070 (Turner et al.), 6,124,371 (Stanssens et al.), and 6,057,380 (Birbaum et al.), and U.S. Pat. Appl. Pub. No. 2011/01900412 (Studer et al.).

A composition including a photolabile base can be packaged as a one-part product including the photolabile base, or a two-part product in which at least one of the parts includes the photolabile base and can be mixed just before it is applied to surface of the substrate. The photolabile base can be added to the composition in any amount suitable to initiate curing. In some embodiments, the photolabile base is present in an amount in a range from 0.05 weight percent to about 5 weight percent (in some embodiments, 0.1 weight percent to 2.5 weight percent, or 0.1 weight percent to 2 weight percent), based on the total weight of the composition.

In some embodiments of the method according to the present disclosure, a composition comprising a photolabile base also includes a second amine. The second amine can be useful, for example, when at least a portion of the composition is in shadow (e.g., between opaque substrates unable to transmit some portion of visible light or otherwise shielded from the light source) and/or if the curable

sealant composition is highly filled with an opaque filler. The second amine may be the same or different from the first amine. In some embodiments, a temperature sufficient for the second amine to at least partially cure the curable sealant is ambient temperature (that is, no external heat source is necessary). The second amine can also be useful for curing a composition in the absence of a photolabile base.

5 The first amine (generated by the photolabile base) and second amine can independently be any compound including one to four basic nitrogen atoms that bear a lone pair of electrons. The first amine and second amine can independently include primary, secondary, and tertiary amine groups. The nitrogen atom(s) in the first amine and second amine can be bonded to alkyl groups, aryl groups, arylalkylene groups, alkylarylene, alkylarylenealkylene groups, or a combination thereof. The first amine and second
10 amine can also be cyclic amines, which can include one or more rings and can be aromatic or non-aromatic (e.g., saturated or unsaturated). One or more of the nitrogen atoms in the amine can be part of a carbon-nitrogen double bond. While in some embodiments, the first amine and second amine independently include only carbon-nitrogen, nitrogen-hydrogen, carbon-carbon, and carbon-hydrogen bonds, in other embodiments, the first amine and second amine can include other functional groups (e.g.,
15 hydroxyl or ether group). However, it is understood by a person skilled in the art that a compound including a nitrogen atom bonded to a carbonyl group is an amide, not an amine, and has different chemical properties from an amine. The first amine and second amine can include carbon atoms that are bonded to more than one nitrogen atom. Thus, the first amine and second amine can independently be a guanidine or amidine. As would be understood by a person skilled in the art, a lone pair of electrons on
20 one or more nitrogens of the first amine and second amine distinguishes them from quaternary ammonium compounds, which have a permanent positive charge regardless of pH.

 Examples of useful first and second amines include propylamine, butylamine, pentylamine, hexylamine, triethylamine, dimethylethanolamine, benzyldimethylamine, dimethylaniline, tribenzylamine, triphenylamine, tetramethylguanidine (TMG), 1,8-diazabicyclo[5.4.0]undec-7-ene
25 (DBU), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), 1,4-diazabicyclo[2.2.2]octane (DABCO), quinuclidine, diphenylguanidine (DPG), dimethylaminomethyl phenol, and tris(dimethylaminomethyl)phenol. In some embodiments, the first amine and second amine are each independently tertiary amines, amidines, or guanidines.

 The second amine and its amount may be selected to provide the curable sealant with a desirable
30 amount of open time (that is, the length of time it takes for the curable sealant to become at least partially gelled) after it is mixed or thawed. In some embodiments, the composition has an open time of at least 10 minutes, at least 30 minutes, at least one hour, or at least two hours. The amount of the second amine and its conjugate acid pKa both affect the open time. A composition with a smaller amount of a second amine having a higher pKa may have the same open time as a composition having a larger amount of a second
35 amine having a lower pKa. For a second amine with a moderate conjugate acid pKa value in a range from about 7 to about 10, an amount of second amine in a range from 0.05 weight percent to about 10

weight percent (in some embodiments, 0.05 weight percent to 7.5 weight percent, or 1 weight percent to 5 weight percent) may be useful. For a second amine with a higher conjugate acid pKa value of about 11 or more, an amount of second amine in a range from 0.005 weight percent to about 3 weight percent (in some embodiments, 0.05 weight percent to about 2 weight percent) may be useful. In some embodiments in which the second amine is different from the first amine, the second amine has a lower conjugate acid pKa value than the first amine. This may be useful, for example, for achieving a desirable amount of open time and a desirably fast formation of a non-tacky skin. In some embodiments in which the second amine is different from the first amine, the first amine and the second amine have the same conjugate acid pKa value.

In some embodiments, the second amine may be phase-separated in the composition. In these embodiments, the second amine can be a solid (e.g., dicyandiamide), present in a solid adduct (e.g., such as an adduct of an amine and an epoxy resin), or segregated within a solid (e.g., a semi-crystalline polymer). As a phase-separated amine, the second amine is not reactive with or reacts very slowly with the curable components in the composition at ambient temperature. Further details about compositions including a phase-separated amine can be found in Int. Pat. App. Pub. No. WO2018/085546 (Zook et al.). The composition may also include a second amine that is not phase-separated, such as any of those described above, and an amine that is phase-separated.

While the first amine is photochemically generated from a photolabile base, the first and second amines themselves are generally not considered photolabile bases. That is, they do not undergo photochemical reactions that generate an amine by photocleavage, photoelimination, or another mechanism.

In some embodiments of the composition useful for practicing the present disclosure, the composition includes a photosensitizer. Useful photosensitizers include aromatic ketones (e.g., substituted or unsubstituted benzophenones, substituted or unsubstituted thioxanthenes, substituted or unsubstituted anthraquinones, and combinations thereof), dyes (e.g., oxazines, acridines, phenazines, rhodamines, and combinations thereof), 3-acylcoumarins (e.g., substituted and unsubstituted 3-benzoylcoumarins and substituted and unsubstituted 3-naphthoylcoumarins, and combinations thereof), anthracenes (e.g., substituted and unsubstituted anthracenes), 3-(2-benzothiazolyl)-7-(diethylamino)coumarin (coumarin 6), 10-acetyl-2,3,6,7-tetrahydro-1H,5H,11H-[1]benzopyrano[6,7,8-ij]quinolizin-11-one (coumarin 521), other carbonyl compounds (e.g., camphorquinone, 4-phenylacetophenone, benzil, and xanthone, and combinations thereof), and combinations thereof. In some embodiments, the photosensitizer has an absorbance in the blue light range. In some embodiments, the photosensitizer is camphorquinone. In some embodiments, coumarin photosensitizers that are triplet photosensitizers with a wavelength of maximum absorbance, λ_{max} , between 390 to 510 nm are used in combination with camphorquinone. Examples of such coumarin photosensitizers include 3,3'-carbonylbis(5,7-dimethoxycoumarin), 3-benzoyl-7-diethylaminocoumarin, 7-diethylamino-3-

thenoylcoumarin, 3-(2-benzofuroyl)-7-diethylaminocoumarin, 7-diethylamino-5',7'-dimethoxy-3,3'-carbonylbiscoumarin, 3,3'-carbonylbis(7-diethylaminocoumarin), 9-(7-diethylamino-3-coumarinoyl)-1,2,4,5-tetrahydro-3H,6H,10H[1]benzopyrano[9,9a,1-g]quinolazine-10-one, and 9,9'-carbonylbis(1,2,4,5-tetrahydro-3H,6H,10H[1]benzopyrano[9,9a,1-g]quinolazine-10-one). Further details about compositions including a photolabile base, camphorquinone, and such coumarins can be found in Int. Pat. App. Pub. No. WO2018/085534 (Clough et al.). The amount of photosensitizer can vary widely, depending upon, for example, its nature, the nature of other component(s) of the photoactivatable composition, and the particular curing conditions. When the photosensitizer is present in the composition, amounts ranging from about 0.1 weight percent to about 15 weight percent can be useful. In some embodiments, the photosensitizer is included in the curable sealant in an amount from 0.5 percent to 10 percent by weight, 0.5 percent to 7.5 percent by weight, or 1 percent to 7.5 percent by weight, based on the total weight of the composition.

In some embodiments, compositions useful for practicing the method of the present disclosure include at least one oxidizing agent. Oxidizing agents can be useful, for example, when the composition includes a polysulfide oligomer or polymer. In some embodiments, oxidizing agents can minimize the degradation or interchanging of disulfide bonds in the sealant network. In other embodiments, oxidizing agents can be a component for curing the curable sealant. Useful oxidizing agents include a variety of organic and inorganic oxidizing agents (e.g., organic peroxides and metal oxides). Examples of metal oxides useful as oxidizing agents include calcium dioxide, manganese dioxide, zinc dioxide, lead dioxide, lithium peroxide, and sodium perborate hydrate. Other useful inorganic oxidizing agents include sodium dichromate. Examples of organic peroxides useful as oxidizing agents include those described above. Other useful organic oxidizing agents include para-quinone dioxime.

Compositions in any of their embodiments described above, which are useful for practicing the method of the present disclosure, can also contain fillers. Conventional inorganic fillers such as silica (e.g., fumed silica), calcium carbonate, aluminum silicate, and carbon black may be useful as well as low density fillers. In some embodiments, the curable sealant disclosed herein includes at least one of silica, hollow ceramic elements, hollow polymeric elements, calcium silicates, calcium carbonate, or carbon black. Silica, for example, can be of any desired size, including particles having an average size above 1 micrometer, between 100 nanometers and 1 micrometer, and below 100 nanometers. Silica can include nanosilica and amorphous fumed silica, for example. Suitable low-density fillers may have a specific gravity ranging from about 1.0 to about 2.2 and are exemplified by calcium silicates, fumed silica, precipitated silica, and polyethylene. Examples include calcium silicate having a specific gravity of from 2.1 to 2.2 and a particle size of from 3 to 4 microns ("HUBERSORB HS-600", J. M. Huber Corp.) and fumed silica having a specific gravity of 1.7 to 1.8 with a particle size less than 1 ("CAB-O-SIL TS-720", Cabot Corp.). Other examples include precipitated silica having a specific gravity of from 2 to 2.1 ("HISIL TS-7000", PPG Industries), and polyethylene having a specific gravity of from 1 to 1.1 and a particle

size of from 10 to 20 microns ("SHAMROCK S-395" Shamrock Technologies Inc.). Hollow ceramic elements can include hollow spheres and spheroids. The hollow ceramic elements and hollow polymeric elements may have one of a variety of useful sizes but typically have a maximum dimension of less than 10 millimeters (mm), more typically less than one mm. The specific gravities of the microspheres range from about 0.1 to 0.7 and are exemplified by polystyrene foam, microspheres of polyacrylates and polyolefins, and silica microspheres having particle sizes ranging from 5 to 100 microns and a specific gravity of 0.25 ("ECCOSPHERES", W. R. Grace & Co.). Other examples include elastomeric particles available, for example, from Akzo Nobel, Amsterdam, The Netherlands, under the trade designation "EXPANCEL". Other examples include alumina/silica microspheres having particle sizes in the range of 5 to 300 microns and a specific gravity of 0.7 ("FILLITE", Pluess-Stauffer International), aluminum silicate microspheres having a specific gravity of from about 0.45 to about 0.7 ("Z-LIGHT"), and calcium carbonate-coated polyvinylidene copolymer microspheres having a specific gravity of 0.13 ("DUALITE 6001AE", Pierce & Stevens Corp.). Further examples of commercially available materials suitable for use as hollow, ceramic elements include glass bubbles marketed by 3M Company, Saint Paul, Minnesota, as "3M GLASS BUBBLES" in grades K1, K15, K20, K25, K37, K46, S15, S22, S32, S35, S38, S38HS, S38XHS, S42HS, S42XHS, S60, S60HS, iM30K, iM16K, XLD3000, XLD6000, and G-65, and any of the HGS series of "3M GLASS BUBBLES"; glass bubbles marketed by Potters Industries, Carlstadt, N.J., under the trade designations "Q-CEL HOLLOW SPHERES" (e.g., grades 30, 6014, 6019, 6028, 6036, 6042, 6048, 5019, 5023, and 5028); and hollow glass particles marketed by Silbrico Corp., Hodgkins, IL under the trade designation "SIL-CELL" (e.g., grades SIL 35/34, SIL-32, SIL-42, and SIL-43). Such fillers, alone or in combination, can be present in a sealant in a range from 10 percent by weight to 55 percent by weight, in some embodiments, 20 percent by weight to 50 percent by weight, based on the total weight of the composition. The presence of filler in the composition provides the advantageous effect of increasing the open time of the composition in some cases.

Other fillers useful in the curable sealant compositions are special purpose fillers. Such fillers are used to impart properties such as fire resistance. Examples of suitable fillers providing fire resistance include aluminum trihydroxide (ATH) and magnesium dihydroxide.

Compositions in any of their embodiments described above, which are useful for practicing the method of the present disclosure, can also contain at least one of cure accelerators, colorants (e.g., pigments and dyes), thixotropic agents, and solvents. The solvent can conveniently be any material (e.g., *N*-methyl-2-pyrrolidone, tetrahydrofuran, ethyl acetate, or those described below) capable of dissolving a component of the composition. Suitable pigments and dyes can include those that do not absorb in the wavelength range that is desirable for curing the composition. Examples of pigments and dyes useful in the compositions according to the present disclosure can be found in Int. Pat. App. Pub. No.

WO2018/085190 (Townsend et al.).

Compositions in any of their embodiments described above, which are useful for practicing the method of the present disclosure, can also contain adhesion promoters. In some embodiments, useful adhesion promoters include organosilanes have amino functional groups (e.g., N-2-(aminoethyl)-3-aminopropyltrimethoxysilane and (3-aminopropyl)trimethoxysilane). In some embodiments, useful adhesion promoters have groups polymerizable by, for example, actinic radiation. Examples of polymerizable moieties are materials that contain olefinic functionality such as styrenic, vinyl (e.g., vinyltriethoxysilane, vinyltri(2-methoxyethoxy) silane), acrylic and methacrylic moieties (e.g., 3-methacryloxypropyltrimethoxysilane). Some functional silanes useful as adhesion promoters are commercially available, for example, from Momentive Performance Materials, Inc., Waterford, N.Y., under the trade designations "SILQUEST A-187" and "SILQUEST A-1100".

Compositions in any of their embodiments described above, which are useful for practicing the method of the present disclosure, can also contain wetting agents. Examples of suitable wetting agents include a silicone, modified silicone, silicone acrylate, hydrocarbon solvent, fluorine-containing compound, non-silicone polymer or copolymer such as a copolyacrylate, and mixtures thereof. Examples of nonionic surfactants suitable as wetting agents in the curable sealants disclosed herein include block copolymers of polyethylene glycol and polypropylene glycol, polyoxyethylene (7) lauryl ether, polyoxyethylene (9) lauryl ether, polyoxyethylene (18) lauryl ether, and polyethoxylated alkyl alcohols such as those available, for example, from Air Products and Chemicals Inc., Allentown, Penn., under the trade designation "SURFYNOL SE-F". Fluorochemical surfactants such as those available under the trade designation "FLUORAD" from 3M Company of St. Paul, Minn.) may also be useful. In some embodiments, the composition useful for practicing the present disclosure includes at least about 0.001 wt%, at least about 0.01 wt%, or at least about 0.02 wt% of at least one wetting agent and up to about 2 wt%, up to about 1.5 wt%, or up to about 1 wt% of at least one wetting agent, based on the total weight of the composition.

Compositions in any of their embodiments described above, which are useful for practicing the method of the present disclosure, can be packaged either as two-part products or one-part products. For the two-part products including a curable composition that can at least partially cure at room temperature, once the user mixes the two parts, the reaction begins, and the composition starts to form into an elastomeric solid. After mixing, the time that the composition remains usable is called the application life or open time. Throughout the application life, viscosity of the composition gradually increases until the composition is too viscous to be applied. In practice, users choose products with differing application lives and cure times depending on the specific application. For one-part products that can at least partially cure at room temperature, users can avoid a complicated mixing step, but the product is typically shipped and stored in a freezer before application. One-part products that are cured by actinic radiation (e.g., that do not include a second initiator for curing at room temperature or elevated temperature) may be able to be shipped and stored at room temperature before application.

In some embodiments, cured sealant prepared from the method according to the present disclosure may be useful in these applications, for example, because of their fuel resistance and low glass transition temperatures. In some embodiments, the cured sealant prepared according to the present disclosure has a low glass transition temperature, in some embodiments less than -20 °C, in some
5 embodiments less than -30 °C, in some embodiments less than -40 °C, and in some embodiments less than -50 °C. In some embodiment, the cured sealant prepared according to the present disclosure has high jet fuel resistance, characterized by a volume swell of less than 30% and a weight gain of less than 20% when measured according to Society of Automotive Engineers (SAE) International Standard AS5127/1.

10 Some Embodiments of the Disclosure

In a first embodiment, the present disclosure provides a method of irradiating a composition through a substrate, the method comprising:

providing a composition comprising a polythiol, a second component, and at least one of a photoinitiator or photosensitizer that absorbs light having a wavelength greater than 400 nanometers;

15 positioning the composition adjacent to the substrate, wherein over a wavelength range of 350 nanometers (nm) to 390 nm, the substrate has an average percent transmittance of less than 50 percent; and

irradiating the composition through the substrate with light having a wavelength greater than 400 nanometers, wherein irradiating causes the polythiol to react with the second component.

20 In a second embodiment, the present disclosure provides the method of the first embodiment, wherein over a wavelength range of 400 nm to 750 nm, the substrate has an average percent transmittance of at least 50 percent.

In a third embodiment, the present disclosure provides the method of the first or second embodiment, wherein over a wavelength range of 400 nm to 750 nm, the substrate has an average percent
25 transmittance of at least 55, 60, 65, 70, 75, 80, 85, or 90 percent.

In a fourth embodiment, the present disclosure provides the method of any one of the first to third embodiments, wherein the substrate has a length, a width, and a thickness, wherein the thickness is the smallest dimension of the substrate, and wherein for an area defined by the length and width of the substrate, at least 99 percent of the area of the substrate has an average percent transmittance over a
30 wavelength range of 400 nm to 750 nm of at least 50, 55, 60, 65, 70, 75, 80, 85, or 90 percent.

In a fifth embodiment, the present disclosure provides the method of any one of the first to fourth embodiments, wherein the substrate comprises at least one of a polyacrylate, a polymethacrylate, a polycarbonate, a polyester, an epoxy, or a polyurethane.

In a sixth embodiment, the present disclosure provides the method of any one of the first to fifth
35 embodiments, wherein the substrate comprises poly(methyl methacrylate).

In a seventh embodiment, the present disclosure provides the method of any one of the first to sixth embodiments, wherein the substrate has a thickness of at least 2, 3, 4, 5, 6, 7, 8, 9, or 10 millimeters.

In an eighth embodiment, the present disclosure provides the method of any one of the first to seventh embodiments, wherein the substrate comprises at least one of ceramic fibers or nanoparticulate filler.

In a ninth embodiment, the present disclosure provides the method of any one of the first to eighth embodiments, wherein the substrate is a window of a vehicle.

In a tenth embodiment, the present disclosure provides the method of any one of the first to ninth embodiments, wherein the substrate is a window of an aircraft.

In an eleventh embodiment, the present disclosure provides the method of the ninth or tenth embodiment, wherein the composition is at least one of an adhesive for adhering the window to a window frame or a window sealant.

In a twelfth embodiment, the present disclosure provides a method of making a window assembly, the method comprising:

providing a composition comprising a polythiol, a second component, and at least one of a photoinitiator or photosensitizer that absorbs light having a wavelength greater than 400 nanometers;

positioning the composition adjacent to a window; and

irradiating the composition through the window with light having a wavelength greater than 400 nanometers, wherein irradiating causes the polythiol to react with the second component.

In a thirteenth embodiment, the present disclosure provides the method of the twelfth embodiment, wherein over a wavelength range of 350 nm to 390 nm, the window has an average percent transmittance of less than 50 percent.

In a fourteenth embodiment, the present disclosure provides the method of the twelfth or thirteenth embodiment, wherein over a wavelength range of 400 nm to 750 nm, the window has an average percent transmittance of at least 50 percent.

In a fifteenth embodiment, the present disclosure provides the method of any one of the twelfth to fourteenth embodiments, wherein over a wavelength range of 400 nm to 750 nm, the window has an average percent transmittance of at least 55, 60, 65, 70, 75, 80, 85, or 90 percent.

In a sixteenth embodiment, the present disclosure provides the method of any one of the twelfth to fifteenth embodiments, wherein the window comprises at least one of a polyacrylate, a polymethacrylate, a polycarbonate, a polyester, an epoxy, or a polyurethane.

In a seventeenth embodiment, the present disclosure provides the method of any one of the twelfth to sixteenth embodiments, wherein the window comprises poly(methyl methacrylate).

In an eighteenth embodiment, the present disclosure provides the method of any one of the twelfth to seventeenth embodiments, wherein the window has a thickness of at least 2, 3, 4, 5, 6, 7, 8, 9, or 10 millimeters.

In a nineteenth embodiment, the present disclosure provides the method of any one of the twelfth to eighteenth embodiments, wherein the window comprises at least one of ceramic fibers or nanoparticulate filler.

5 In a twentieth embodiment, the present disclosure provides the method of any one of the twelfth to fifteenth embodiments, wherein window comprises glass.

In a twenty-first embodiment, the present disclosure provides the method of any one of the twelfth to twentieth embodiments, wherein the window is an aircraft window.

10 In a twenty-second embodiment, the present disclosure provides the method of any one of the twelfth to twenty-first embodiments, wherein irradiating the composition provides at least one of an adhesive for adhering the window to a window frame or a sealant for the window assembly.

In a twenty-third embodiment, the present disclosure provides the method of any one of the first to twenty-second embodiments, wherein the light having a wavelength greater than 400 nanometers comprises blue light.

15 In a twenty-fourth embodiment, the present disclosure provides the method of any one of the first to twenty-third embodiments, wherein irradiating causes the polythiol to react with the second component to form an at least partially crosslinked network.

In a twenty-fifth embodiment, the present disclosure provides the method of any one of the first to twenty-fourth embodiments, wherein the polythiol is monomeric.

20 In a twenty-sixth embodiment, the present disclosure provides the method of any one of the first to twenty-fourth embodiments, wherein the polythiol is oligomeric or polymeric.

In a twenty-seventh embodiment, the present disclosure provides the method of the twenty-sixth embodiment, wherein the polythiol is a polythioether.

25 In a twenty-eighth embodiment, the present disclosure provides the method of the twenty-seventh embodiment, wherein the polythiol is an oligomer or polymer prepared from components comprising a dithiol and a diene or divinyl ether.

In a twenty-ninth embodiment, the present disclosure provides the method of the twenty-sixth embodiment, wherein the polythiol is a polysulfide oligomer or polymer.

30 In a thirtieth embodiment, the present disclosure provides the method of the twenty-ninth embodiment, wherein the composition further comprises an oxidizing agent.

In a thirty-first embodiment, the present disclosure provides the method of any one of the first to thirtieth embodiments, wherein the second component comprises a polyepoxide comprising more than one epoxide group.

In a thirty-second embodiment, the present disclosure provides the method of the thirty-first embodiment, wherein the polyepoxide is monomeric.

35 In a thirty-third embodiment, the present disclosure provides the method of the thirty-first embodiment, wherein the polyepoxide is oligomeric or polymeric.

In a thirty-fourth embodiment, the present disclosure provides the method of any one of the thirty-first to thirty-third embodiments, wherein the polyepoxide is aromatic.

In a thirty-fifth embodiment, the present disclosure provides the method of any one of the thirty-first to thirty-third embodiments, wherein the polyepoxide is non-aromatic.

5 In a thirty-sixth embodiment, the present disclosure provides the method of any one of the thirty-first to thirty-fifth embodiments, wherein the polyepoxide comprises three or more epoxide groups.

In a thirty-seventh embodiment, the present disclosure provides the method of any one of the first to thirtieth embodiments, wherein the composition comprises a Michael acceptor comprising more than one Michael acceptor group.

10 In a thirty-eighth embodiment, the present disclosure provides the method of any one of the thirty-first to thirty-seventh embodiments, wherein the composition comprises the photoinitiator, and wherein the photoinitiator comprises a photolatent base catalyst.

In a thirty-ninth embodiment, the present disclosure provides the method of the thirty-eighth embodiment, wherein the photolatent base catalyst generates a first amine upon exposure to the light
15 having the wavelength greater than 400 nanometers.

In a fortieth embodiment, the present disclosure provides the method of the thirty-ninth embodiment, wherein the first amine comprises at least one of a tertiary amine, an amidine, or a guanidine.

20 In a forty-first embodiment, the present disclosure provides the method of the thirty-ninth or fortieth embodiment, wherein the composition further comprises a catalytic amount of a second amine, which may be the same or different from the first amine.

In a forty-second embodiment, the present disclosure provides the method of the forty-first embodiment, wherein at least one of the first amine or second amine is triethylamine, dimethylethanolamine, benzyldimethylamine, dimethylaniline, tribenzylamine, triphenylamine, tetramethylguanidine (TMG), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), 1,4-diazabicyclo[2.2.2]octane (DABCO), quinuclidine, diphenylguanidine (DPG), dimethylaminomethyl phenol, and tris(dimethylaminomethyl)phenol.
25

In a forty-third embodiment, the present disclosure provides the method of any one of the first to thirtieth embodiments, wherein the second component comprises at least one unsaturated compound comprising more than one carbon-carbon double bond, at least one carbon-carbon triple bond, or a combination thereof.
30

In a forty-fourth embodiment, the present disclosure provides the method of the forty-third embodiment, wherein the at least one unsaturated compound comprises two carbon-carbon double bonds, and wherein the curable composition further comprises a second unsaturated compound comprising three carbon-carbon double bonds.
35

In a forty-fifth embodiment, the present disclosure provides the method of the forty-third or forty-fourth embodiment, wherein the composition comprises the photoinitiator, and wherein the photoinitiator comprises a free-radical photoinitiator.

5 In a forty-sixth embodiment, the present disclosure provides the method of the forty-fifth embodiment, wherein the composition further comprises an organic peroxide.

In a forty-seventh embodiment, the present disclosure provides the method of the forty-sixth embodiment, wherein the composition further comprises an organoborane-amine complex.

In a forty-eighth embodiment, the present disclosure provides the method of the forty-seventh embodiment, wherein the composition further comprises a nitrogen-containing base (an amine).

10 In a forty-ninth embodiment, the present disclosure provides the method of any one of the first to forty-eighth embodiments, wherein the composition comprises the photosensitizer.

In a fiftieth embodiment, the present disclosure provides a method of making an aircraft, the method comprising the method of any one of the first to forty-ninth embodiments.

15 In a fifty-first embodiment, the present disclosure provides a window assembly made by the method of any one of the first to forty-ninth embodiments, the window assembly comprising a window and a composition on at least a portion of the window, the composition comprising an at least partially crosslinked network from reaction of the polythiol and the second component, wherein the composition comprises at least one of the photosensitizer or a residue from the photoinitiator.

20 In a fifty-second embodiment, the present disclosure provides an aircraft, automobile, marine vessel, or building comprising the window assembly of the fifty-first embodiment.

EXAMPLES

25 In order that this disclosure can be more fully understood, the following examples are set forth. It should be understood that these examples are for illustrative purposes only and are not to be construed as limiting this disclosure in any manner.

Table 1: Materials

Designation	Description	Source
A187	Glycidoxypolytrimethoxysilane available under the designation "ANDISIL 187 SILANE"	AB Specialty Silicones, Waukegan, IL. United States
AC-X92	Thiol-terminated polythioether oligomer with the equivalent weight of 1482 g/mol synthesized as described in "Polythioether Example 1" in PCT Publ. No. WO 2016/130673	3M Company, St. Paul, MN. United States
DABCO	1,4-diazabicyclo[2.2.2]octane 33% solution in dipropylene glycol	Alfa Aesar, Ward Hill, MA. United States
DAEBPA	Diallyl ether of bisphenol A	Bimax, Glen Rock, PA. United States
D-E135	Expanding polymeric microsphere available under the designation "DUALITE E135-040D"	Chase Corporation, Westwood, MA. United States
HA187	1:1 Hydrolyzed glycidoxypolytrimethoxysilane	3M Company, St. Paul, MN. United States
IM30K	Glass bubbles available under the designation "3M iM30K HI-STRENGTH GLASS BUBBLES"	3M Company, St. Paul, MN. United States
OR819	Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide available under the trade designation "OMNIRAD 819"	IGM Resins, St. Charles, IL. United States
PCNB	PCN Blue Plasticizer Paste 11S695	Penn Color of Doylestown, PA. United States
R-202	Fumed silica available under the trade designation "AEROSIL R202"	Evonik of Essen, Germany
S322	Coated calcium carbonate available under the trade designation "SOCAL 332"	Imerys, Paris, France
TAC	Triallyl cyanurate	Sartomer Inc., Exton, PA. United States
TAIC	Triallyl isocyanurate	Tokyo Chemical Industry Co., Portland, OR. United States
TBEC	<i>tert</i> -Butylperoxy 2-ethylhexyl carbonate	Sigma-Aldrich, St. Louis, MO. United States
TnBB-MOPA	Tri- <i>n</i> -butylborane methoxypropylamine	BASF Chemical Co., Ludwigshafen, Germany
UPF	Precipitated calcium carbonate available under the designation "ULTRA-PFLEX"	Specialty Minerals, Inc., Bethlehem, PA. United States

Test Methods:

All test methods with the exception of the depth of cure test are based on those found in SAE International Aerospace Standard AS5127/1, Rev. C.

Depth of Cure

A 0.635 cm (¼ in) deep cylindrical silicone rubber mold was placed on glass slides and loaded with a sealant sample. Each molded specimen was irradiated with a Clearstone LED array (455 nm), obtained from Clearstone Technologies, Inc., Hopkins, Minn., United States, at 100% power from a distance of 2.54 cm (1 inch) for 15 seconds. Following this, the uncured material on the bottom side of the sample was scraped away with a spatula, leaving only a cured disc. The underside of the cured disc was quickly irradiated with the LED array to remove tack, and the thickness of the cured disc was measured with a 500-196-30 Digimatic Digital Caliper from Mitutoyo of Kanagawa, Japan.

Hardness, Tensile Strength and Elongation at Break

Freshly mixed sealant was placed into an open-faced polytetrafluoroethylene (PTFE) mold with cavity dimensions 9.525 cm x 4.064 cm x 0.318 cm (3.75 in x 1.6 in x 0.125 in). The excess sealant was scraped off with a flat-bladed scraper. The molded sealant sample was cured by placing it under the Clearstone LED array (455 nm) at the distance described above and irradiated at 100% power for 45 seconds.

Hardness Measurement

The instantaneous hardness was determined in accordance with ASTM D2240 using a Model 2000 Type A Durometer from Rex Gauge Company of Buffalo Grove, Ill., United States, after the sealant sample was allowed to cure under the given conditions. The reading was taken on two 0.318 cm (0.125 in) thick specimens, stacked back to back (for a “Top Hardness” measurement) or front to front (for a “Bottom Hardness”. If the thickness was less than 0.318 cm (0.125 in), then multiple pieces were stacked to obtain a total thickness of at least 0.635 cm (0.25 in).

Tensile Strength and Elongation at Break

After curing, three tensile specimens were cut from the sheet using the small dogbone-shaped die specified in ASTM D638V. These specimens were tested in accordance with ASTM D638V using a jaw separation rate of 50.8 cm ± 2.54 cm per minute (20 inches ± 1 inch per minute). The thickness of each specimen was recorded and used to calculate the value of tensile strength.

Example 1:

Step 1: Blending of Cure-on-Demand Sealant (Part A)

Part A was prepared by mixing the DABCO and AC-X92 in a MAX 200 DAC cup (FlackTek, Inc. of Landrum, SC, United States) using a spatula and heating at 60°C (140°F) for two hours. The mixture was allowed to cool to ambient temperature (25°C) and A187, IM30K, R-202, TnBB-MOPA, and UPF were added to the cup. Quantities of the ingredients (in grams) are represented in Table 2. The cup

was then speed mixed for 60 seconds at 1600 RPM (SPEEDMIXER model DAC 400 FVZ from FlackTek, Inc.). The sides and bottom of the cup were scraped with a spatula and the cup was speed mixed for an additional 30 seconds at 1600 RPM.

5

Table 2: Part A Composition

Ingredient	Quantity (grams)
AC-X92	185.38
DABCO	0.36
A187	0.93
IM30K	9.82
R-202	3.63
TnBB-MOPA	0.91
UPF	64.88

Step 2: Blending of Cure-on-Demand Sealant (Part B)

Part B was prepared by speed mixing (SPEEDMIXER model DAC 400 FVZ, FlackTek, Inc.) the ingredients, DAEBPA, OR819, R-202, TAC, and TBEC in a MAX 100 DAC cup (FlackTek, Inc.) for 60 seconds at 1600 RPM. Quantities of the ingredients (in grams) are represented in Table 3. The sides and bottom of the cup were scraped with a spatula and the cup speed mixed for an additional 30 seconds at 1600 RPM.

10

Table 3: Part B Composition

Ingredient	Quantity (grams)
DAEBPA	17.98
OR819	2.44
R-202	2.3
TAC	2.82
TBEC	6.41

15

Step 3: Mixing of Part A and Part B Sealant

Cured sealant was prepared by speed mixing 90.92 g of Part A and 9.08 g of Part B in a MAX 100 DAC cup for 60 seconds at 1600 RPM. The sides and bottom of the cup were scraped with a spatula and the cup was speed mixed for an additional 30 seconds at 1600 RPM. The Depth of Cure was found to be 0.330 cm (0.130 in) when determined using the Depth of Cure test method described previously.

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Tensile strength, elongation, and hardness measurements for the mixture were then determined according to the Tensile Strength and Elongation at Break test method and the Hardness Measurement test method described previously. Light cure refers to a sample irradiated with a Clearstone LED array for 30 seconds at distance 2.54 cm (1 in) and allowed to sit for 14 days. 1+1 dark cure refers to one day of curing at ambient temperature, followed by one day of curing in a 60°C oven. 2+4 dark cure refers to two days of curing at ambient temperature, followed by four days of curing in a 60°C oven. Results are represented in Table 4.

Table 4: Test Results for Part A and Part B Mixture at Various Cure Conditions

Sample	Tensile Strength kPa (psi)	Elongation at Break %	Hardness, Shore A
light cure	2300 ± 35 (333 ± 5)	228 ± 8	50
1+1 dark cure	2237 ± 28 (324 ± 4)	500 ± 11	41
2+4 dark cure	2452 ± 90 (355 ± 13)	459 ± 37	44

Example 2

Cured sealant was prepared by speed mixing 72.74 g of Part A from Example 1 and 7.26 g of Part B from Example 1 in a MAX 100 DAC cup for 60 seconds at 1600 RPM. The sides and bottom of the cup were scraped with a spatula and the cup speed mixed for an additional 30 seconds at 1600 RPM. The freshly mixed sealant was placed into an open-faced PTFE mold whose cavity dimensions were 9.525 cm x 4.064 cm x 0.318 cm (3.75 inches x 1.6 inches x 0.125 inches) and the excess sealant was scraped off flush with a flat-bladed scraper. The sealant filled PTFE molded sample was then placed against a 0.99 cm (0.39 inch) thick PMMA aircraft window (B747 Series N14OU4005-15 REV B PMA, Nordam Transparency Div., Tulsa, OK, United States). The specimen was then irradiated through the window with a 3M Blue Light Gun (450 +/- 5 nm LED source) at a distance of 2.54 cm (1 inch) for 30 seconds. The PTFE mold was removed, and the sealant had cured to a depth of 0.138 cm (0.125 inch).

Example 3

Freshly mixed sealant as prepared in Example 2 was placed into an open-faced PTFE mold whose cavity dimensions were 9.525 cm x 4.064 cm x 0.318 cm (3.75 inches x 1.6 inches x 0.125 inches) and the excess sealant was scraped off flush with a flat-bladed scraper. The sealant-filled, PTFE-molded sample was then placed against a 0.99 cm (0.39 inch) thick PMMA aircraft window. The specimen was then irradiated through the window with a 365 nm Helios G1 LED array at a distance of 2.54 cm (1 inch)

for 60 seconds. The PTFE mold was removed and the sealant was uncured except for a 0.076 cm (0.03 inch) thick skin immediately against the PMMA window.

Example 4

Step 1: Blending of Cure-on-Demand Sealant (Part A)

Part A was prepared by mixing the DABCO and AC-X92 in a MAX 200 DAC cup (FlackTek, Inc. of Landrum, SC. United States) using a spatula and heating at 60°C (140°F) for two hours. The mixture was allowed to cool to ambient temperature (25°C) and D-E135, R-202, S322 and TnBB-MOPA were added to the cup. Quantities of the ingredients (in grams) are represented in Table 5. The cup was then speed mixed for 60 seconds at 1600 RPM (SPEEDMIXER model DAC 400 FVZ from FlackTek, Inc.). The sides and bottom of the cup were scraped with a spatula and the cup was speed mixed for an additional 30 seconds at 1600 RPM.

Table 5: Part A Composition

Ingredient	Quantity (grams)
AC-X92	147.16
DABCO	0.02
D-E135	2.42
R-202	0.02
S322	48.56
TnBB-MOPA	1.10

Step 2: Blending of Cure on Demand Sealant (Part B)

Part B was prepared by speed mixing (SPEEDMIXER model DAC 400 FVZ, FlackTek, Inc.) the ingredients, DAEBPA, D-E135, HA187, OR819, PCNB, R-202, TAIC, and TBEC in a MAX 10 DAC cup (FlackTek, Inc.) for 60 seconds at 1600 RPM. Quantities of the ingredients (in grams) are represented in Table 6. The sides and bottom of the cup were scraped with a spatula and the cup speed mixed for an additional 30 seconds at 1600 RPM.

Table 6: Part B Composition

Ingredient	Quantity (grams)
DAEBPA	102.14
D-E135	11.50
HA187	34.98
OR819	8.16
PCNB	0.08
R-202	17.26
TAIC	6.52
TBEC	19.36

Step 3: Mixing of Part A and Part B Sealant

Cured sealant was prepared by speed mixing 100.00 g of Part A and 12.79 g of Part B in a MAX 100 DAC cup for 60 seconds at 1600 RPM. The sides and bottom of the cup were scraped with a spatula and the cup was speed mixed for an additional 30 seconds at 1600 RPM. The freshly mixed sealant was placed into an open-faced PTFE mold whose cavity dimensions were 9.525 cm x 4.064 cm x 0.318 cm (3.75 inches x 1.6 inches x 0.125 inches) and the excess sealant was scraped off flush with a flat-bladed scraper. The sealant-filled, PTFE-molded sample was then placed against a 0.99 cm (0.39 inch) thick PMMA aircraft window (B747 Series N14OU4005-15 REV B PMA, Nordam Transparency Div., Tulsa, OK, United States). The specimen was then irradiated through the window with a 3M Blue Light Gun (450 +/- 5 nm LED source) at a distance of 2.54 cm (1 inch) for 30 seconds. The PTFE mold was removed, and the sealant had cured to a depth of 0.138 cm (0.125 inch).

Various modifications and alterations of this disclosure may be made by those skilled the art without departing from the scope and spirit of the disclosure, and it should be understood that this invention is not to be unduly limited to the illustrative embodiments set forth herein.

What is claimed is:

1. A method of irradiating a composition through a substrate, the method comprising:
providing a composition comprising a polythiol, a second component, and at least one of a
5 photoinitiator or photosensitizer that absorbs light having a wavelength greater than 400 nanometers;
positioning the composition adjacent to the substrate, wherein over a wavelength range of 350
nanometers (nm) to 390 nm, the substrate has an average percent transmittance of less than 50 percent;
and
irradiating the composition through the substrate with light having a wavelength greater than 400
10 nanometers, wherein irradiating causes the polythiol to react with the second component.
2. The method of claim 1, wherein over a wavelength range of 400 nm to 750 nm, the substrate has
an average percent transmittance of at least 50 percent.
- 15 3. The method of claim 1 or 2, wherein the substrate comprises at least one of a polyacrylate, a
polymethacrylate, a polycarbonate, a polyester, an epoxy, or a polyurethane.
4. The method of any one of claims 1 to 3, wherein the substrate comprises at least one of ceramic
fibers or nanoparticulate filler.
- 20 5. The method of any one of claims 1 to 4, wherein the substrate has a thickness of at least two
millimeters.
6. The method of any one of claims 1 to 5, wherein the substrate is a window of a vehicle.
- 25 7. The method of claim 6, wherein irradiating the composition provides at least one of an adhesive
for adhering the window to a window frame or a sealant for the window.
8. A method of making a window assembly, the method comprising:
30 providing a composition comprising a polythiol, a second component, and at least one of a
photoinitiator or photosensitizer that absorbs light having a wavelength greater than 400 nanometers;
positioning the composition adjacent to a window; and
irradiating the composition through the window with light having a wavelength greater than 400
nanometers, wherein irradiating causes the polythiol to react with the second component.
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9. The method of any one of claims 1 to 8, wherein the light having a wavelength greater than 400 nanometers comprises blue light.

10. The method of any one of claims 1 to 9, wherein the second component comprises at least one unsaturated compound comprising more than one carbon-carbon double bond, at least one carbon-carbon triple bond, or a combination thereof.

11. The method of claim 10, wherein the composition comprises the photoinitiator, and wherein the photoinitiator comprises a free-radical photoinitiator.

12. The method of claim 11, wherein the composition further comprises an organoborane-amine complex, an organic peroxide, and a nitrogen-containing base.

13. The method of any one of claims 1 to 9, wherein the second component comprises a polyepoxide comprising more than one epoxide group.

14. The method of claim 13, wherein the composition comprises the photoinitiator, and wherein the photoinitiator comprises a photolatent base.

15. The method of any one of claims 1 to 14, wherein the polythiol is a polythioether.

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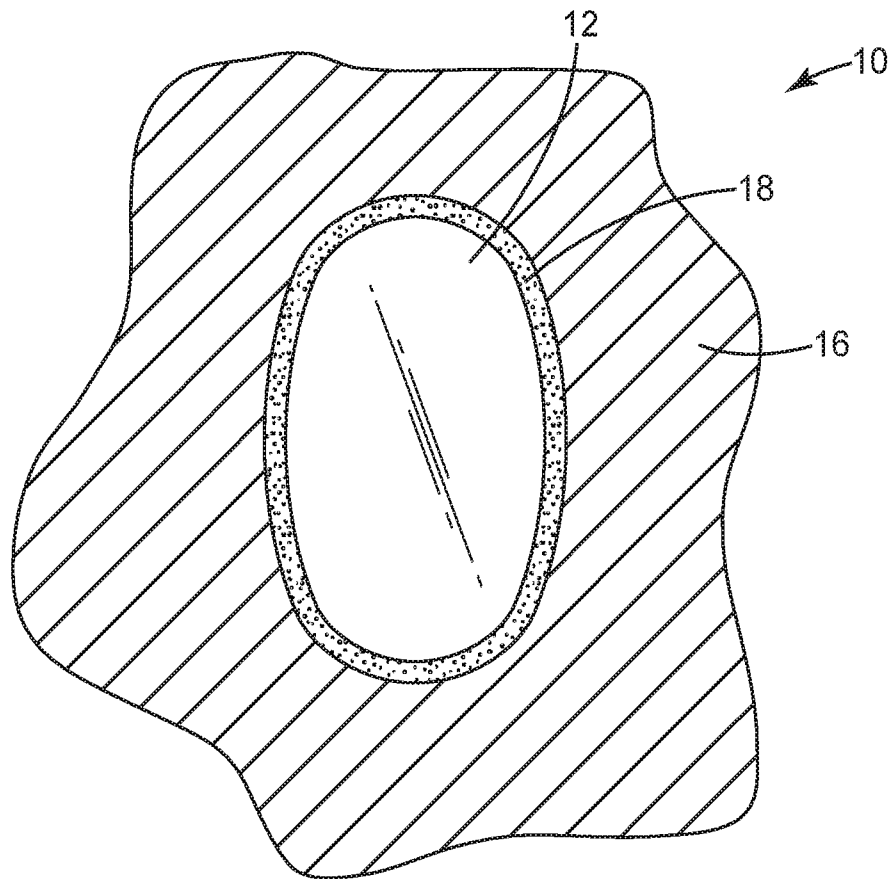


FIG. 1

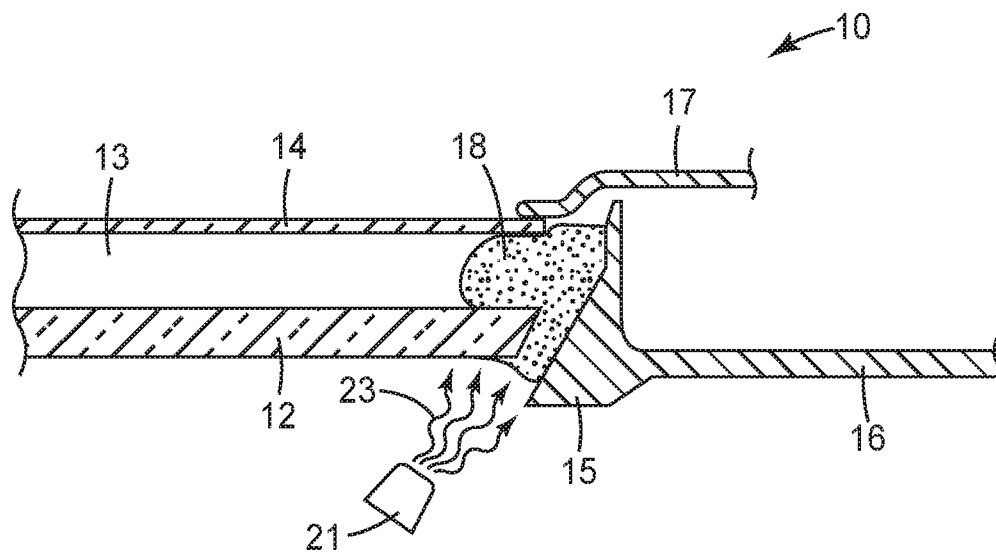


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No

PCT/IB2020/053166

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C08G75/045 B64C1/14
 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)
 C08G C08L C09D C09J B64C B64F

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 Y	US 2016/069378 A1 (ZOOK JONATHAN D [US] ET AL) 10 March 2016 (2016-03-10) paragraph [0003] examples 1,7 figure 2c	1-5, 9-11,15 12-14
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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

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

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

"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

9 June 2020

Date of mailing of the international search report

19/06/2020

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

O'Sullivan, Timothy

INTERNATIONAL SEARCH REPORT

International application No

PCT/IB2020/053166

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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