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(54) **Title**: COMPOSITION INCLUDING A POLYTHIOL AND A POLYEPOXIDE AND METHODS RELATING TO THE COMPOSITION

(57) **Abstract**: A composition including a polythiol having more than one thiol groups, a polyepoxide having more than one epoxide group, a catalytic amount of a second amine, and a photolatent base catalyst. The photolatent base catalyst can photochemically generate a first amine, which may be the same as or different from the second amine. A polymer network preparable from the composition, and a method for making the polymer network are also disclosed.

COMPOSITION INCLUDING A POLYTHIOL AND A POLYEPOXIDE AND METHODS RELATING TO THE COMPOSITION

Cross-Reference to Related Applications

This application claims priority to U.S. Provisional Application Nos. 62/154,469 and 62/154,502, filed April 29, 2015, the disclosures of which are incorporated by reference in their entirety herein.

Background

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.). A desirable combination of properties for aerospace sealants, which is difficult to obtain, is 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).

In other technologies, photochemical generation of bases may be useful for a variety of polymerization reactions. For example, photochemically generated bases may be useful for catalyzing epoxide homopolymerization, Michael additions, and thiol- or polyol-isocyanate reactions. Japanese Patent Application Publication JP2009-126974 describes a thiol-epoxide reaction catalyzed by a photogenerated base.

Summary

Compositions and methods according to the present disclosure include a polythiol, a polyepoxide, and two catalysts. One catalyst is a photolatent base suitable for photochemically curing the composition by generating a first amine. The second catalyst is a second amine suitable for curing the composition, for example, under ambient conditions. The photolatent base provides a cure-on-demand feature to the composition according the present disclosure when the composition is exposed to a light trigger, for example, to provide at least a non-tacky surface or, in some cases, to fully cure the composition. The presence of the second amine in the composition provides several advantages. The second amine provides the composition with a backup curing mechanism and ensures curing in cases in which photochemical irradiation is not an option, does not reach the entire composition (e.g., in unexposed areas) or is inadvertently omitted. As shown in the Examples, below, the second amine does not interfere with the photochemical cure using the photolatent base, and the presence of the photolatent base does not interfere with the traditional cure provided by the second amine. Thus, the composition can be useful, for example, as a one-part or two-part sealant composition with an optional cure-on-demand feature.

In one aspect, the present disclosure provides a composition that includes a polythiol having more than one thiol group, a polyepoxide having more than one epoxide group, a catalytic amount of a second amine, and a photolatent base catalyst. The photolatent base catalyst can photochemically generate a first amine, different from the second amine.

In another aspect, the present disclosure provides a polymer network preparable from the composition described above, in which at least some of the thiol groups and epoxide groups have reacted to form thioether groups and hydroxyl groups.

In another aspect, the present disclosure provides a method of making a polymer network. The method includes providing the composition described above and at least one of exposing the composition to light to generate the first amine to at least partially cure the composition or allowing the composition to achieve a temperature sufficient to at least partially cure the composition.

In another aspect, the present disclosure provides a method of making a polymer network. The method includes providing a composition including a polythiol having more than one thiol group, a polyepoxide having more than one epoxide group, a catalytic amount of a second amine, and a photolatent base catalyst. The photolatent base catalyst can photochemically generate a first amine, which may be the same as or different from the second amine. After providing this composition, the method further includes at least one of exposing the composition to light to generate the first amine to at least partially cure the composition or allowing the composition to achieve a temperature sufficient for the second amine to at least partially cure the composition.

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 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.

"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, or nitro groups. Examples of aryl groups include phenyl, naphthyl, biphenyl, fluorenyl as well as furyl, thienyl, pyridyl, quinolinyl, isoquinolinyl, indolyl, isoindolyl, triazolyl, pyrrolyl, tetrazolyl, imidazolyl, pyrazolyl, oxazolyl, and thiazolyl.

All numerical ranges are inclusive of their endpoints and non-integral values between the endpoints unless otherwise stated.

Detailed Description

Existing sealant products now in use in the aircraft industry are typically either two-part products or one-part products. For the two-part products, once the user mixes the two parts, the reaction begins and the sealant starts to form into an elastomeric solid. After mixing, the time that the sealant remains usable is called the application life or open time. Throughout the application life, viscosity of the sealant gradually increases until the sealant is too viscous to be applied. Application life and cure time are typically related in that short-application-life products cure quickly. Conversely, long-application-life products cure slowly. In practice, customers chose products with differing application lives and cure times depending on the specific application. This requires the customer to maintain inventories of multiple products to address the production flow requirements of building and repairing aircraft. For one-part products, users can avoid a complicated mixing step, but the product has to be shipped and stored in a freezer before application. Advantageously, in many embodiments, compositions according to the present disclosure can be useful as one-part sealants that can simultaneously have a long application life but can be cured on demand.

Polythiols and polyepoxides useful for practicing the present disclosure have more than one thiol group and epoxide group, respectively. In some embodiments, the polythiol includes at least two thiol groups, and 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 thiol groups contributed by polythiols having at least three thiol groups may be useful.

A variety of polythiols having more than one thiol group and polyepoxides having more than one epoxide group are useful in the composition 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., $-NR^1-$) groups and optionally substituted by alkoxy or hydroxyl. Useful monomeric polythiols may be dithiols or polythiols with more than 2 (in some embodiments, 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. Combinations of any of these or with any of the dithiols mentioned above may be useful.

In some embodiments, the polythiol in the curable composition 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 $CH_2=CH-O-(-R^2-O-)_m-CH=CH_2$, in which m is a number from 0 to 10 and R^2 is a 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 -CH(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., -CH_2CH(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 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 HS-R^3-[S-$(CH_2)_2$-O-[-R^4-O-]$_m$-$(CH_2)_2$-S-R^3-]$_n$-SH, wherein each R^3 and 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, -[$(CH_2)_p$-X-]$_q$-$(-CH_2)_r$, in which at least one -CH_2- is optionally substituted with a methyl group, X is one selected from the group consisting of O, S and –NR^5-, 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-3,5,5-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 BASF under the trade designation "IRGACURE". 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-ynes 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 thermal initiators described above are used, and the resulting mixture is heated to provide the polythioethers.

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.

A variety of polyepoxides having more than one epoxide group are useful in the composition 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., $-NR^1-$) 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., $-O-C_6H_5-CH_2-C_6H_5-O-$) 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. 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 tetrakis glycidyl-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 C_2 to C_5 alkylene, in some embodiments, C_2 to C_3 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 according to the present disclosure and/or 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 curable composition so that there is a stoichiometric equivalence of mercaptan groups and epoxide groups.

Compositions and methods according to the present disclosure include a photolatent base catalyst. A photolatent base catalyst photochemically generates a base that can catalyze the reaction between the polythiol and the polyepoxide. In the compositions and methods disclosed herein, the base is a first amine. Compositions and methods according to the present disclosure also include a second amine. In

some embodiments, the second amine is different from the first amine. In some embodiments, for example, some embodiments of the methods disclosed herein, the first amine and the second amine are the same amine.

The first amine 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 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., 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, lone pair of electrons on 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 (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 (including amidines) or guanidines.

The second amine and its amount may be selected to provide the composition with a desirable amount of open time (that is, the length of time it takes for the composition 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 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 cure-on-demand. 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.

As shown in the Examples below, the composition according to the present disclosure typically has a working time that can be useful for the production of very large structures, as is typical in the aircraft industry, and does not require heating above ambient conditions to cure. Thus, use of the composition as a sealant may avoid unpredictable performance that may be associated with overheating either the sealant material, the structure to be sealed, or both.

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

A variety of photolatent bases can be useful for photochemically generating the first amine. Many useful photolatent 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. Photolatent 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 photolatent bases described in the review as useful for generating primary or secondary amines include certain O-acyloximes, sulfonamides, and formamides. Acetophenones, benzophenones, and acetonaphthones 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 photolatent 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 photolatent bases useful for practicing the present disclosure.

In some embodiments, the photolatent base useful for practicing the present disclosure is a 1,3-diamine compound represented by the formula $N(R_7)(R_6)$-$CH(R_5)$-$N(R_4)$-$C(R_1)(R_2)(R_3)$ such as those described in U.S. Pat. No. 7,538,104 (Baudin et al.). Such compounds can be considered arylalkylenyl substituted reduced amidines or guanidines. In formula $N(R_7)(R_6)$-$CH(R_5)$-$N(R_4)$-$C(R_1)(R_2)(R_3)$, R_1 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 C_1-C_{18} alkyl, C_2-C_{18} alkenyl, C_2-C_{18} alkynyl, C_1-C_{18} haloalkyl, $-NO_2$, $-NR_{10}R_{11}$, -CN, $-OR_{12}$, $-SR_{12}$, $-C(O)R_{13}$, $-C(O)OR_{14}$, halogen, groups of the formula $N(R_7)(R_6)$-$CH(R_5)$-$N(R_4)$-$C(R_2)(R_3)$- where R_2-R_7 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_2 and R_3 are each independently selected from hydrogen, C_1-C_{18} alkyl, phenyl, substituted phenyl (that is, substituted one or more times by at least one monovalent group selected from C_1-C_{18} alkyl, -CN, $-OR_{12}$, $-SR_{12}$, halogen, C_1-C_{18} haloalkyl, and combinations thereof), and combinations thereof; R_5 is selected from C_1-C_{18} alkyl, $-NR_8R_9$, and combinations thereof; R_4, R_6, R_7, R_8, R_9, R_{10} and R_{11} are each independently selected from hydrogen, C_1-C_{18} alkyl, and combinations thereof; or R_4 and R_6 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_5 and R_7, independently of R_4 and R_6, 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_5 is $-NR_8R_9$, then R_7 and R_9 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; R_{12} and R_{13} are each independently selected from hydrogen, C_1-C_{19} alkyl, and combinations thereof; and R_{14} is selected from C_1-C_{19} alkyl and combinations thereof. The alkyl and haloalkyl groups can be linear or branched and, in some embodiments, contain 1 to about 12 carbon atoms (in some embodiments, 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 12 carbon atoms (in some embodiments, 2 to about 6 carbon atoms). The alkynyl groups can be linear or branched and, in some embodiments, contain 2 to about 12 carbon atoms (in some embodiments, 2 to about 6 carbon atoms).

In some embodiments of formula $N(R_7)(R_6)$-$CH(R_5)$-$N(R_4)$-$C(R_1)(R_2)(R_3)$, R_1 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, thioxanthyl, phenoxathiinyl, pyrrolyl, imidazolyl, pyrazolyl, pyrazinyl, pyrimidinyl, pyridazinyl, indolizinyl, isoindolyl, indolyl, indazolyl, purinyl, quinolizinyl, isoquinolyl, quinolyl, phthalazinyl, naphthyridinyl, quinoxalinyl, 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, $-NO_2$, $-NR_{10}R_{11}$, -CN, $-OR_{12}$, $-SR_{12}$, $-C(O)R_{13}$, $-C(O)OR_{14}$, halogen, a radical of the formula $N(R_7)(R_6)$-$CH(R_5)$-$N(R_4)$-$C(R_2)(R_3)$-, or a combination thereof, where R_2-R_7 and R_{10}-R_{14} are as defined above. In some embodiments of formula $N(R_7)(R_6)$-$CH(R_5)$-$N(R_4)$-$C(R_1)(R_2)(R_3)$, R_1 is a substituted or unsubstituted biphenylyl radical, wherein each phenyl group is independently substituted with from zero to three (preferably, zero or one) substituents selected from C_1-C_{18} alkyl, C_2-C_{18} alkenyl, -OH, -CN, $-OR_{10}$, $-SR_{10}$, halogen, radicals of the formula $N(R_7)(R_6)$-$CH(R_5)$-$N(R_4)$-$C(R_2)(R_3)$-, and combinations thereof, where R_2-R_7 and R_{10}-R_{14} are as defined above. In some embodiments of formula $N(R_7)(R_6)$-$CH(R_5)$-$N(R_4)$-$C(R_1)(R_2)(R_3)$, R_1 is selected from phenyl, 3-methoxyphenyl, 4-methoxyphenyl, 2,4,6-trimethoxyphenyl, 2,4-dimethoxyphenyl, and combinations thereof.

In some embodiments of formula $N(R_7)(R_6)$-$CH(R_5)$-$N(R_4)$-$C(R_1)(R_2)(R_3)$, R_2 and R_3 each are independently selected from hydrogen, C_1-C_6 alkyl, and combinations thereof (in some embodiments, both are hydrogen); R_4 and R_6 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_5 and R_7 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_5 is $-NR_8R_9$, R_9 and R_7 together form a C_2-C_6 alkylene bridge that is unsubstituted or substituted by one or more groups selected from C_1-C_4 alkyl radicals and combinations thereof.

Examples of suitable photolatent 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)-11′-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.

Other suitable photolatent bases useful for the compositions according to 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.).

In some embodiments, compositions according to the present disclosure in any of the embodiments described above and below include the photolatent base catalyst in an amount from 0.1 percent to 10.0 percent by weight, based on the total weight of the composition. In some embodiments, the photolatent base catalyst is included in the composition in an amount from 0.5 percent to 10 percent, or 0.5 percent to 5 percent by weight, or 1 to 5 percent by weight, based on the total weight of the composition.

In some embodiments, useful photolatent bases absorb light in a wavelength range from 200 nm to 650 nm. For some applications (e.g., sealants), compositions according to the present disclosure (which include the photolatent base) absorb light in the ultraviolet A (UVA) and/or blue light regions, for example, in a wavelength range from 315 nm to 550 nm or 315 nm to 500 nm. UVA light can be considered to have a wavelength range of 315 nm to 400 nm, and blue light can be considered to have a wavelength range of 450 nm to 495 nm.

In some embodiments, the composition according to the present disclosure and/or useful for practicing the methods according to the present disclosure further include at least one photosensitizer. A photosensitizer can be useful, for example, if the photolatent base 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 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 composition (e.g., the photolatent base). Useful photosensitizers include aromatic ketones (e.g., substituted or unsubstituted benzophenones, substituted or unsubstituted thioxanthones, 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. 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. For example, amounts ranging from about 0.1 weight percent to about 15 weight percent can be useful for some applications. In some embodiments, the photosensitizer is included in the composition 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.

When used in sealant applications, for example, compositions according to 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 composition according to the present disclosure 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 ("HI-SIL 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.). The term "ceramic" refers to glasses, crystalline ceramics, glass-ceramics, and combinations thereof. 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 500 micrometers, more typically less than 100 micrometers. 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". Yet 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 sealant composition.

When used in sealant applications, for example, compositions according to the present disclosure can also contain at least one of cure accelerators, surfactants, adhesion promoters, thixotropic agents, pigments, 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 the photolatent base or another component of the composition.

In some embodiments, compositions according to the present disclosure include at least one oxidizing agent. Oxidizing agents can be useful, for example, when the composition according to the present disclosure includes a polysulfide oligomer or polymer. In these compositions, oxidizing agents can minimize the degradation or interchanging of disulfide bonds in the sealant network. 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 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). Other useful organic oxidizing agents include para-quinone dioxime.

As shown in the Examples, below, compositions according to the present disclosure cure remarkably well in the presence of filler. When the samples were exposed to 455 nm blue light, cure depths of greater than one millimeter were achieved. Such cure depths were achieved even when manganese dioxide was used as an oxidant. In polysulfide-based sealants, manganese dioxide is

commonly added as an oxidation agent with excess to prevent disulfide bond degradation or interchanging. However, manganese dioxide is black and typically tends to limit the depth of curing.

Compositions according to the present disclosure can be made by combining a polythiol comprising more than one thiol groups, a polyepoxide comprising more than one epoxide group, a catalytic amount of a second amine, and a photolatent base catalyst, wherein the photolatent base catalyst can photochemically generate a first amine. The polythiol, polyepoxide, second amine, and photolatent base catalyst can be those as described above in any of their embodiments. It should be noted that the second amine is present in the composition even before light exposure causes the photolatent base catalyst to generate the first amine. The polythiol, polyepoxide, the catalytic amount of the second amine, the photolatent base, and any other components described in any of the above embodiments may be provided as a one-part composition. To make a one-part composition, the components may be added in any convenient order. It may be useful to store such a composition frozen and away from light before it is applied (e.g., as a sealant) and cured. The composition may also arise from combining components of a two-part system. For example, a first component comprising the polyepoxide can conveniently be combined with a second component comprising the polythiol, the catalytic amount of the second amine, and the photolatent base to generate the composition according to the present disclosure. In another example, a first component may comprise the polyepoxide and the photolatent base, and a second component may comprise the polythiol and the catalytic amount of the second amine. Other combinations may also be useful.

In some embodiments, compositions according to the present disclosure can be made by providing a starting composition comprising the polythiol comprising more than one thiol group, the polyepoxide comprising more than one epoxide group, and the catalytic amount of the second amine. The starting composition may be stored frozen as a one-part composition or stored as a two-part composition and mixed shortly before use. The starting composition may, in some embodiments, be applied to a substrate to be coated or sealed, for example, leaving a surface of the starting composition exposed. A solution comprising the photolatent base catalyst can then be applied to the surface of the starting composition. The solution comprising the photolatent base can be applied by any convenient method, for example, dip coating, knife coating, reverse roll coating, brushing, and spraying (e.g., aerosol spraying or electrostatic spraying). The solution may be allowed to penetrate into the composition for any desired length of time to allow the photolatent base to combine with the polythiol, polyepoxide, and the second amine. In some embodiments, the solution further comprises a photosensitizer (e.g., any of the photosensitizers described above). Following the application of the solution comprising the photolatent base to the surface of the starting composition, at least a non-tacky skin can be made on the surface by exposing the applied photolatent base to an appropriate light source. The non-tacky skin can advantageously serve to protect the underlying composition while it continues to cure (e.g., by means of the second amine).

In these embodiments, the solution including the photolatent base and optionally the photosensitizer can include any suitable solvent or solvents capable of dissolving these components. The components may be present in the solvent at any suitable concentration, (e.g., from about 5 percent to about 90 percent by weight based on the total weight of the solution). Illustrative examples of suitable solvents include aliphatic and alicyclic hydrocarbons (e.g., hexane, heptane, and cyclohexane), aromatic solvents (e.g., benzene, toluene, and xylene), ethers (e.g., diethyl ether, glyme, diglyme, and diisopropyl ether), esters (e.g., ethyl acetate and butyl acetate), alcohols (e.g., ethanol and isopropyl alcohol), ketones (e.g., acetone, methyl ethyl ketone, and methyl isobutyl ketone), sulfoxides (e.g., dimethyl sulfoxide), amides (e.g., N,N-dimethylformamide and N,N-dimethylacetamide), halogenated solvents (e.g., methylchloroform, 1,1,2-trichloro-1,2,2-trifluoroethane, trichloroethylene, and trifluorotoluene), and mixtures thereof. When an aromatic photosensitizer is present, an aromatic solvent may be useful.

In some embodiments, the method of making a polymer network includes exposing the composition disclosed herein in any of its embodiments to light to generate the first amine to at least partially cure the composition. The light source and exposure time can be selected, for example, based on the nature and amount of the composition. Sources of ultraviolet and/or visible light can be useful (for example, wavelengths ranging from about 200 nm to about 650 nm, from about 315 nm to 550 nm, or from about 315 nm to 500 nm can be useful). Suitable light includes sunlight and light from artificial sources, including both point sources and flat radiators. In some embodiments, the light source is a source of at least one of UVA or blue light. 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 argon lamps; electronic flashlights; xenon flashlights; photographic flood lamps; light-emitting diodes; laser light sources (for example, excimer lasers); and combinations thereof. The distance between the light source and the coated substrate can vary widely, depending upon the particular application and the type and/or power of the light source. For example, distances up to about 150 cm, distances from about 0.01 cm to 150 cm, or a distance as close as possible without touching the composition can be useful.

Depending on various factors, exposure to light might be sufficient to cure the composition to the desired non-tackiness and hardness. However, the thickness of the composition, the presence and nature of filler, the existence and size of areas shielded from light, and other factors may prevent the curing of the composition to the desired non-tackiness and hardness. For some applications, exposure to light may not be possible or may be inadvertently omitted after applying the composition to a substrate. In these embodiments, the method of making a polymer network includes allowing the composition to achieve a temperature sufficient for the second amine to at least partially cure the composition. In some embodiments, the temperature sufficient for the second amine to at least partially cure the composition is

ambient temperature (that is, no external heat source is necessary). In these embodiments, the catalytic amount of the second amine serves as a useful back-up cure mechanism for the composition.

For any of the embodiments of the methods according to the present disclosure, exposing the composition to light at least partially cures the composition. In some of these embodiments, at least the surface of the composition is cured to an extent that the surface becomes non-tacky. A non-tacky surface may be one in which the surface no longer tightly adheres to L-LP-690 standard low density polyethylene film. Such a non-tacky surface may be achieved after exposure of the composition disclosed herein to a light source for up to 10 minutes, up to 5 minutes, up to 3 minutes, up to 2 minutes, or, in some cases, up to 1 minute or up to 30 seconds. Without exposure to light, in some embodiments, the composition according to the present disclosure exhibits at least one of a non-tacky surface or a 30 Shore "A" hardness in less than 24 hours, in some embodiments, less than 12 hours or 10 hours under ambient conditions. With or without exposure to light, in some embodiments, the compositions according to the present disclosure can achieve a 45 to 50 Shore "A" hardness in up to 2 weeks, up to 1 week, up to 5 days, up to 3 days, or up to 1 day.

Polymer networks prepared with polythiols and polyepoxides as described above in any of their embodiments are useful for a variety of applications. For example, such polymer networks can be useful as sealants, for example, aviation fuel resistant sealants. Aviation fuel resistant sealants are widely used by the aircraft industry for many purposes. Commercial and military aircraft are typically built by connecting a number of structural members, such as longitudinal stringers and circular frames. The aircraft skin, whether metal or composite, is attached to the outside of the stringers using a variety of fasteners and adhesives. These structures often include gaps along the seams, joints between the rigidly interconnected components, and overlapping portions of the exterior aircraft skin. The composition according to the present disclosure can be useful, for example, for sealing such seams, joints, and overlapping portions of the aircraft skin. The composition may be applied, for example, to aircraft fasteners, windows, access panels, and fuselage protrusions. As a sealant, the composition disclosed herein may prevent the ingress of weather and may provide a smooth transition between the outer surfaces to achieve desired aerodynamic properties. The composition according to the present disclosure may likewise be applied to interior assembles to prevent corrosion, to contain the various fluids and fuels necessary to the operation of an aircraft, and to allow the interior of the aircraft (e.g., the passenger cabin) to maintain pressurization at higher altitudes. Among these uses are the sealing of integral fuel tanks and cavities.

Aircraft exterior and interior surfaces, to which sealants may be applied, may include metals such as titanium, stainless steel, and aluminum, and/or composites, any of which may be anodized, primed, organic-coated or chromate-coated. For example, a dilute solution of one or more phenolic resins, organo-functional silanes, titanates or zirconantes, and a surfactant or wetting agent dissolved in organic solvent or water may be applied to an exterior or interior surface and dried.

Sealants may optionally be used in combination with a seal cap, for example, over rivets, bolts, or other types of fasteners. A seal cap may be made using a seal cap mold, filled with a curable sealant, and placed over a fastener. The curable sealant may then be cured. In some embodiments, the seal cap and the curable sealant may be made from the same material. In some embodiments, the seal cap may be made from a curable composition disclosed herein. For more details regarding seal caps, see, for example, Int. Pat. App. Pub. No. WO2014/172305 (Zook et al.).

In some embodiments, compositions 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 polymer network according to the present disclosure has a low glass transition temperature, in some embodiments less than -20 °C, in some embodiments less than -30 °C, in some embodiments less than -40 °C, and in some embodiments less than -50 °C. In some embodiment, the polymer network 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.

Some Embodiments of the Disclosure

In a first embodiment, the present disclosure provides a composition comprising a polythiol comprising more than one thiol group, a polyepoxide comprising more than one epoxide group, a catalytic amount of a second amine, and a photolatent base catalyst, wherein the photolatent base catalyst can photochemically generate a first amine, different from the second amine.

In a second embodiment, the present disclosure provides the composition of the first embodiment, wherein the first amine and second amine are each independently a tertiary amine or a guanidine.

In a third embodiment, the present disclosure provides the composition of the first or second embodiment, wherein the first amine and second amine are each independently an amidine or a guanidine.

In a fourth embodiment, the present disclosure provides the composition of any one of the first to third embodiments, 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), diphenylguanidine (DPG), dimethylaminomethyl phenol, and tris(dimethylaminomethyl)phenol.

In a fifth embodiment, the present disclosure provides the composition of any one of the first to fourth embodiments, wherein at least one of the first amine or second amine comprises at least one of tetramethylguanidine, diphenylguanidine, 1,4-diazabicyclo[2.2.2]octane (DABCO), quinuclidine, 1,8-diazabicyclo[5.4.0]undec-7-ene, or 1,5-diazabicyclo[4.3.0]non-5-ene.

In a sixth embodiment, the present disclosure provides the composition of any one of the first to fifth embodiments, wherein the first amine has a higher conjugate acid pKa than the second amine.

In a seventh embodiment, the present disclosure provides the composition of any one of the first to sixth embodiments, wherein the first amine comprises at least one of tetramethylguanidine, diphenylguanidine, 1,8-diazabicyclo[5.4.0]undec-7-ene, quinuclidine, or 1,5-diazabicyclo[4.3.0]non-5-ene.

In an eighth embodiment, the present disclosure provides the composition of any one of the first to seventh embodiments, wherein the second amine is 1,4-diazabicyclo[2.2.2]octane.

In a ninth embodiment, the present disclosure provides the composition of any one of the first to eighth embodiments, wherein the polythiol is monomeric.

In a tenth embodiment, the present disclosure provides the composition of any one of the first to eighth embodiments, wherein the polythiol is oligomeric or polymeric.

In an eleventh embodiment, the present disclosure provides the composition of the tenth embodiment, wherein the polythiol is a polythioether.

In a twelfth embodiment, the present disclosure provides the composition of the eleventh embodiment, wherein the polythiol is an oligomer or polymer prepared from components comprising a dithiol and a diene or divinyl ether.

In a thirteenth embodiment, the present disclosure provides the composition of the tenth embodiment, wherein the polythiol is a polysulfide oligomer or polymer.

In a fourteenth embodiment, the present disclosure provides the composition of the thirteenth embodiment, further comprising an oxidizing agent.

In a fifteenth embodiment, the present disclosure provides the composition of the fourteenth embodiment, wherein the oxidizing agent comprises at least one of calcium dioxide, manganese dioxide, zinc dioxide, lead dioxide, lithium peroxide, sodium perborate hydrate, sodium dichromate, or an organic peroxide.

In a sixteenth embodiment, the present disclosure provides the composition of any one of the first to fifteenth embodiments, further comprising filler.

In a seventeenth embodiment, the present disclosure provides the composition of the sixteenth embodiment, wherein the filler comprises at least one of silica, carbon black, calcium carbonate, aluminum silicate, or lightweight particles having a density of up to 0.7 grams per cubic centimeter.

In an eighteenth embodiment, the present disclosure provides the composition of any one of the first to seventeenth embodiments, wherein the polyepoxide is monomeric.

In a nineteenth embodiment, the present disclosure provides the composition of any one of the first to seventeenth embodiments, wherein the polyepoxide is oligomeric or polymeric.

In a twentieth embodiment, the present disclosure provides the composition of any one of the first to nineteenth embodiments, wherein the polyepoxide is aromatic.

In a twenty-first embodiment, the present disclosure provides the composition of any one of the first to nineteenth embodiments, wherein the polyepoxide is non-aromatic.

In a twenty-second embodiment, the present disclosure provides the composition of any one of the first to twenty-first embodiments, wherein the polyepoxide comprises three or more epoxide groups.

In a twenty-third embodiment, the present disclosure provides the composition of any one of the first to twenty-second embodiments, further comprising a photosensitizer.

In a twenty-fourth embodiment, the present disclosure provides the composition of the twenty-third embodiment, wherein the photosensitizer has an absorbance in at least one of an ultraviolet A or blue light range.

In a twenty-fifth embodiment, the present disclosure provides the composition of the twenty-fourth embodiment, wherein the photosensitizer has an absorbance in the blue light range.

In a twenty-sixth embodiment, the present disclosure provides the composition of any one of the first to twenty-fifth embodiments, wherein the composition has an open time of at least ten minutes.

In a twenty-seventh embodiment, the present disclosure provides a polymer network preparable from the composition of any one of the first to twenty-sixth embodiments, wherein at least some of the thiol groups and epoxide groups have reacted to form thioether groups and hydroxyl groups.

In a twenty-eighth embodiment, the present disclosure provides a sealant comprising the polymer network of the twenty-seventh embodiment.

In a twenty-ninth embodiment, the present disclosure provides a method of making an at least partially crosslinked polymer network, the method comprising:

providing the composition of any one of the first to twenty-sixth embodiments;

and at least one of:

exposing the composition to light to generate the first amine to at least partially cure the composition; or

allowing the composition to achieve a temperature sufficient for the second amine to at least partially cure the composition.

In a thirtieth embodiment, the present disclosure provides a method of making an at least partially crosslinked polymer network, the method comprising:

providing a composition comprising a polythiol comprising more than one thiol group, a polyepoxide comprising more than one epoxide group, a catalytic amount of a second amine, and a photolatent base catalyst, wherein the photolatent base catalyst can photochemically generate a first amine;

and subsequently at least one of:

exposing the composition to light to generate the first amine to at least partially cure the composition; or

allowing the composition to achieve a temperature sufficient for the second amine to at least partially cure the composition,

wherein the first amine and second amine are either the same or different.

In a thirty-first embodiment, the present disclosure provides the method of the thirtieth 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.

In a thirty-second embodiment, the present disclosure provides the method of the thirtieth or thirty-first embodiment, wherein the first amine and the second amine are the same.

In a thirty-third embodiment, the present disclosure provides the method of any one of the thirtieth to thirty-second embodiments, wherein at least one of the first amine or second amine comprises at least one of tetramethylguanidine, diphenylguanidine, 1,8-diazabicyclo[5.4.0]undec-7-ene, quinuclidine, or 1,5-diazabicyclo[4.3.0]non-5-ene.

In a thirty-fourth embodiment, the present disclosure provides the method of any one of thirtieth to thirty-third embodiments, wherein the first amine is present at a higher mole percent than the second amine.

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

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

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

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

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

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

In a forty-first embodiment, the present disclosure provides the method of the fortieth embodiment, wherein the oxidizing agent comprises at least one of calcium dioxide, manganese dioxide, zinc dioxide, lead dioxide, lithium peroxide, sodium perborate hydrate, sodium dichromate, or an organic peroxide.

In a forty-second embodiment, the present disclosure provides the method of any one of the thirtieth to forty-first embodiments, wherein the composition further comprises filler.

In a forty-third embodiment, the present disclosure provides the method of the forty-second embodiment, wherein the filler comprises at least one of silica, carbon black, calcium carbonate, aluminum silicate, or lightweight particles having a density of up to 0.7 grams per cubic centimeter.

In a forty-fourth embodiment, the present disclosure provides the method of any one of the thirtieth to forty-third embodiments, wherein the polyepoxide is monomeric.

In a forty-fifth embodiment, the present disclosure provides the method of any one of the thirtieth to forty-third embodiments, wherein the polyepoxide is oligomeric or polymeric.

In a forty-sixth embodiment, the present disclosure provides the method of any one of the thirtieth to forty-fifth embodiments, wherein the polyepoxide is aromatic.

In a forty-seventh embodiment, the present disclosure provides the method of any one of the thirtieth to forty-fifth embodiments, wherein the polyepoxide is non-aromatic.

In a forty-eighth embodiment, the present disclosure provides the method of any one of the thirtieth to forty-seventh embodiments, wherein the polyepoxide comprises three or more epoxide groups.

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

In a fiftieth embodiment, the present disclosure provides the method of the forty-ninth embodiment, wherein the photosensitizer has an absorbance in at least one of a ultraviolet A or blue light range.

In a fifty-first embodiment, the present disclosure provides the method of the fiftieth embodiment, wherein the photosensitizer has an absorbance in the blue light range.

In a fifty-second embodiment, the present disclosure provides the method of any one of the thirtieth to fifty-first embodiments, wherein the composition has an open time of at least ten minutes.

In a fifty-third embodiment, the present disclosure provides the method of any one of the thirtieth to fifty-second embodiments, wherein the method includes exposing the composition to light.

In a fifty-fourth embodiment, the present disclosure provides a method of making the composition of any one of the first to twenty-sixth embodiments, the method comprising:

providing a starting composition comprising the polythiol comprising more than one thiol group, the polyepoxide comprising more than one epoxide group, and the catalytic amount of the second amine; and

applying a solution comprising the photolatent base catalyst to a surface of the starting composition.

In a fifty-fifth embodiment, the present disclosure provides the method of the fifty-fourth embodiment, further comprising allowing the solution to penetrate into the starting composition.

In a fifty-sixth embodiment, the present disclosure provides the method of the fifty-fourth or fifty-fifth embodiment, wherein applying comprises spraying the solution.

In a fifty-seventh embodiment, the present disclosure provides the method of any one of the fifty-fourth to fifty-sixth embodiments, wherein the solution further comprises a photosensitizer.

In a fifty-eighth embodiment, the present disclosure provides the method of the fifty-seventh embodiment, wherein the photosensitizer has an absorbance in at least one of a ultraviolet A or blue light range.

In a fifty-ninth embodiment, the present disclosure provides the method of the fifty-eighth embodiment, wherein the photosensitizer has an absorbance in the blue light range.

In a sixtieth embodiment, the present disclosure provides the method of any one of the fifty-fourth to fifty-ninth embodiments, further comprising exposing the composition to light to generate the first amine to at least partially cure at least a portion of the composition.

In a sixty-first embodiment, the present disclosure provides the method of the fifty-third or sixtieth embodiment, wherein the light comprises at least one of ultraviolet A light or blue light.

In a sixty-second embodiment, the present disclosure provides the method of the sixty-first embodiment, wherein the light comprises blue light.

In a sixty-third embodiment, the present disclosure provides the method of any one of the twenty-ninth to sixty-second embodiments, wherein exposing the composition to light to at least partially cure the composition comprises forming at least a non-tacky surface.

In a sixty-fourth embodiment, the present disclosure provides the method of any one of the twenty-ninth to sixty-second embodiments, wherein exposing the composition to light to at least partially cure the composition comprises at least partially gelling the composition.

In a sixty-fifth embodiment, the present disclosure provides the method of any one of the twenty-ninth to sixty-second embodiments, wherein exposing the composition to light to at least partially cure the composition comprises fully curing the composition.

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.

EXAMPLES

Unless otherwise noted, all reagents were obtained or are available from Sigma-Aldrich Company, St. Louis, Missouri, or may be synthesized by known methods. Unless otherwise reported, all ratios are by weight percent.

The following abbreviations are used to describe the examples:

°C:	degrees Centigrade
cm:	centimeter
LED:	light emitting diode
mL:	milliliter
mg:	milligram
mm:	millimeter
MPa:	megaPascal
MW:	molecular weight
nm:	nanometer
rpm:	revolutions per minute
T_g:	glass transition temperature
UV:	ultraviolet

Abbreviations for the materials used in the examples are as follows:

CGI-90:	Photolatent base obtained from BASF, Ludwigshafen, Germany
CPQ:	Camphorquinone, a photosensitizer obtained from Sigma-Aldrich Company.
DABCO:	A 33% by weight solution of 1,4-Diazabicyclo[2.2.2]octane in dipropylene glycol, obtained under the trade designation "DABCO 33-LV" from Air Products & Chemicals, Inc., Allentown, Pennsylvania.
DEA:	9,10-diethoxyanthracene, a photosensitizer obtained from Alfa Aesa, Ward Hill, Massachusetts.
DMDO:	1,8-Dimercapto-3,6-dioxaoctane, obtained from Arkena, Inc., King of Prussia, Pennsylvania.
DVE-3:	Triethyleneglycol divinylether, obtained under the trade designation "RAPI-CURE DVE-3" from Ashland Specialty Ingredients, Wilmington, Delaware.
E-8220:	A diglycidylether of bisphenol F, obtained under the trade designation "EPALLOY 8220" from Emerald Performance Materials, LLC, Cuyahoga Falls, Ohio.
GE-23:	A diepoxidized polyglycol obtained under the trade designation "ERISYS GE-23" from Emerald Performance Materials, LLC.
GE-30:	Trimethylolpropane triglycidylether, obtained under the trade designation "ERISYS GE-30" from Emerald Performance Materials Company.
IPA:	Isopropyl alcohol.
ITX:	Isopropylthioxanthone, a photosensitizer obtained from Sigma-Aldrich Company.
TAC:	Triallylcyanurate, obtained from Sartomer, Inc., Exton, Pennsylvania.

UPF: A surface-treated precipitated calcium carbonate, obtained under the trade designation "ULTRA-PFLEX" from Minerals Technologies, Inc. New York, New York.

VAZO-52: 2,2'-azobis(2,4-dimethyl-pentanenitrile), obtained under the trade designation "VAZO 52" from E.I. du Dupont de Nemours and Company, Wilmington, Delaware.

VAZO-67: 2,2'-azobis(2-methylbutyronitrile), obtained under the trade designation "VAZO-67" from E.I. du Dupont de Nemours and Company.

LP-33: A liquid polysulfide polymer, obtained under the trade designation "THIOKOL LP-33" from Toray Fine Chemicals Co., Ltd., Urayasu, Japan.

AC-380A: Part A of a two-part polysulfide-based, manganese cured, sealant, obtained under the trade designation "AEROSPACE SEALANT AC-380 CLASS B-1/2" from 3M Company, St. Paul, Minnesota.

AC-380B: Part B of a two-part polysulfide-based, manganese cured, sealant, obtained under the trade designation "AEROSPACE SEALANT AC-380 CLASS B-1/2" from 3M Company.

AC-1: A thiol terminated polythioether oligomer with the equivalent weight of 1458 was synthesized as follows. Into a 12-liter round bottom flask equipped with an air-driven stirrer, thermometer, and a dropping funnel, was added 4,706 grams (25.8 moles) DMDO and 999 grams (3.0 moles) E-8220 at 21°C. 1.7 grams DABCO (0.02 weight percent) was mixed in as a catalyst. The system was flushed with nitrogen, then mixed and heated for four hours at between 60 - 70°C. 150 grams (0.6 mole) TAC was added along with approximate 0.4 grams VAZO-67. The material was mixed and heated at approximately 60°C for 3 hours. 3,758 grams (18.6 moles) DVE-3 was then added drop-wise to the flask over 4 hours, keeping the temperature between 60 - 70°C. An additional 1.2 grams VAZO-67 was then added in approximately 0.4 gram increments over approximately 8 hours. The temperature was then raised to 100°C and the material degassed for approximately 1 hour. The resultant polythioether was approximately 3200 MW with 2.2 functionality.

AC-2: A thiol terminated polythioether oligomer with the equivalent weight of 283 was synthesized as follows. Into a 250-millliter round bottom flask equipped with an air-driven stirrer, thermometer, and a dropping funnel, was added 128 grams (0.7 moles) DMDO. The system was flushed with nitrogen, then mixed and heated for 1 hour at between 55 - 60°C. 0.03 grams VAZO-52 was then added and dissolved. 71 grams (0.4 moles) DVE-3 was then added drop-wise to the flask over 30 minutes, keeping the temperature between 55 - 65°C. 0.1 gram VAZO-52 was added and the material was

allowed to stir for three hours. The temperature was then raised to 100°C and the material degassed for approximately 1 hour. The resultant polythioether was approximately 567 MW with 2.0 functionality.

AC-3: A thiol terminated polythioether oligomer with the equivalent weight of 476 was synthesized as follows. Into a 250-millliter round bottom flask equipped with an air-driven stirrer, thermometer, and a dropping funnel, was added 115 grams (0.6 moles) DMDO. The system was flushed with nitrogen, then mixed and heated for 1 hour at between 55 - 60°C. 0.03 grams VAZO-52 was then added and dissolved. 85 grams (0.4 moles) DVE-3 was then added drop-wise to the flask over 30 minutes, keeping the temperature between 55 - 65°C. Another 0.03 gram VAZO-52 was added and the material was allowed to stir for three hours. The temperature was then raised to 100°C and the material degassed for approximately 1 hour. The resultant polythioether was approximately 951 MW with 2.0 functionality.

Mixture 1 (M-1)

A 20 mL amber glass vial was charged with 0.109 grams "CGI-90" photolatent base at 21°C. To this was added 4.000 grams DMDO, 3.906 grams GE-23 and 3.028 grams GE-30. The vial was then sealed and placed on a laboratory roller mill for 2 hours at 25 rpm until the components were dissolved.

Mixtures 2-6 (M-2 - M-6)

The procedure generally described for preparing Mixture M-1 was repeated, wherein the components were added to an amber vial in the sequence and quantities listed in Table 1.

Example 1

The procedure generally described for preparing Mixture M-6 was repeated, wherein the contents of the vial was transferred to a jar, 0.022 grams DABCO was added and the mixture homogeneously dispersed by means of a high speed mixer at 2,000 rpm for 1 minute at 21°C.

TABLE 1

mixture	Composition (grams)						
	CGI-90	ITX	CPQ	DMDO	GE-23	GE-30	DABCO
M-1	0.109	0	0	4.000	3.906	3.028	0
M-2	0.109	0.109	0	4.000	3.906	3.028	0
M-3	0.328	0	0	4.000	3.906	3.028	0
M-4	0.328	0.328	0	4.000	3.906	3.028	0
M-5	0.328	0.547	0	4.000	3.906	3.028	0
M-6	0.328	0	0.328	4.000	3.906	3.028	0
Ex.1	0.328	0	0.328	4.000	3.906	3.028	0.022

Examples with Oligomer 1 (Ex. O-1)

A 20 mL amber glass vial was charged with 0.328 grams "CGI-90" photolatent base and an equal quantity of CPQ at 21°C. To this was added 10.000 grams AC-51 and 0.947 grams GE-30. The vial was then sealed and placed on a laboratory roller mill for 2 hours at 25 rpm until the CGI-90 and the CPQ were dissolved. The mixture was then transferred to an opaque jar, to which 0.274 grams DABCO was added, and the mixture homogenously dispersed by means of a high speed mixer at 2,000 rpm for 1 minute at 21°C.

Examples with Oligomers 2-10 (Ex. O-2 – Ex. O-10)

The procedure generally described for preparing Examples with Oligomer O-1 was repeated, wherein the components were added to an amber vial in the sequence and quantities listed in Table 2. With respect to oligomers O-6, O-9 and O-10, the UPF was dispersed along with the DABCO.

TABLE 2

Ex.	Composition (grams)										
	CGI-90	CPQ	ITX	DEA	AC-1	AC-2	AC-3	GE-30	E-8220	DABCO	UPF
Ex. O-1	0.328	0.328	0	0	10.000	0	0	0.947	0	0.274	0
Ex. O-2	0.328	0.328	0	0	10.000	0	0	0.947	0	0.033	0
Ex. O-3	0.328	0.328	0	0	10.000	0	0	0.947	0	0.547	0
Ex. O-4	0.312	0.312	0	0	0	7.000	0	3.413	0	0.031	0
Ex. O-5	0.310	0.310	0	0	0	0	8.000	2.309	0	0.031	0
Ex. O-6	0.328	0.328	0	0	10.000	0	0	0.947	0	0.033	3.284
Ex. O-7	0.328	0	0.328	0	10.000	0	0	0.947	0	0.033	0
Ex. O-8	0.328	0	0	0.328	10.000	0	0	0.947	0	0.033	0
Ex. O-9	0.323	0	0.780	0	10.000	0	0	0	1.139	0.033	3.342
Ex.O-10	0.323	0	0.780	0	10.000	0	0	0	1.139	0.033	5.570

Evaluations

Exposure Source

LED: A 455 nm LED, model CT-2000, obtained from Clearstone Technologies, Inc., Hopkins, Minnesota.

H-Lamp: A mercury UV lamp, model F-600, obtained from Heraeus Holding, GmbH, Hanau, Germany.

Exposure Cure Time

The time, in minutes at 21°C, for the composition to fully cure in a silicone rubber mold when continuously exposed to either the LED or the H-lamp at a distance of 2.54 cm. Mold dimensions were 2.54 by 2.54 cm by 2.54 mm, and 2.54 by 2.54 cm by 0.76 mm, for the LED and H-lamp exposures, respectively.

Working Time

The time, in hours at 21°C, for the composition in the amber vial to gel and become unusable.

Catalyst Cure Time

The time, in hours at 21°C, for the composition to fully cure in a 2.54 by 2.54 cm by 2.54 mm silicone rubber mold without the LED or H-lamp exposure.

Curing results for the thiol epoxy monomers and thiol epoxy oligomers are listed in Table 3 and Table 4, respectively.

Tensile Strength

The composition was transferred to a 7.12 by 1.27 cm by 2.54 mm silicon rubber mold laminated in between a glass slide and a polyester release liner and cured at 21°C by (a) exposure to the LED, at a distance of 2.54 cm, for 2 minutes through the glass slide, followed by 1 minute through the release liner, or (b) catalyst cured for 24 hours. A sample of the cured material was then die cut for the tensile strength test according to ASTM D-638V. Results are listed in Table 5.

TABLE 3

Mixture	Exposure Source	Cure Time		
		Exposure Cure Time (minutes)	Working Time (hours)	Catalyst Cure (hours)
M-1	H-Bulb	Did not cure	Not Measured	Not Measured
M-2	H-Bulb	Did not cure	Not Measured	Not Measured
M-3	H-Bulb	2.0	Not Measured	Not Measured
M-4	H-Bulb	1.25	Not Measured	Not Measured
M-4	LED	2.5	Not Measured	Not Measured
M-5	LED	2.0	Not Measured	Not Measured
M-6	LED	2.0	Not Measured	Not Measured
Ex. 1	LED	2.0	> 2	Approx. 8

TABLE 4

Example	Exposure Source	Cure Time		
		Exposure Cure Time (minutes)	Working Time (hours)	Catalyst Cure (hours)
Ex. O-1	LED	Not Measured	Approx. 3.5	Not Measured
Ex. O-2	LED	1.5	Approx. 2.0	Approx. 8
Ex. O-3	LED	Not Measured	< 1	Not Measured
Ex. O-4	LED	1.5	Approx. 1.5	Not Measured
Ex. O-5	LED	2.0	> 2.0	Not Measured
Ex. O-6	LED	2.0	Approx. 3.5	Not Measured
Ex. O-7	LED	1.0	Approx. 2.5	Not Measured
Ex. O-8	LED	7.5	Approx. 2.0	Not Measured
Ex. O-9	LED	1.5	> 1.75	10 - 16
Ex. O-10	LED	1.5	> 1.75	10 - 16

TABLE 5

Oligomer	Cure Type	Elongation (%)	Tensile Strength (Mpa)	Tg (°C)
Ex. O-9	LED	355	1.78	Not Measured
Ex. O-9	Catalyst	453	1.78	Not Measured
Ex. O-10	LED	661	2.77	-53
Ex. O-10	Catalyst	900	3.42	Not Measured

Sprayable Catalyst A

A 20 mL amber glass vial was charged with 0.7208 grams "CGI-90" photolatent base, 0.7191 grams CPQ and 3.0932 grams IPA at 21°C. The mixture was vortex mixed until the "CGI-90" photolatent base and CPQ were completely dissolved. The mixture was then transferred to an aerosol sprayer.

Sprayable Catalyst B

A 20 mL amber glass vial was charged with 1.0 gram "CGI-90" photolatent base, 1.0 gram ITX and 7.0 grams IPA at 21°C. The mixture was vortex mixed until the "CGI-90" photolatent base and ITX were completely dissolved. The mixture was then transferred to an aerosol sprayer.

Curable Composition 1

A 20 mL amber glass vial was charged with 1.0 gram GE-30, 0.5 grams "CGI-90" photolatent base and 0.5 grams ITX at 21°C. The vial was then sealed and placed on a laboratory roller mill for 2 hours at 25 rpm until the "CGI-90" photolatent base was dissolved. The contents of the vial were then transferred to a plastic jar and 10.0 grams AC-380A manually mixed into the composition by means of a spatula.

Curable Compositions 1A and 1B

20 grams AC-380A was manually mixed with 2.0 grams GE-30 at 21°C in a plastic jar by means of a spatula. The curable composition was then divided into equal parts, 1-A and 1-B.

Curable Compositions 2

A 20 mL amber glass vial was charged with 1.0 gram GE-30, 0.5 grams "CGI-90" photolatent base and 0.5 grams ITX at 21°C. The vial was then sealed and placed on a laboratory roller mill for 2 hours at 25 rpm until the "CGI-90" photolatent base was dissolved. The contents of the vial were then transferred to a plastic jar and 10.0 grams AC-380A and 0.1 grams AC-380B manually mixed into the composition by means of a spatula.

Curable Compositions 2A and 2B

20 grams AC-380A was manually mixed with 2.0 grams GE-30 and 0.2 grams AC-380B at 21°C in a plastic jar by means of a spatula. The curable composition was then divided into equal parts, 2-A and 2-B.

Curable Compositions 3 - 5

The procedure generally described for preparing Curable Composition 2 was repeated, according to the quantities listed in Table 6.

Curable Compositions 3A and 3B through 5A and 5B

The procedure generally described for preparing Curable Compositions 2A and 2B was repeated, according to the quantities listed in Table 6.

Curable Composition 6

A 20 mL amber glass vial was charged with 8.0 grams LP-33, 2.0 gram GE-30, 0.5 grams "CGI-90" photolatent base and 0.5 grams ITX at 21°C. The vial was then sealed and placed on a laboratory roller mill for 2 hours at 25 rpm until the "CGI-90" photolatent base was dissolved.

Curable Composition 7

A 20 mL amber glass vial was charged with 8.0 grams LP-33, 2.0 gram GE-30, 0.5 grams "CGI-90" photolatent base and 0.5 grams ITX at 21°C. The vial was then sealed and placed on a laboratory roller mill for 2 hours at 25 rpm until the "CGI-90" photolatent base was dissolved. The contents of the vial were then transferred to a plastic jar and 0.1 gram AC-380B was manually mixed into the composition by means of a spatula.

Curable Compositions 8 - 9

The procedure generally described for preparing Curable Composition 7 was repeated, according to the quantities listed in Table 6.

TABLE 6

Curable Composition	Components (grams)					
	AC-380A	GE-30	AC-380B	LP-33	CGI-90	ITX
1	10.0	1.0	0	0	0.5	0.5
1A	10.0	1.0	0	0	0	0
1B	10.0	1.0	0	0	0	0
2	10.0	1.0	0.1	0	0.5	0.5
2A	10.0	1.0	0.1	0	0	0
2B	10.0	1.0	0.1	0	0	0
3	10.0	1.0	0.5	0	0.5	0.5
3A	10.0	1.0	0.5	0	0	0
3B	10.0	1.0	0.5	0	0	0
4	10.0	1.0	1.0	0	0.5	0.5
4A	10.0	1.0	1.0	0	0	0
4B	10.0	1.0	1.0	0	0	0
5	10.0	0	1.0	0	0.5	0.5
5A	10.0	0	1.0	0	0	0
5B	10.0	0	1.0	0	0	0
6	0	2.0	0	8.0	0.5	0.5
7	0	2.0	0.1	8.0	0.5	0.5
8	0	2.0	0.5	8.0	0.5	0.5
9	0	2.0	1	8.0	0.5	0.5

The compositions were transferred to 1.88 by 3.15 cm by 2.8 mm Teflon™ molds and subjected to one of the following curing protocols using a model CT2000 LED, obtained from Clearstone Technologies, Inc., Hopkins, Minnesota.

Sprayable Curing

Curable compositions 1A, 2A, 3A, 4A and 5A were evenly sprayed with approximately 35 mg Sprayable Catalyst A, allowed to dry for 1 minute at 21°C, then exposed to the LED, at 50% power, for 1 minute at a distance of 2.54 cm.

Curable compositions 1B, 2B, 3B, 4B and 5B were evenly sprayed with approximately 35 mg Sprayable Catalyst B, then dried and exposed to the LED and as per the "A" compositions above.

The thickness of cured compositions are listed in Table 7.

TABLE 7

Cured Composition	Cured Thickness (mm)
1A	0.23
1B	0.24
2A	0.25
2B	0.25
3A	0.23
3B	0
4A	>0.1
4B	0
5A	0
5B	0

Direct Curing

Curable Compositions 1 – 5 were exposed to the LED, at 50% power, for 1 minute at a distance of 2.54 cm. A second series of curable compositions were exposed for the same time and at the same distance at 100% LED power.

Curable Compositions 6 - 9 were cured in a similar fashion to compositions 1 – 5, at 50 and 75% LED power levels.

Thickness of the cured compositions 1 -5 and 6 -9 are listed in Tables 8 and 9, respectively.

TABLE 8

Cured Composition	Cured Thickness (mm)	
	@ 50% LED Power	@ 100% LED Power
1	0.25	0.20
2	0.20	>0.1
3	0.24	>0.1
4	>0.1	Surface charred
5	0.30	Surface charred

TABLE 9

Cured Composition	Cured Thickness (mm)	
	@ 50% LED Power	@ 75% LED Power
6	0	2.45
7	0	1.09
8	0	1.63
9	0	Sample charred

A second amine can be added, such as DABCO, can be added to any one of Curable Compositions 1, 1A, 1B, 2, 2A, 2B, 3, 3A, 3B, 4, 4A, 4B, 5, 5A, 5B, and 6 to 9. In these examples, areas not exposed to light can cure.

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 composition comprising a polythiol comprising more than one thiol group, a polyepoxide comprising more than one epoxide group, a catalytic amount of a second amine, and a photolatent base catalyst, wherein the photolatent base catalyst can photochemically generate a first amine, different from the second amine.

2. The composition of claim 1, wherein the first amine and second amine are each independently a tertiary amine or a guanidine.

3. The composition of claim 1 or 2, wherein at least one of the first amine or second amine comprises at least one of tetramethylguanidine, diphenylguanidine, 1,4-diazabicyclo[2.2.2]octane, 1,8-diazabicyclo[5.4.0]undec-7-ene, or 1,5-diazabicyclo[4.3.0]non-5-ene.

4. The composition of any one of claims 1 to 3, wherein the first amine has a higher conjugate acid pKa than the second amine.

5. The composition of any one of claims 1 to 4, wherein the polythiol is monomeric.

6. The composition of any one of claims 1 to 4, wherein the polythiol is an oligomeric or polymeric polythioether.

7. The composition of any one of claims 1 to 4, wherein the polythiol is an oligomeric or polymeric polysulfide.

8. The composition of any one of claims 1 to 7, further comprising an oxidizing agent or a filler.

9. The composition of any one of claims 1 to 8, wherein the polyepoxide is monomeric.

10. The composition of any one of claims 1 to 8, wherein the polyepoxide is an oligomeric or polymeric epoxy resin.

11. The composition of any one of claims 1 to 10, further comprising a photosensitizer.

12. A polymer network preparable from the composition of any one of claims 1 to 11, wherein at least some of the thiol groups and epoxide groups have reacted to form thioether groups and hydroxyl groups.

13. A method of making a polymer network, the method comprising:

providing the composition of any one of claims 1 to 11;

and at least one of:

exposing the composition to light to generate the first amine to at least partially cure the composition; or

allowing the composition to achieve a temperature sufficient to at least partially cure the composition.

14. A method of making a polymer network, the method comprising:

providing a composition comprising a polythiol comprising more than one thiol group, a polyepoxide comprising more than one epoxide group, a catalytic amount of a second amine, and a photolatent base catalyst, wherein the photolatent base catalyst can photochemically generate a first amine;

and subsequently at least one of:

exposing the composition to light to generate the first amine to at least partially cure the composition; or

allowing the composition to achieve a temperature sufficient for the second amine to at least partially cure the composition,

wherein the first amine and second amine are either the same or different.

15. The method of claim 13 or 14, wherein the light comprises at least one of ultraviolet A light or blue light.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/030021

A. CLASSIFICATION OF SUBJECT MATTER

C08G 59/66 (2006.01) C08G 59/40 (2006.01) C08G 59/68 (2006.01) C08G 75/00 (2006.01)

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)

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)

Database: EPODOC, WPIAP, JAPIO, TXTE, Google patents, Google Scholar, Espacenet. CPC Marks: C08G59/4014, C08G 59/686, C08G59/66, C08G75/02, C08G75/14, C08G75/12, C08G59/00, C08L63/00, C09J163/00, C08G75/00, C08L81/00, C09J181/00, Keywords: epoxide, epoxy resin, polyepoxide, Polythiol, Polythioether, polysul[f,ph]ide, polymercapt, Photolatent base, latent curing, cured, curable, amine, catalyst, accelerat, Photo, light, radiate, UV, ultra violet and similar. Applicant/inventor name: 3M, Jonathan ZOOK, Susan DEMOSS, Sheng YE, Andrew DAVIS, Tao GONG, Charlie BLACKWELL

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	

[X] Further documents are listed in the continuation of Box C [X] See patent family annex

* Special categories of cited documents:

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

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"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	Date of mailing of the international search report
15 July 2016	15 July 2016

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INTERNATIONAL SEARCH REPORT C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		International application No. **PCT/US2016/030021**
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	JP 2010095686 A (ASAHI KASEI E MATERIALS CORP) 30 April 2010 Para 0087-0090, Examples 1-2	1-15
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P,X	WO 2015/121341 A1 (CARL ZEISS JENA GMBH) 20 August 2015 Claims 1 and 9; Page 18, line 36	1-15

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/US2016/030021**

This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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End of Annex

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.