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(54) Title: METHOD OF APPLYING A SEALANT TO AN AIRCRAFT COMPONENT

(57) **Abstract:** The method includes applying a curable sealant to a surface of the aircraft component, forming a non-tacky skin on an exposed portion of the curable sealant within a first time periodwhile allowing a portion of the curable sealant adjacent the surface of the aircraft component to be liquid for a second time period. The second time period is at least twice the first time period. The curable sealant comprises at least one of an adhesion promoter or a wetting agent.

METHOD OF APPLYING A SEALANT TO AN AIRCRAFT COMPONENT

Cross-Reference to Related Application

This application claims priority to U.S. Provisional Application Nos. 62/416,948 and 62/416,970, filed November 3, 2016, the disclosure of which is incorporated by reference in its 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).

Other crosslinked sulfur-containing polymers have been made, for example, by reaction of a thiol-terminated sulfur-containing compound with a polyene in the presence of a photoinitiator as described in U.S. Pat. Appl. Nos. 2012/0040103 (Keledjian et al.) and 2016/0032058 (Ye et al.).

Summary

When photochemical curing thiol-terminated sulfur-containing compounds to make sealants, it has been generally considered desirable to achieve full cure as quickly as possible. In contrast, the present disclosure relates to a method of applying aerospace sealants to form a durable, tack-free surface skin but remain un-gelled beneath the crosslinked skin. This method offers the advantage of providing a material having a FOD (foreign object debris) free surface while leaving a portion of the applied sealant un-gelled so that smaller molecules, such as wetting agents and adhesion promoters, are free to migrate to the interface between the sealant and the aircraft component. The method of the present disclosure can allow manufacturers to more quickly assemble aircraft by reducing time wasted waiting for sealant to become tack-free.

In one aspect, the present disclosure provides a method of applying a sealant to an aircraft component. The method includes applying a curable sealant including at least one of an adhesion promoter or wetting agent to a surface of the aircraft component, forming a non-tacky skin on an exposed portion of the curable sealant within a first time period while allowing a portion of the curable sealant adjacent the surface of the aircraft component to be liquid for a second time period. The second time period is at least twice the first time period.

In some embodiments, the method according to the present disclose includes providing a composition comprising a polythiol comprising more than one thiol group and a curing agent comprising more than one crosslinking group. A solution including a photoinitiator is then applied to the surface of the composition. Following the application of the solution including the photoinitiator to the surface of the composition, a non-tacky skin can be made on the surface by exposing the composition to an appropriate light source. In other embodiments in which the curable sealant includes a photoinitiator, the light source, power level, temperature, and presence of fillers, for example, can be tuned to achieve a non-tacky skin while allowing portion of the curable sealant adjacent the surface of the aircraft component to remain liquid for a desirable time period. In still other embodiments, the curable sealant includes at least one of an oxygen-activated curing agent or a moisture-activated curing agent. When such curing agents are exposed to oxygen or moisture, respectively, non-tacky skin can be formed while allowing portion of the curable sealant adjacent the surface of the aircraft component to remain liquid for a desirable time period.

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 “liquid” refers to being able to flow at ambient temperature. In some embodiments, the term “liquid” refers to being un-gelled and/or still having remaining open time. In some embodiments, the term “liquid” refers to having sufficient flow in order to wet out a surface when manually spread with a spatula at 21°C.

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, cyano, 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 (e.g., 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.80, 4, 5, etc.).

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 choose 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. Thus there exists a need for an aircraft sealing material that can simultaneously satisfy the need of having a long application life but can also be cured on demand by the customer.

With existing materials, sealant applicators mix the first and second components as described above and then apply the mixed sealant to the area to be sealed. The sealant is tooled to ensure the shape of the joint meets the desired geometry and so the sealant is free of voids, air pockets, pinholes and other possible defects. The sealed area must then be protected for an extended period of time to allow the sealant to become tack and FOD-free and hard enough to be durable so that additional work operations can be performed in the vicinity of the sealed structure without damaging the applied sealant. Customer specifications establish maximum allowable times for each of these application characteristics, for example SAE AMS-S-8802 requires a 2 hour application life sealant to be tack-free in 40 hours and cured to 30 Share A within 72 hours. Aircraft manufacturers use a variety of methods to eliminate this waiting time including the use of energy intensive forced air heaters, detackifier products which potentially disrupt adhesion of other materials or dissolve in fuel creating particles that could clog filters, and the erection of physical barriers such as tents to protect the uncured and tacky sealant.

The performance properties of aircraft sealing materials may rely on the ability of small molecules to surface segregate. Principle among these properties is adhesion. Adhesion with sealant materials is most generally created using one or more wetting agents and/or adhesion promoters. We have observed that, unlike application life and cure time, the time required for a sealant to adhere to a given substrate is inversely related to cure time. That is, materials that cure through to the substrate rapidly require longer to develop adhesion to the substrate. Rapid gelation and network formation inhibits the mobility of small molecules within the cured matrix thus extending the time required for adhesion to form between the sealant and substrate. The present disclosure addresses an unmet need for materials capable of rapidly forming a tough and durable FOD-free skin and also adhering well to the substrate. The method according to the present disclosure allows the sealant to remain liquid beneath that skin so that wetting agents and adhesion promoters are able to migrate to the substrate before the curable sealant gels.

In the method of the present disclosure, a curable sealant including at least one of an adhesion promoter or wetting agent is applied to a surface of the aircraft component. A non-tacky skin is formed on an exposed portion of the curable sealant within a first time period, while a portion of the curable sealant adjacent the surface of the aircraft component is allowed to remain liquid for a second time period. A non-tacky surface may be one in which the surface no longer tightly adheres to L-LP-690 standard low density polyethylene film as determined using ASTM C679. A non-tacky surface may also be one that is FOD-free according to the following evaluation. After curing, fine aluminum shavings can be spread on to the cured sealant surface and allowed to remain undisturbed for 30 seconds at 70°F (21.1°C). The sealant can then be inverted to allow the shavings to fall off, after which the sealant surface can be gently brushed using a fine fiber paintbrush to remove any remaining aluminum shavings. The surface can be considered FOD-free, akin to non-tacky, if no aluminum shavings remain on the surface after inversion and/or after brushing.

In some embodiments, the first time period is up to four hours. In some embodiments, the first time period is up to three hours, two hours, one hour, 45 minutes, 30 minutes, 20 minutes, 15 minutes, ten minutes, or five minutes. In embodiments, for example, in which actinic radiation is used to form a non-tacky skin on the exposed surface of the curable sealant, the first time period can be up to 60, 45, 30, 25, 20, 15, or ten seconds. The second time period is at least twice the first time period. The second time period is generally sufficient to allow for at least one of the adhesion promoter or wetting agent to interact with the surface of the aircraft component. In some embodiments, the second time period is at least three, five, ten, 20, 25, 50, or 100 times the first time period. In embodiments, for example, in which actinic radiation is used to form a non-tacky skin on the exposed surface of the curable sealant, the second time period can be at least 200, 500, 1000, 2000, or even at least 5000 times the first time period. The first time period and second time period generally begin simultaneously. Thus, it should be understood that the portion of the curable sealant adjacent the surface of the aircraft component is allowed to remain liquid at the same time and subsequent to forming the non-tacky skin.

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.

In some embodiments, curable compositions useful for practicing the present disclosure comprise at least one adhesion promoter. Adhesion promoter may be present in amount from 0.1 wt % to 15 wt % of the curable sealant, less than 5 wt %, less than 2 wt %, and in some embodiments, less than 1 wt %, based on the total weight of the curable sealant. Examples of adhesion promoters include phenolics, such as a phenolic resin available under the trade designation “METHYLON”, epoxy resins such as low molecular weight bisphenol A diglycidyl ethers, organosilanes, such as epoxy-, mercapto- or amino-functional silanes, organotinates, and organozirconates. Examples of mercaptosilanes useful as adhesion promoters include gamma-mercaptopropyltrimethoxysilane, gamma-mercaptopropyltriethoxysilane, gamma-mercaptopropylmethyldimethoxysilane, gamma-mercaptopropylmethyldiethoxysilane, mercaptomethyltrimethoxysilane, mercaptomethyltriethoxysilane, and combinations thereof. In some embodiments, useful organosilanes have amino functional groups (e.g., N-2-(aminoethyl)-3-aminopropyltrimethoxysilane and (3-aminopropyl)trimethoxysilane). In some embodiments, useful adhesion promoters have groups polymerizable by, for example, actinic radiation. Examples of polymerizable moieties are materials that contain olefinic functionality such as styrenic, vinyl (e.g., vinyltriethoxysilane, vinyltri(2-methoxyethoxy) silane), acrylic and methacrylic moieties (e.g., 3-metacrylroxypropyltrimethoxysilane). Some functional silanes useful as adhesion promoters are commercially available, for example, from Momentive Performance Materials, Inc., Waterford, N.Y., under the trade designations “SILQUEST A-187” and “SILQUEST A-1100”. Other useful adhesion promoters are known in the art. In some embodiments of mercaptan-functional adhesion promoters, the adhesion promoter has a mercaptan equivalent weight of less than 5000, 4000, 3000, 2000, or 1000 as determined by mercaptan titration so that they may more easily migrate within the curable sealant composition. Other functional adhesion promoters (e.g., amino- or epoxy-silanes) can also have equivalent weights of less than 5000, 4000, 3000, 2000, or 1000 as determined by titration. Typical titanate and zirconate coupling agents are known to those skilled in the art and a detailed overview of the uses and selection criteria for these materials can be found in Monte, S.J., Kenrich Petrochemicals, Inc., "Ken-React® Reference Manual - Titanate, Zirconate and Aluminate Coupling Agents", Third Revised Edition, March, 1995.

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

In some embodiments of the method according to the present disclosure, the curable sealant comprises a polythiol comprising more than one thiol group. In some embodiments, the polythiol includes at least two thiol groups. Generally, in order to achieve chemical crosslinking between polymer chains, greater than two thiol groups and/or greater than two crosslinking groups are present in at least some of the polythiol and curing agent molecules, respectively. In some embodiments, mixtures of curing agents and/or polythiols having at least 5 percent functional equivalents of thiol groups contributed by polythiols having at least three thiol groups may be useful.

A variety of polythiols having more than one thiol group are useful in the method according to the present disclosure. In some embodiments, the polythiol is monomeric. In these embodiments, the polythiol may be an alkylene, arylene, alkylarylene, arylalkylene, or alkylenearylalkylene having at least two mercaptan groups, wherein any of the alkylene, alkylarylene, arylalkylene, or alkylenearylalkylene are optionally interrupted by one or more ether (i.e., -O-), thioether (i.e., -S-), or amine (i.e., -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. Combination of any of these or with any of the dithiols mentioned above may be useful.

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

Polythioethers can be prepared, for example, by reacting dithiols with dienes, diynes, divinyl ethers, diallyl ethers, ene-ynes, or combinations of these under free-radical conditions. Useful dithiols include any of the dithiols listed above. Examples of suitable divinyl ethers include divinyl ether, ethylene glycol divinyl ether, butanediol divinyl ether, hexanediol divinyl ether, diethylene glycol divinyl ether, triethylene glycol divinyl ether, tetraethylene glycol divinyl ether, cyclohexanedimethanol divinyl ether, polytetrahydrofuryl divinyl ether, and combinations of any of these. Useful divinyl ethers of formula $CH_2=CH-O-(-R^2-O-)_m-CH=CH_2$, in which m is a number from 0 to 10, R^2 is C_2 to C_6 branched alkylene can be prepared by reacting a polyhydroxy compound with acetylene. Examples of compounds of this type include compounds in which R^2 is an alkyl-substituted methylene group such as $-CH(CH_3)-$ (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 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.

In some embodiments, the curable sealant comprises a polyepoxide comprising more than one epoxide group. Epoxides are useful, for example, as curing agents for polythiols. In some embodiments, the polyepoxide includes at least two epoxide groups. Generally, in order to achieve chemical crosslinking between polymer chains, greater than two thiol groups and/or greater than two epoxide groups are present in at least some of the polythiol and polyepoxide molecules, respectively. When using a polythiol having two thiol groups, for example, a mixture of polyepoxides may be useful in which at least one polyepoxide has two epoxide groups, and at least one polyepoxide has at least three epoxide groups. Mixtures of polyepoxides and/or polythiols having at least 5 percent functional equivalents of epoxide groups contributed by polyepoxides having at least three epoxide groups or at least 5 percent functional equivalents of thiol groups contributed by polythiols having at least three thiol groups may be useful. A variety of polyepoxides having more than one epoxide group are useful in the method according to the present disclosure. In some embodiments, the polyepoxide is monomeric. In some embodiments, the polyepoxide is oligomeric or polymeric (that is, an epoxy resin). A monomeric polyepoxide may be an alkylene, arylene, alkylarylene, arylalkylene, or alkylenearylalkylene having at least two epoxide groups, wherein any of the alkylene, alkylarylene, arylalkylene, or alkylenearylalkylene are optionally interrupted by one or more ether (i.e., -O-), thioether (i.e., -S-), or amine (i.e., -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 useful in the methods according to the present disclosure, the polyepoxide is an oligomeric or polymeric diepoxide. In some embodiments, epoxides may be chain extended to have any desirable epoxy equivalent weight. Chain extending epoxy resins can be carried out by reacting a monomeric diepoxide, for example, with a diol in the presence of a catalyst to make a linear polymer. In some embodiments, the resulting epoxy resin (e.g., either an aromatic or non-aromatic epoxy resin) may have an epoxy equivalent weight of at least 150, 170, 200, or 225 grams per equivalent. In some embodiments, the aromatic epoxy resin may have an epoxy equivalent weight of up to 2000, 1500, or 1000 grams per equivalent. In some embodiments, the aromatic epoxy resin may have an epoxy equivalent weight in a range from 150 to 2000, 150 to 1000, or 170 to 900 grams per equivalent. Epoxy equivalent weights may be selected, for example, so that the epoxy resin may be used as a liquid.

Mixtures of polythiols and mixtures of polyepoxides, including any of those described above, may also be useful. Typically the amounts of the polythiol(s) and polyepoxide(s) are selected for the composition so that there is a stoichiometric equivalence of mercaptan groups and epoxide groups.

In some embodiments, the curable sealant comprises at least one unsaturated compound comprising more than one carbon-carbon double bond, carbon-carbon triple bond, or a combination thereof. These unsaturated compounds are useful, for example, as curing agents for polythiols. In some embodiments, the unsaturated compound includes at least two carbon-carbon double bonds, carbon-carbon triple bonds, or combinations thereof. Generally, in order to achieve chemical crosslinking between polymer chains, greater than two thiol groups and/or greater than two carbon-carbon double bonds, carbon-carbon triple bonds, or a combinations thereof are present in at least some of the polythiol and unsaturated compounds, respectively. It should be understood that the unsaturated compound having carbon-carbon double bonds and/or carbon-carbon triple bonds are reactive and generally not part of an aromatic ring. In some of these embodiments, the carbon-carbon double and triple bonds are terminal groups in a linear aliphatic compound. However, styryl groups and allyl-substituted aromatic rings may be useful. The unsaturated compound may also include one or more ether (i.e., -O-), thioether (i.e., -S-), amine (i.e., -NR^1-), or ester (e.g., so that the compound is an acrylate or methacrylate) groups and one or more alkoxy or hydroxyl substituents. In some embodiments, the unsaturated compound does not include ester groups or carbonate groups. In these embodiments, the unsaturated compound is not an acrylate, methacrylate, vinyl ester, or vinyl carbonate. Unsaturated compounds without ester and carbonate groups may be more chemically stable than unsaturated compounds that contain these groups. Suitable unsaturated compounds include dienes, diynes, divinyl ethers, diallyl ethers, ene-ynes, and trifunctional versions of any of these. Combinations of any of these groups may also be useful. Examples of useful unsaturated compounds having more than one carbon-carbon double bond and/or carbon-carbon triple bond include any of those described above in connection with the preparation of polythioethers. When using polythiols having two thiol groups, a mixture of unsaturated compounds may be useful in which at least one unsaturated compound has two carbon-carbon double or triple bonds, and at least one unsaturated compound has at least three carbon-carbon double or triple bonds. Mixtures of unsaturated compounds having at least 5 percent functional equivalents of carbon-carbon double or triple bonds contributed by polyenes having at least three carbon-carbon double or triple bonds may be useful.

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

Curable sealants useful for practicing the method of the present disclosure can also contain fillers. Conventional inorganic fillers such as silica (e.g., fumed silica), calcium carbonate, aluminum silicate, and carbon black may be useful as well as low density fillers. In some embodiments, the curable sealant disclosed herein includes at least one of silica, hollow ceramic elements, hollow polymeric elements, calcium silicates, calcium carbonate, or carbon black. Silica, for example, can be of any desired size, including particles having an average size above 1 micrometer, between 100 nanometers and 1 micrometer, and below 100 nanometers. Silica can include nanosilica and amorphous fumed silica, for example. Suitable low density fillers may have a specific gravity ranging from about 1.0 to about 2.2 and are exemplified by calcium silicates, fumed silica, precipitated silica, and polyethylene. Examples include calcium silicate having a specific gravity of from 2.1 to 2.2 and a particle size of from 3 to 4 microns (“HUBERSORB HS-600”, J. M. Huber Corp.) and fumed silica having a specific gravity of 1.7 to 1.8 with a particle size less than 1 (“CAB-O-SIL TS-720”, Cabot Corp.). Other examples include precipitated silica having a specific gravity of from 2 to 2.1 (“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 10 millimeters (mm), more typically less than one mm. The specific gravities of the microspheres range from about 0.1 to 0.7 and are exemplified by polystyrene foam, microspheres of polyacrylates and polyolefins, and silica microspheres having particle sizes ranging from 5 to 100 microns and a specific gravity of 0.25 (“ECCOSPHERES”, W. R. Grace & Co.). Other examples include elastomeric particles available, for example, from Akzo Nobel, Amsterdam, The Netherlands, under the trade designation "EXPANCEL". Other examples include alumina/silica microspheres having particle sizes in the range of 5 to 300 microns and a specific gravity of 0.7 (“FILLITE”, Pluess-Stauffer International), aluminum silicate microspheres having a specific gravity of from about 0.45 to about 0.7 (“Z-LIGHT”), and calcium carbonate-coated polyvinylidene copolymer microspheres having a specific gravity of 0.13 (“DUALITE 6001AE”, Pierce & Stevens Corp.). Further examples of commercially available materials suitable for use as hollow, ceramic elements include glass bubbles marketed by 3M Company, Saint Paul, Minnesota, as “3M GLASS BUBBLES” in grades K1, K15, K20, K25, K37, K46, S15, S22, S32, S35, S38, S38HS, S38XHS, S42HS, S42XHS, S60, S60HS, iM30K, iM16K, XLD3000, XLD6000, and G-65, and any of the HGS series of “3M GLASS BUBBLES”; glass bubbles marketed by Potters Industries, Carlstadt, N.J., under the trade designations "Q-CEL HOLLOW SPHERES" (e.g., grades 30, 6014, 6019, 6028, 6036, 6042, 6048, 5019, 5023, and 5028); and hollow glass particles marketed by Silbrico Corp., Hodgkins, IL under the trade designation "SIL-CELL" (e.g., grades SIL 35/34, SIL-32, SIL-42, and SIL-43). Such fillers, alone or in combination, can be present in a sealant in a range from 10 percent by weight to 55 percent by weight, in some embodiments, 20 percent by weight to 50 percent by weight, based on the total weight of the curable sealant composition. The presence of filler in the curable sealant provides the advantageous effect of increasing the open time of the curable sealant in some cases.

Curable sealants useful for practicing the method of the present disclosure can also contain at least one of cure accelerators, colorants (e.g., pigments and dyes), thixotropic agents, and solvents. The solvent can conveniently be any material (e.g., *N*-methyl-2-pyrrolidone, tetrahydrofuran, ethyl acetate, or those described below) capable of dissolving a component of the curable sealant. Suitable pigments and dyes can include those that do not absorb in the wavelength range that is desirable for curing the composition. Examples of pigments and dyes useful in the compositions according to the present disclosure can be found in co-pending U.S. Pat. App. Serial No. 62/416,958 (Townsend et al.), filed on November 3, 2016.

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

In some embodiments of the method according to the present disclosure, forming a non-tacky skin on an exposed portion of the curable sealant comprises exposing the exposed portion of the curable sealant to actinic radiation. In some of these embodiments, the curable sealant includes a photoinitiator. Photoinitiators suitable for curing a polythiol with a curing agent comprising an unsaturated compound having at least one carbon-carbon double bond and/or carbon-carbon triple bond include a free-radical photoinitiator. In some embodiments, the free radical photoinitiator is a cleavage-type photoinitiator. Cleavage-type photoinitiators include acetophenones, alpha-aminoalkylphenones, benzoin ethers, benzoyl oximes, acylphosphine oxides and bisacylphosphine oxides and mixtures thereof. Examples of useful photoinitiators include benzoin ethers (e.g., benzoin methyl ether or benzoin butyl ether); substituted acetophenone (e.g., 2,2-dimethoxy-2-phenylacetophenone or 2,2-diethoxyacetophenone); 1-hydroxycyclohexyl phenyl ketone; and acylphosphonate derivatives (e.g., bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide, diphenyl-2,4,6-trimethylbenzoylphosphine oxide, isopropoxyphenyl-2,4,6-trimethylbenzoylphosphine oxide, or dimethyl pivaloylphosphonate). Other useful photoinitiators include those described above in connection with the preparation of polythioethers. Many photoinitiators are available, for example, from BASF under the trade designation “IRGACURE”. The photoinitiator may be selected, for example, based on the desired wavelength for curing and compatibility with the curable sealant. Two or more of any of these photoinitiators may also be used together in any combination.

In some embodiments, a photoinitiator can be added to the curable sealant before it is applied to the surface of the aircraft component. For example, the curable sealant can be packaged as a one-part product including the photoinitiator, or a two-part product in which at least one of the parts includes the photoinitiator can be mixed just before it is applied to surface of the aircraft component. The photoinitiator can be added to the curable sealant in any amount suitable to initiate curing. In some embodiments, the photoinitiator is present in an amount in a range from 0.05 weight percent to about 5 weight percent (in some embodiments, 0.1 weight percent to 2.5 weight percent, or 0.1 weight percent to

2 weight percent), based on the total weight of the curable sealant. In some embodiments, a solution of the photoinitiator can be applied to the exposed surface of the curable sealant after the curable sealant is applied to the surface of the aircraft component. Further details about applying a solution of a photoinitiator to the exposed portion of the curable sealant before exposing the exposed portion of the curable sealant to actinic radiation can be found below in connection with the discussion of the application of photolatent bases.

In some embodiments of the method according to the present disclosure, curable sealants in which a non-tacky skin is formed on an exposed surface thereof using a free-radical photoinitiator also include a second initiator or initiator system. The presence of a second initiator can be useful, for example, for curing the remaining uncured sealant after the second time period has passed. In some embodiments, the second initiator comprises s a peroxide and an amine, wherein the peroxide and the amine together provide a peroxide-amine redox initiator. In some embodiments, the amine is a tertiary amine. In some embodiments, the amine is selected from the group consisting of dihydroxyethyl-p-toluidine, N,N-diisopropylethylamine, and N, N, N', N", N"-pentamethyl-diethylenetriamine. In some embodiments, the peroxide is selected from the group consisting of di-tert-butyl peroxide, methyl ethyl ketone peroxide, and benzoyl peroxide.

In some embodiments, the second initiator comprises an organic hydroperoxide either alone or in combination with a nitrogen-containing base. Organic hydroperoxides have the general structure R-OOH, wherein R is an alkyl group, aryl group, arylalkylene group, alkylarylene group, alkylarylenealkylene group, or a combination thereof. Examples of useful organic hydroperoxides include cumene hydroperoxide, *tert*-butyl hydroperoxide, *tert*-amyl hydroperoxide, 1,1,3,3-tetramethylbutyl hydroperoxide, isopropylcumyl hydroperoxide, p-menthane hydroperoxide (i.e., 1-methyl-1-(4-methylcyclohexyl)ethyl hydroperoxide), diisopropylbenzene hydroperoxide (e.g., 3,5-diisopropylhydroperoxide). In some embodiments, the organic hydroperoxide includes a ketone peroxide (e.g., methyl ethyl ketone peroxide, acetone peroxide, and cyclohexanone peroxide). While organic hydroperoxides tend to be some of the more stable peroxides and require some of the highest temperatures for thermal initiation, we have found that in the presence of a polythiol and unsaturated compound in the composition of the present disclosure, the organic hydroperoxide can initiate curing at room temperature. In some embodiments, compositions according to the present disclosure further comprise a nitrogen-containing base. In some embodiments, a combination of a nitrogen-containing base and an organic hydroperoxide can be considered a redox initiator. The nitrogen atom(s) in the nitrogen-containing base can be bonded to alkyl groups, aryl groups, arylalkylene groups, alkylarylene, alkylarylenealkylene groups, or a combination thereof. The nitrogen-containing base can also be a cyclic compound, which can include one or more rings and can be aromatic or non-aromatic (e.g., saturated or unsaturated). Cyclic nitrogen-containing bases can include a nitrogen as at least one of the atoms in a 5- or 6-membered ring. In some embodiments, the nitrogen-containing base includes only carbon-nitrogen,

nitrogen-hydrogen, carbon-carbon, and carbon-hydrogen bonds. In some embodiments, the nitrogen-containing base can be substituted with at least one of alkoxy, aryl, arylalkylenyl, haloalkyl, haloalkoxy, halogen, nitro, hydroxy, hydroxyalkyl, mercapto, cyano, aryloxy, arylalkyleneoxy, heterocyclyl, or hydroxyalkyleneoxyalkylenyl. In some embodiments, the nitrogen-containing base is a tertiary amine. Examples of useful tertiary amines include triethylamine, dimethylethanolamine, benzyldimethylamine, dimethylaniline, tribenzylamine, triphenylamine, N,N-dimethyl-para-toluidine, N,N-dimethyl-ortho-toluidine, tetramethylguanidine (TMG), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), 1,4-diazabicyclo[2.2.2]octane (DABCO), quinuclidine, dimethylaminomethyl phenol, tris(dimethylaminomethyl)phenol, N,N-dihydroxyethyl-p-toluidine, N,N-diisopropylethylamine, and N, N, N', N", N"-pentamethyl-diethylenetriamine. Useful nitrogen-containing bases also include guanidines such as diphenylguanidine (DPG). In some embodiments, the nitrogen-containing base comprises a substituted or unsubstituted nitrogen-containing ring. In some embodiments, the substituted or unsubstituted nitrogen-containing ring has 5 or 6 atoms in the ring. The substituted or unsubstituted nitrogen-containing ring can be aromatic or nonaromatic and can have up to 4 nitrogen atoms in the ring. The ring can optionally include other heteroatoms (e.g., S and O). Substituted aromatic or nonaromatic rings can be substituted by one or more substituents independently selected from the group consisting of alkyl, aryl, arylalkylenyl, alkoxy, haloalkyl, haloalkoxy, halogen, nitro, hydroxy, hydroxyalkyl, mercapto, cyano, aryloxy, arylalkyleneoxy, heterocyclyl, hydroxyalkyleneoxyalkylenyl, amino, alkylamino, dialkylamino, (dialkylamino)alkyleneoxy, and oxo. The alkyl substituent can be unsubstituted or substituted by at least one of alkoxy having up to 4 carbon atoms, halo, hydroxy, or nitro. In some embodiments, the aryl or arylalkylenyl is unsubstituted or substituted by at least one of alkyl having up to 4 carbon atoms, alkoxy having up to 4 carbon atoms, halo, hydroxy, or nitro. In some embodiments, the nitrogen-containing base is a substituted or unsubstituted pyridine, pyrazine, imidazole, pyrazole, tetrazole, triazole, oxazole, thiazole, pyrimidine, pyridazine, triazine, tetrazine, or pyrrole. Any of these may be substituted with halogen (e.g., iodo, bromo, chloro, fluoro), alkyl (e.g., having from 1 to 4, 1 to 3, or 1 to 2 carbon atoms), arylalkylenyl (e.g., benzyl), or aryl (phenyl). In some embodiments, the nitrogen-containing base, is a substituted or unsubstituted imidazole or pyrazole. The imidazole or pyrazole may be substituted with halogen (e.g., iodo, bromo, chloro, fluoro), alkyl (e.g., having from 1 to 4, 1 to 3, or 1 to 2 carbon atoms), arylalkylenyl (e.g., benzyl), or aryl (phenyl). Examples of useful nitrogen-containing rings include 1-benzylimidazole, 1,2-dimethylimidazole, 4-iodopyrazole, 1-methylbenzimidazole, 1-methylpyrazole, 3-methylpyrazole, 4-phenylimidazole, and pyrazole.

Organic peroxides, in some embodiments, organic hydroperoxides, can be added in any amount suitable to initiate curing. In some embodiments, the organic peroxide is present in an amount in a range from 0.05 weight percent to about 10 weight percent (in some embodiments, 0.1 weight percent to 5 weight percent, or 0.5 weight percent to 5 weight percent). The organic peroxide and its amount may be selected to provide the composition with a desirable second time period (that is, the length of time a portion of the curable sealant adjacent the surface of the aircraft remains liquid) 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 nitrogen-containing base, which in some embodiments, provides a redox curing system in the presence of an organic peroxide, and its amount may be selected to provide the composition with a desirable second time period (that is, the length of time a portion of the curable sealant adjacent the surface of the aircraft remains liquid) 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 nitrogen-containing base and its conjugate acid pKa can both affect the open time. A composition with a smaller amount of a nitrogen-containing base having a higher pKa may have the same open time as a composition having a larger amount of a nitrogen-containing base having a lower pKa. In some embodiments, the nitrogen-containing base is present in an amount in a range from 0.05 weight percent to about 10 weight percent (in some embodiments, 0.1 weight percent to 5 weight percent, or 0.5 weight percent to 5 weight percent).

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

A variety of photolatent bases can be useful in the method of the present disclosure. 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 $N(R_7)(R_6)\text{-}CH(R_5)\text{-}N(R_4)\text{-}C(R_1)(R_2)(R_3)$ 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 $N(R_7)(R_6)\text{-}CH(R_5)\text{-}N(R_4)\text{-}C(R_1)(R_2)(R_3)$, 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 alkyl, alkenyl, alkynyl, 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 $N(R_7)(R_6)\text{-}CH(R_5)\text{-}N(R_4)\text{-}C(R_2)(R_3)\text{-}$ 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, alkyl, phenyl, substituted phenyl (that is, substituted one or more times by at least one monovalent group selected from alkyl, -CN, $-OR_{12}$, $-SR_{12}$, halogen, haloalkyl, and combinations thereof), and combinations thereof; R_5 is selected from 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, 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; and R_{12}, R_{13}, and R_{14} are each independently selected from hydrogen, alkyl, and combinations thereof. Any of the alkyl and haloalkyl groups above can be linear or branched and, in some embodiments, contain 1 to about 19 carbon atoms (in some embodiments, 1 to about 18, 1 to about 12, or 1 to about 6 carbon atoms). In some embodiments, halogen atoms are chlorine, fluorine, and/or bromine (in some embodiments, chlorine and/or fluorine). The alkenyl groups can be linear or branched and, in some embodiments, contain 2 to about 18 carbon atoms (in some embodiments, 2 to about 12 or 2 to about 6 carbon atoms). The alkynyl groups can be linear or branched and, in some embodiments, contain 2 to about 18 carbon atoms (in some embodiments, 2 to about 12 or 2 to about 6 carbon atoms).

In some embodiments of formula $N(R_7)(R_6)\text{-}CH(R_5)\text{-}N(R_4)\text{-}C(R_1)(R_2)(R_3)$, 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. An example of a photolatent base is available from BASF under the trade designation “CGI 90”, which is reported to generate 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) upon exposure to actinic radiation (see, e.g., US2013/0345389 (Cai et al.).

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

In some embodiments, a photolatent base can be added to the curable sealant before it is applied to the surface of the aircraft component. For example, the curable sealant can be packaged as a one-part product including the photolatent base, or a two-part product in which at least one of the parts includes the photolatent base can be mixed just before it is applied to surface of the aircraft component. The photolatent base can be added to the curable sealant in any amount suitable to initiate curing. In some embodiments, the photolatent base is present in an amount in a range from 0.05 weight percent to about 5 weight percent (in some embodiments, 0.1 weight percent to 2.5 weight percent, or 0.1 weight percent to 2 weight percent), based on the total weight of the curable sealant. In some embodiments, a solution of the photolatent base can be applied to the exposed surface of the curable sealant after the curable sealant is applied to the surface of the aircraft component.

In some embodiments of the method according to present disclosure, the curable sealant is applied to a surface of the aircraft component, and the non-tacky skin is formed on the exposed portion of the curable sealant upon exposure to actinic radiation. When it is applied, the curable sealant can comprise a polythiol comprising more than one thiol group and a curing agent comprising more than one crosslinkable group. The curable sealant may be stored as a one-part product (e.g., frozen if necessary) or stored as a two-part product and mixed shortly before use. A solution comprising a photoinitiator or photolatent base described above can then be applied to the surface of the composition. The solution comprising the photoinitator or 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 curable sealant for any desired length of time to allow the photolatent base to combine with the polythiol and curing agent, for example. In some embodiments, the solution further comprises a photosensitizer. Following the application of the solution comprising the photoinitiator or photolatent base to the surface of the composition, a non-tacky skin can be made on the surface by exposing the applied photoinitiator or photolatent base to an appropriate light source. The length of time that the solution is allowed to penetrate the curable sealant can influence the depth of the light cure and thickness of the cured skin at the surface of the curable sealant.

The solution including the photoinitiator or 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). In some embodiments, each component may be present in a range from 10 to 85 or 25 to 75 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.

As shown in the Examples, below, the method according to the present disclosure can provide at least a non-tacky skin on the surface of the composition even when the composition contains filler. When the samples were exposed to 455 nm blue light, cure depths of up to 0.25 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.

Applying a solution including a photolatent base to the exposed portion of a curable sealant can be useful, for example, for adding a second curing mechanism to an existing product. For example, a traditional one-part or two-part sealant can include a polythiol, a polyepoxide, and an amine or other accelerator. The accelerator may be present to provide the sealant composition with a balance of a desirable open time and cure time. For example, the composition may be designed to have 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. The compositions may be designed 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. The solution described herein can be sprayed on the exposed surface of the sealant composition, which can then be exposed to light to provide at least a protective, non-tacky skin on the surface of the composition. Underneath the protective skin, the composition can continue to cure by means of its accelerator.

In some embodiments of the method according to the present disclosure, curable sealants in which a non-tacky skin is formed on an exposed surface thereof using a photolatent base also include a second amine. The presence of a second amine can be useful, for example, for curing the remaining uncured sealant after the second time period has passed. The second amine can also be useful, for example, for curing areas shielded from the light source. The second amine may be the same or different from the first amine. In some embodiments, a temperature sufficient for the second amine to at least partially cure the curable sealant is ambient temperature (that is, no external heat source is necessary).

The first amine (generated by the photolatent base) and second amine can independently be any compound including one to four basic nitrogen atoms that bear a lone pair of electrons. The first amine and second amine can independently include primary, secondary, and tertiary amine groups. The nitrogen atom(s) in the first amine and second amine can be bonded to alkyl groups, aryl groups, arylalkylene groups, alkylarylene, alkylarylenealkylene groups, or a combination thereof. The first amine and second 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, a 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, amidines, or guanidines.

The second amine and its amount may be selected to provide the curable sealant with a desirable amount of open time (that is, the length of time it takes for the curable sealent to become at least partially gelled) after it is mixed or thawed and a desirable second time period during which it remains liquid at the interface of the aircraft component. 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 formation of a non-tacky skin. In some embodiments in which the second amine is different from the first amine, the first amine and the second amine have the same conjugate acid pKa value.

In some embodiments, the second amine may be phase-separated from the curable sealant. In these embodiments, the second amine can be a solid (e.g., dicyandiamide), present in a solid adduct (e.g., such as an adduct of an amine and an epoxy resin), or segregated within a solid (e.g., a semi-crystalline polymer). As a phase-separated amine, the second amine is not reactive with or reacts very slowly with the curable components in the sealant at ambient temperature. Further details about compositions including a phase-separated amine can be found in co-pending U.S. Pat. App. Serial No. 62/416,970 (Zook et al.), filed on November 3, 2016. The curable sealant may also include a second amine that is not phase separated, such as any of those described above, and an amine this phase-separated.

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.

In some embodiments of the method according to present disclosure, the non-tacky skin is formed on the exposed portion of the curable sealant upon exposure to actinic radiation. In some of these embodiments, useful photoinitiators and photolatent bases absorb light in a wavelength range from 200 nm to 650 nm. For some applications, curable sealants that include a photoinitiator or 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 in which the non-tacky skin is formed upon exposure to actinic radiation, the curable sealant or the solution including a photoinitiator or photolatent base that is applied to the curable sealant further includes at least one photosensitizer. A photosensitizer can be useful, for example, if the photoinitiator or photolatent base does not have a strong absorbance in a wavelength range that is desired for curing the curable sealant. 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 curable sealant or solution (e.g., the photoinitiator or 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. In some embodiments, coumarin photosensitizers that are triplet photosensitizers with a wavelength of maximum absorbance, λ_{max}, between 390 to 510 nm are used in combination with camphorquinone. Examples of such coumarin photosensitizers include 3,3'-carbonylbis(5,7-dimethoxycoumarin), 3-benzoyl-7-diethylaminocoumarin, 7-diethylamino-3-thenoylcoumarin, 3-(2-benzofuroyl)-7-diethylaminocoumarin, 7-diethylamino-5',7'-dimethoxy-3,3'-carbonylbiscoumarin, 3,3'-carbonylbis(7-diethylaminocoumarin), 9-(7-diethylamino-3-coumarinoyl)-1,2,4,5-tetrahydro-3H,6H,10H[1]benzopyrano[9,9a,1-gh]quinolazine-10-one, and 9,9'-carbonylbis(1,2,4,5-tetrahydro-3H,6H,10H[1]benzopyrano[9,9a,1-gh]quinolazine-10-one). Further details about compositions including a photolatent base, camphorquinone, and such coumarins can be found in co-pending U.S. Pat. App. Serial No. 62/417,158 (Clough et al.), filed on November 3, 2016. 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. In embodiments in which the photosensitizer is in the solution including the photoinitiator or photolatent base, the photosensitizer may be present in the solution at any suitable concentration, (e.g., from about 5 percent to about 90 percent by weight, 10 percent to 85 percent by weight, or 25 percent to 75 percent by weight, based on the total weight of the solution). When the photosensitizer is present in the curable sealant, amounts ranging from about 0.1 weight percent to about 15 weight percent can be useful. In some embodiments, the photosensitizer is included in the curable sealant in an amount from 0.5 percent to 10 percent by weight, 0.5 percent to 7.5 percent by weight, or 1 percent to 7.5 percent by weight, based on the total weight of the curable sealant.

The method of making a polymer network according to the present disclosure includes exposing the composition disclosed herein in any of its embodiments to light to generate the first amine to at least partially cure at least the surface of 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.

As shown in the Examples, below, the power of the light source can be adjusted to form a non-tacky skin while leaving a portion of curable sealant adjacent the surface of the aircraft component to remain liquid for a desirable second time period. See, for example, the data in Tables 8 and 9. The power level can be selected to form a desirable thickness of non-tacky skin on the surface of a sealant.

In some embodiments, the curable sealant comprises at least one of an oxygen-activated curing agent or a moisture-activated curing agent. In some embodiments, the curable sealant comprises an oxygen-activated curing agent. For example, polythiols as described above in any of their embodiments can be combined with a thiuram disulfide in conjunction with a member selected from the group consisting of an iron salt, iron oxide, iron hydroxide, iron metal complex, manganese salt, manganous oxide, manganese hydroxide, and manganese metal complex. For example, polythiols as described above in any of their embodiments can be combined with a dithiocarbamate selected from the group consisting of iron dithiocarbamate and manganese dithiocarbamate. A non-tacky skin can be formed on such compositions by exposure to an environment containing oxygen, and a portion of the curable sealant not exposed to oxygen (e.g., adjacent the surface of the aircraft component) will take longer to cure. Further information regarding such oxygen-activated curing agents can be found, for example, in U.S. Pat. No. 3,991,039 (Gunter).

In some embodiments, the curable sealant comprises a moisture-activated curing agent. For example, polysulfides as described above in any of their embodiments can be combined with an oxidizing agent such as dinitrobenzene, alkali metal peroxides (e.g., sodium peroxide), alkali metal salt peroxides (e.g., sodium pyrophosphate peroxide, sodium carbonate peroxide, sodium perborate), alkaline earth metal peroxides (e.g., calcium peroxide and barium peroxide) and other metal peroxides (e.g., zinc peroxide manganese dioxide), and ammonium dichromate, and an alkaline desiccating deliquescent accelerating agent adapted and sufficient to maintain said polymer in dry condition during shipment and storage and to attract and absorb moisture from its surroundings after deposition in place to hasten the curing of said polymer by said curing agent. Such alkaline desiccating deliquescent accelerating agents include sodium oxide, sodium peroxide, potassium hydroxide, sodium hydroxide, sodium acetate, sodium carbonate, sodium phosphate, sodium molybdate, calcium oxide, barium oxide, calcium peroxide, barium peroxide, calcium hydroxide, and strontium hydroxide. A non-tacky skin can be formed on such compositions by exposure to an environment containing moisture, and a portion of the curable sealant not exposed to moisture (e.g., adjacent the surface of the aircraft component) will take longer to cure. Further information regarding such moisture-activated curing agents can be found, for example, in U.S. Pat. No. 3,225,017 (Seegman). Any of the oxidizing agents described above can also be used in combination with molecular sieves and a cure accelerator selected from monomeric and polymeric acrylated liquid polysulfide compounds having an acrylate functionality of at least 2 to cure a mercaptan-terminated liquid polysulfide. A non-tacky skin can be formed on such compositions by exposure to an environment containing moisture. Further details regarding such moisture-activated curing agents can be found, for example, in U.S. Pat. No. 5,409,985 (Robinson).

Curable sealants in the method according to the present disclosure can be cured into, 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 method according to the present disclosure can be useful, for example, for sealing such seams, joints, and overlapping portions of the aircraft skin. The curable sealant may be applied, for example, to aircraft fasteners, windows, access panels, and fuselage protrusions. The sealant disclosed herein may prevent the ingress of weather and may provide a smooth transition between the outer surfaces to achieve desired aerodynamic properties. The method according to the present disclosure may likewise be carried out on 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. For more details regarding seal caps, see, for example, Int. Pat. App. Pub. No. WO2014/172305 (Zook et al.).

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

Some Embodiments of the Disclosure

In a first embodiment, the present disclosure provides a method of applying a sealant to an aircraft component, the method comprising:

applying a curable sealant to a surface of the aircraft component, wherein the curable sealant comprises at least one of an adhesion promoter or a wetting agent; and

forming a non-tacky skin on an exposed portion of the curable sealant within a first time periodwhile allowing a portion of the curable sealant adjacent the surface of the aircraft component to be liquid for a second time period, wherein the second time period is at least twice the first time period.

In a second embodiment, the present disclosure provides the method of the first embodiment, wherein the first time period is up to four hours.

In a third embodiment, the present disclosure provides the method of the first or second embodiment, wherein the first time period is up to one minute.

In a fourth embodiment, the present disclosure provides the method of any one of the first to third embodiments, wherein the non-tacky skin is formed on the exposed portion of the curable sealant within up to one hour, and wherein the portion of the curable sealant adjacent the surface of the aircraft component remains liquid for at least two hours.

In a fifth embodiment, the present disclosure provides the method of any one of the first to fourth embodiments, wherein the second time period is at least ten times the first time period.

In a sixth embodiment, the present disclosure provides the method of any one of the first to fifth embodiments, wherein the second time period is at least one hundred times the first time period.

In a seventh embodiment, the present disclosure provides the method of any one of the first to sixth embodiments, wherein the second time period is sufficient to allow for at least one of the adhesion promoter or wetting agent to migrate to the surface of the aircraft component.

In an eighth embodiment, the present disclosure provides the method of the any one of the first to seventh embodiments, wherein the sealant develops a 30 Shore "A" hardness in less than or equal to 24 hours.

In a ninth embodiment, the present disclosure provides the method of any one of the first to eighth embodiments, wherein the curable sealant is applied to a seam or joint between portions of aircraft skin.

In a tenth embodiment, the present disclosure provides the method of any one of the first to ninth embodiments, wherein the curable sealant is applied to at least one of an aircraft fastener, an aircraft window, an aircraft access panel, a fuselage protrusion, or an aircraft fuel tank.

In an eleventh embodiment, the present disclosure provide the method of any one of the first to tenth embodiments, wherein the adhesion promoter comprises at least one of a phenolic resin or an amino-, mercapto-, or epoxy-functional silane.

In a twelfth embodiment, the present disclosure provides the method of any one of the first to eleventh embodiments, wherein the wetting agent comprises at least one of a silicone, fluorinated, or hydrocarbon surfactant.

In a thirteenth embodiment, the present disclosure provides the method of any one of the first to twelfth embodiments, wherein the curable sealant comprises a polythiol comprising more than one thiol group.

In a fourteenth embodiment, the present disclosure provides the method of the thirteenth embodiment, wherein the polythiol is monomeric.

In a fifteenth embodiment, the present disclosure provides the method of the thirteenth embodiment, wherein the polythiol is oligomeric or polymeric.

In a sixteenth embodiment, the present disclosure provides the method of the fifteenth embodiment, wherein the polythiol is a polythioether.

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

In an eighteenth embodiment, the present disclosure provides the method of the fifteenth embodiment, wherein the polythiol is a polysulfide oligomer or polymer.

In a nineteenth embodiment, the present disclosure provides the method of the eighteenth embodiment, wherein the curable sealant further comprises an oxidizing agent.

In a twentieth embodiment, the present disclosure provides the method of any one of thirteenth to nineteenth embodiments, wherein the curable sealant comprises a polyepoxide comprising more than one epoxide group.

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

In a twenty-second embodiment, the present disclosure provides the method of the twentieth embodiment, wherein the polyepoxide is oligomeric or polymeric.

In a twenty-third embodiment, the present disclosure provides the method of any one of the twentieth to twenty-second embodiments, wherein the polyepoxide is aromatic.

In a twenty-fourth embodiment, the present disclosure provides the method of any one of the twentieth to twenty-second embodiments, wherein the polyepoxide is non-aromatic.

In a twenty-fifth embodiment, the present disclosure provides the method of any one of the twentieth to twenty-fourth embodiments, wherein the polyepoxide comprises three or more epoxide groups.

In a twenty-sixth embodiment, the present disclosure provides the method of any one of the thirteenth to twenty-fifth embodiments, wherein the curable sealant comprises a Michael acceptor comprising more than one Michael acceptor group.

In a twenty-seventh embodiment, the present disclosure provides the method of any one of the thirteenth to twenty-sixth embodiments, wherein the curable sealant further comprises a photolatent base catalyst.

In a twenty-eighth embodiment, the present disclosure provides the method of the twenty-seventh embodiment, wherein forming a non-tacky skin on an exposed portion of the curable sealant comprises exposing the exposed portion of the curable sealant to actinic radiation.

In a twenty-ninth embodiment, the present disclosure provides the method of any one of the thirteenth to twenty-sixth embodiments, further comprising applying a solution comprising a photolatent base catalyst to the exposed portion of the curable sealant before exposing the exposed portion of the curable sealant to actinic radiation.

In a thirtieth embodiment, the present disclosure provides the method of the twenty-ninth embodiment, wherein the solution further comprises a solvent comprising at least one of an aliphatic or alicyclic hydrocarbon, an aromatic solvent, ether, ester, alcohol, ketone, sulfoxide, amide, or halogenated solvent.

In a thirty-first embodiment, the present disclosure provides the method of any one of the twenty-seventh to thirtieth embodiments, wherein the photolatent base catalyst generates a first amine upon exposure to actinic radiation.

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

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

In a thirty-fourth embodiment, the present disclosure provides the method of the thirty-third 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-fifth embodiment, the present disclosure provides the method of any one of the thirteenth to nineteenth embodiments, wherein the curable sealant comprises at least one unsaturated compound comprising more than one carbon-carbon double bond, carbon-carbon triple bond, or a combination thereof.

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

In a thirty-seventh embodiment, the present disclosure provides the method of the thirty-fifth or thirty-sixth embodiment, wherein the curable sealant further comprises a free-radical photoinitiator.

In a thirty-eighth embodiment, the present disclosure provides the method of the thirty-seventh embodiment, wherein forming a non-tacky skin on an exposed portion of the curable sealant comprises exposing the exposed portion of the curable sealant to actinic radiation.

In a thirty-ninth embodiment, the present disclosure provides the method of the thirty-fifth or thirty-sixth embodiment, further comprising applying a solution comprising a free-radical photoinitiator to the exposed portion of the curable sealant before exposing the exposed portion of the curable sealant to actinic radiation.

In a fortieth embodiment, the present disclosure provides the method of the thirty-ninth embodiment, wherein the solution further comprises a solvent comprising at least one of an aliphatic or alicyclic hydrocarbon, an aromatic solvent, ether, ester, alcohol, ketone, sulfoxide, amide, or halogenated solvent.

In a forty-first embodiment, the present disclosure provides the method of any one of the thirty-fifth to fortieth embodiments, wherein the curable sealant further comprises at least one of a peroxide or hydroperoxide.

In a forty-second embodiment, the present disclosure provides the method of any one of the thirteenth to nineteenth embodiments, wherein the curable sealant comprises at least one of an oxygen-activated curing agent or a moisture-activated curing agent.

In a forty-third embodiment, the present disclosure provides an aircraft component sealed by the method of any one of the first to forty-second embodiments.

In a forty-fourth embodiment, the present disclosure provides an aircraft comprising the aircraft component of the forty-third embodiment.

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
CPP:	Calcium peroxide powder, obtained under the trade designation "IXPER 75C" from Solvay Chemicals, Inc., Houston, Texas.
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.
FERBAM:	Ferric dimethyldithiocarbamate, a fungicide, obtained under the trade designation "FERBAM D1267" from TCI America Portland, Oregon.
G-12:	A liquid polysulfide resin, mol. wt. 4,000, obtained under the trade designation "THIOPLAST G12" from Akzo Nobel Functional Chemicals GmbH.
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.
TMG:	Tetramethyl guanidine, obtained from Sigma-Aldrich Company.
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.

Mixture 7 (M-7)

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
M-7	0.328	0	0.328	4.000	3.906	3.028	0.022

Mixtures with Oligomer 1 (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-1 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.

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

The procedure generally described for preparing Mixtures 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

Mixture	Composition (grams)										
	CGI-90	CPQ	ITX	DEA	AC-1	AC-2	AC-3	GE-30	E-8220	DABCO	UPF
O-1	0.328	0.328	0	0	10.000	0	0	0.947	0	0.274	0
O-2	0.328	0.328	0	0	10.000	0	0	0.947	0	0.033	0
O-3	0.328	0.328	0	0	10.000	0	0	0.947	0	0.547	0
O-4	0.312	0.312	0	0	0	7.000	0	3.413	0	0.031	0
O-5	0.310	0.310	0	0	0	0	8.000	2.309	0	0.031	0
O-6	0.328	0.328	0	0	10.000	0	0	0.947	0	0.033	3.284
O-7	0.328	0	0.328	0	10.000	0	0	0.947	0	0.033	0
O-8	0.328	0	0	0.328	10.000	0	0	0.947	0	0.033	0
O-9	0.323	0	0.780	0	10.000	0	0	0	1.139	0.033	3.342
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 (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
M-7	LED	2.0	> 2	Approx. 8

TABLE 4

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

TABLE 5

Oligomer	Cure Type	Elongation (%)	Tensile Strength (Mpa)	Tg (°C)
O-9	LED	355	1.78	Not Measured
O-9	Catalyst	453	1.78	Not Measured
O-10	LED	661	2.77	-53
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 Sealant 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 Sealants 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 Sealant 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 Sealants 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 Sealants 3 - 5

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

Curable Sealants 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 Sealant 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 Sealant 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 Sealants 8 - 9

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

TABLE 6

Curable Sealant	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^{TM} molds and subjected to one of the following curing protocols using a model CT2000 LED, obtained from Clearstone Technologies, Inc., Hopkins, Minnesota.

Examples 1 to 10

At least one of an adhesion promoter or wetting agent can be added to each of Curable Sealants 1A-5A and 1B to 5B. The curable sealants can then be applied to an aircraft component.

Sprayable Curing

Curable sealants 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

Example	Cured Composition	Cured Thickness (mm)
1	1A	0.23
2	1B	0.24
3	2A	0.25
4	2B	0.25
5	3A	0.23
6	3B	0
7	4A	>0.1
8	4B	0
9	5A	0
10	5B	0

Examples 11 to 19

At least one of an adhesion promoter or wetting agent can be added to each of Curable Sealants 1 to 9. The curable sealants can then be applied to an aircraft component.

Curable Sealants 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

Example	Cured Thickness (mm)	
	@ 50% LED Power	@ 100% LED Power
11	0.25	0.20
12	0.20	>0.1
13	0.24	>0.1
14	>0.1	Surface charred
15	0.30	Surface charred

TABLE 9

Example	Cured Thickness (mm)	
	@ 50% LED Power	@ 75% LED Power
16	0	2.45
17	0	1.09
18	0	1.63
19	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 to provide Examples 20 to 38. In these examples, the second time period can be shorter than the second time period achieved for Examples 1 to 19.

Example 20

A sealant mixture was prepared as follows. 50 grams G-12, 35 grams UPF, 5 grams CPP and 0.5 grams FERBAM were mixed under vacuum in a 200 mL cup for 2 minutes, at 21°C and 1,200 rpm, using a model "DAC 600.1 VAC-P" speed mixer, from Flack Tec, Inc., Landrum, South Carolina. To this was added 0.1 grams TMG and mixing continued for another 30 seconds at 1,200 rpm until the sealant was homogeneous. The cup was removed from the mixer, the cover removed and the contents flushed with nitrogen. The cup was again covered and the sealant allowed to equilibrate at 25°C for 2 hours. The sealant was then transferred to an open 8.8 by 3.1 by 0.25 cm silicone rubber mold and exposed to an atmosphere of 50% relative humidity at 25°C. After 24 hours the sealant had formed a durable, tack-free skin, approximately 1mm thick, over a viscous liquid. After an additional 168 hours exposure to this atmosphere the skin thickness increased had to 1.5 mm.

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

What is claimed is:

1. A method of applying a sealant to an aircraft component, the method comprising:

applying a curable sealant to a surface of the aircraft component, wherein the curable sealant comprises at least one of an adhesion promoter or a wetting agent; and

forming a non-tacky skin on an exposed portion of the curable sealant within a first time period while allowing a portion of the curable sealant adjacent the surface of the aircraft component to be liquid for a second time period, wherein the second time period is at least twice the first time period.

2. The method of claim 1, wherein the first time period is up to four hours.

3. The method of claim 1 or 2, wherein the second time period is at least ten times the first time period, or wherein the second time period is sufficient to allow for at least one of the adhesion promoter or wetting agent to migrate to the surface of the aircraft component.

4. The method of any one of claims 1 to 3, wherein the curable sealant is applied to a seam or joint between portions of aircraft skin.

5. The method of any one of claims 1 to 4, wherein the curable sealant is applied to at least one of an aircraft fastener, an aircraft window, an aircraft access panel, a fuselage protrusion, or an aircraft fuel tank.

6. The method of any one of claims 1 to 5, wherein the curable sealant comprises a polythiol comprising more than one thiol group.

7. The method of claim 6, wherein the polythiol is monomeric.

8. The method of claim 6, wherein the polythiol is an oligomeric or polymeric polythioether or polysulfide.

9. The method of any one of claims 6 to 8, wherein the curable sealant comprises a polyepoxide comprising more than one epoxide group.

10. The method of any one of claims 6 to 8, wherein the curable sealant comprises a Michael acceptor comprising more than one Michael acceptor group.

11. The method of claim 9 or 10, wherein the curable sealant further comprises a photolatent base.

12. The method of claim 9 or 10, further comprising applying a solution comprising a photolatent base catalyst to the exposed portion of the curable sealant before exposing the exposed portion of the curable sealant to actinic radiation.

13. The method of any one of claims 1 to 11, wherein forming a non-tacky skin on an exposed portion of the curable sealant comprises exposing the exposed portion of the curable sealant to actinic radiation.

14. The method of any one of claims 6 to 8, wherein the curable sealant comprises at least one unsaturated compound comprising more than one carbon-carbon double bond, carbon-carbon triple bond, or a combination thereof and a photoinitiator, and wherein forming a non-tacky skin on an exposed portion of the curable sealant comprises exposing the exposed portion of the curable sealant to actinic radiation.

15. The method of any one of claims 6 to 8, wherein the curable sealant comprises at least one of an oxygen-activated curing agent or a moisture-activated curing agent.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/059731

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D5/00 B05D3/00 C09D5/34 C08G59/40 C09D163/00
C09D181/00 C09D7/63 C08K5/05 C08K5/5415
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09D B05D C08G C08K

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2013/192480 A2 (PRC DESOTO INT INC [US]) 27 December 2013 (2013-12-27) page 37, paragraph 162 page 49, paragraph 213 - paragraph 214 -----	1-15
X	WO 2016/090221 A1 (PRC DESOTO INT INC [US]) 9 June 2016 (2016-06-09) page 19, paragraph 92 examples; page 26 - page 35 page 27 - page 28; table 3 -----	1-15
X,P	WO 2016/176548 A1 (3M INNOVATIVE PROPERTIES CO [US]) 3 November 2016 (2016-11-03) page 18, line 5 - line 14 claims 1-14 ----- -/--	1-15

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

☒ See patent family annex.

* Special categories of cited documents :

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search 27 March 2018	Date of mailing of the international search report 09/04/2018
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Mill, Sibel

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2017/059731

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 1-15(partially)
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/059731

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 2 836 562 A1 (CHEMETALL GMBH [DE]) 18 February 2015 (2015-02-18) claims 2,20 -----	1-15

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2017/059731

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		US 2015065599 A1	05-03-2015
		WO 2013153047 A1	17-10-2013

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 1-15(partially)

The second step of claim 1 includes two time periods, which are not clearly defined: the second time period is unclear, since the begin of the measurement of the second time is undisclosed. The person skilled in the art is not in a position to rework the invention. The requirement of Art. 5 PCT is not fulfilled.

Furthermore, the examples shown do not clearly include the presence of a specific adhesion promoter or a wetting agent: indeed, the examples from p. 31 until p. 39 do not disclose such components in the composition; the one sentence on p. 40, l.6-7 discloses "at least one of an adhesion promoter or wetting agent can be added to each of the curale sealants 1A-5A and 1B to 5B". The same sentence is present for Example 11-19, last sentence of p. 40 (l. 22-23). However, no real example is shown and no effect is shown. Neither the type of adhesion promoter or wetting agent is disclosed, nor the method claimed in exemplified on an aircraft substrate. So there is not enough information concerning the invention and the person skilled in the art is left with an undue burden to try to reproduce the invention; the requirement of Art. 5 PCT is n

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guidelines C-IV, 7.2), should the problems which led to the Article 17(2) declaration be overcome.