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(57) Abstract: In one embodiment, a method of bonding a substrate is described. The method comprises providing an epoxy resin composition comprising a first liquid part comprising an epoxy resin; and a second liquid part comprising a combination of curing agents. The second liquid part comprises a first (e.g. ambient temperature) curing agent having an activation temperature at or below 20-25°C and a second latent curing agent having an activation temperature greater than 25°C. The method further comprises applying a mixture of the first and second part such that it contacts at least one substrate and curing the mixture below the activation temperature of the latent curing agent. The method does not include heating the mixture to the activation temperature of the latent curing agent. Rather, the latent curing agent can become activated during use of a substrate or article. In another embodiment, an article is described comprising at least one first substrate bonded with a cured epoxy resin composition wherein the cured epoxy resin composition comprises an uncured latent curing agent having an activation temperature greater than 25°C. Also described is a two-part epoxy resin composition comprising a first liquid part comprising an epoxy resin; and a second liquid part comprising a first curing agent having an activation temperature at or below 20-25°C and a second latent curing agent having an activation temperature greater than 25°C.



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## **TWO-PART EPOXY RESIN COMPOSITIONS WITH LATENT CURING AGENT**

### **Background**

Epoxy resin compositions have been used for the (e.g. aircraft) aerospace industry. The primary use includes the bonding of structural metal and polymer-fiber composite materials.

### **Summary**

Although various epoxy resins have been described, industry would find advantages in new methods, articles, and two-part epoxy resin compositions comprising a latent curing agent.

In one embodiment, a method of bonding a substrate is described. The method comprises providing an epoxy resin composition comprising a first liquid part comprising an epoxy resin; and a second liquid part comprising a combination of curing agents. The second liquid part comprises a first (e.g. ambient temperature) curing agent having an activation temperature at or below 20-25°C and a second latent curing agent having an activation temperature greater than 25°C. The method further comprises applying a mixture of the first and second part such that it contacts at least one substrate and curing the mixture below the activation temperature of the latent curing agent. The method does not include heating the mixture to the activation temperature of the latent curing agent. Rather, the latent curing agent can become activated during use of a substrate or article.

In another embodiment, an article is described comprising at least one first substrate bonded with a cured epoxy resin composition wherein the cured epoxy resin composition comprises an uncured latent curing agent having an activation temperature greater than 25°C.

Also described is a two-part epoxy resin composition comprising a first liquid part comprising an epoxy resin; and a second liquid part comprising a first curing agent having an activation temperature at or below 20-25°C and a second latent curing agent having an activation temperature greater than 25°C.

In some favored embodiments, the latent curing agent has an activation temperature of at least 50, 60, 70, or 80°C and typically no greater than 150°C. In some favored embodiments, the uncured latent curing agent is present in an aircraft or other aerospace article.

### **Detailed Description**

As used herein, “ambient temperature” refers to the temperature range of 20-25°C and can include any temperature within this range, e.g. 20, 21, 22, 23, 24 or 25°C.

As used herein, “total compositions” it is meant the combination of the first liquid part comprising the epoxy resin and the second (curative) part comprising the curing agents.

Presently described are methods of bonding a substrate with epoxy resin compositions, (e.g. aircraft and other aerospace) articles, and two-part epoxy resin compositions.

The two part epoxy resin composition comprises a first liquid part comprising an epoxy resin; and a second liquid part comprising curing agents. Although the first and second part are liquids at ambient temperature, the liquid parts can comprise solid components dissolved or dispersed within the liquid.

The first part of the two-part composition comprises at least one epoxy resin. Epoxy resins are low molecular weight monomers or higher molecular weight polymers which typically contain at least two epoxide groups. An epoxide group is a cyclic ether with three ring atoms, also sometimes referred to as a glycidyl or oxirane group. Epoxy resins are typically liquids at ambient temperature.

In some embodiments, the first part of the two-part composition comprises at least one bisphenol (e.g. A) epoxy resin. Bisphenol (e.g. A) epoxy resins are formed from reacting epichlorohydrin with bisphenol A to form diglycidyl ethers of bisphenol A. The simplest resin of this class is formed from reacting two moles of epichlorohydrin with one mole of bisphenol A to form the bisphenol A diglycidyl ether (commonly abbreviated to DGEBA or BADGE). DGEBA resins are transparent colorless-to-pale-yellow liquids at ambient temperature, with viscosity typically in the range of 5-15 Pa·s at 25°C. Industrial grades normally contain some distribution of molecular weight, since pure DGEBA shows a strong tendency to form a crystalline solid upon storage at ambient temperature. This same reaction can be conducted with other bisphenols, such as bisphenol F. The choice of the epoxy resin used depends upon the end use for which it is intended. Epoxides with flexibilized backbones may be desired where a greater amount of ductility is needed in the bond line. Materials such as diglycidyl ethers of bisphenol A and diglycidyl ethers of bisphenol F can provide desirable structural adhesive properties that these materials attain upon curing, while hydrogenated versions of these epoxies may be useful for compatibility with substrates having oily surfaces.

Examples of commercially available bisphenol epoxy resins include diglycidyl ethers of bisphenol A (e.g. those available under the trade designations EPON 828, EPON 1001, EPON 1004, EPON 2004, EPON 1510, and EPON 1310 from Momentive Specialty Chemicals, Inc., and those under the trade designations D.E.R. 331, D.E.R. 332, D.E.R. 334, and D.E.N. 439 available from Dow Chemical Co.); diglycidyl ethers of bisphenol F (e.g., that are available under the trade designation ARALDITE GY 281 available from Huntsman Corporation) or blends of bisphenol A and F resins such as EPIKOTE 232 from Momentive Specialty Chemicals, Inc.; flame retardant epoxy resins (e.g., that are available under the trade designation DER 560, and brominated bisphenol type epoxy resin, such as available from Dow Chemical Company).

In some embodiments, the amount of bisphenol (e.g. A) epoxy component(s) is no greater than about 30, 29, 28, 27, 26, or 25 wt-% of the first part of the two-part composition. In some embodiments, the amount of bisphenol (e.g. A) epoxy component(s) is no greater than 15 or 20 wt-% of the total composition.

In some embodiments, the first part of the two-part composition comprises at least one novolac epoxy resin. Novolac epoxy resins are formed by reaction of phenols with formaldehyde and subsequent glycidylation with epichlorohydrin produces epoxidised novolacs, such as epoxy phenol novolacs (EPN)

and epoxy cresol novolacs (ECN). These are highly viscous to solid resins with typical mean epoxide functionality of around 2 to 6. A representative commercially available novolac epoxy resin is a semi-solid epoxy novolac resin commercially available from Dow as the trade designation "D.E.N. 431."

In some embodiments, the first part of the two-part composition comprises at least 5, 6, 7, 8, 9, or 10 wt-% and typically no greater than 20 wt-% of a semi-solid epoxy resin having a melt point no greater than about 60°C, such as a novolac epoxy resin. In some embodiments, the amount of semi-solid epoxy resin having a melt point no greater than about 60°C, such as a novolac epoxy resin, is at least 1, 2 or 3 wt-% and no greater than 10 wt-% of the total composition.

Aromatic epoxy resins can also be prepared by reaction of aromatic alcohols such as biphenyl diols and triphenyl diols and triols with epichlorohydrin. Such aromatic biphenyl and triphenyl epoxy resins are not bisphenol epoxy resins. One representative compound is tris-(hydroxyl phenyl)methane-based epoxy available from Huntsman Corporation, Basel, Switzerland as Tactix™ 742.

In some embodiments, the first part of the two-part composition comprises at least 10, 15, 20, 25, or 30 wt-% and typically no greater than 60, 55, 50, or 40 wt-% of an aromatic epoxy resin derived from a biphenyl or triphenyl alcohol having at least 2 or 3 epoxide groups. Such aromatic epoxy resins typically have a molecular weight less than 1000 g/mole. In some embodiments, the amount of aromatic epoxy resin derived from a biphenyl or triphenyl alcohol having at least 2 or 3 epoxide groups is at least 10 or 15 wt-% and no greater than 35 or 30 wt-% of the total composition.

In one embodiment, the first part of the two-part composition comprises a (e.g. butadiene-acrylic copolymer core-shell) rubber. The amount of (e.g. (core shell) rubber is typically at least 10, 20, or 30 wt.-% of the first part of the two-part composition and typically no greater than 60, 50 or 40 wt-%. In some embodiments, the amount of (e.g. (core shell) rubber is at least 5 or 10 and no greater than 20 or 25 wt-% of the total composition. Commercially available core-shell polymers include those available as a dry powder under the trade designations ACRYLOID KM 323, ACRYLOID KM 330, and PARALOID BTA 731, from Dow Chemical Co., and KANE ACE B-564 from Kaneka Corporation. These core-shell polymers may also be available as a predispersed blend (e.g. with a diglycidyl ether of bisphenol A), for example, a ratio of about 10 to 40 parts by weight of the core-shell polymer and are available under the trade designations KANE ACE MX 157, KANE ACE MX 257, KANE ACE MX 125.

There are two primary types of aliphatic epoxy resins, i.e. glycidyl epoxy resins and cycloaliphatic epoxides. Glycidyl epoxy resins are typically formed by the reaction of epichlorohydrin with aliphatic alcohols or polyols to give glycidyl ethers or aliphatic carboxylic acids to give glycidyl esters. The resulting resins may be monofunctional (e.g. dodecanol glycidyl ether), difunctional (diglycidyl ester of hexahydrophthalic acid), or higher functionality (e.g. trimethylolpropane triglycidyl ether). Cycloaliphatic epoxides contain one or more cycloaliphatic rings in the molecule to which the oxirane ring is fused (e.g. 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate). They are formed by the reaction of cyclo-olefins with a peracid, such as peracetic acid. These aliphatic epoxy resins typically display low viscosity at ambient temperature (10-200 mPa·s) and are often used as

reactive diluents. As such, they are employed to modify (reduce) the viscosity of other epoxy resins. This has led to the term 'modified epoxy resin' to denote those containing viscosity-lowering reactive diluents.

Examples of reactive diluents include diglycidyl ether of 1, 4 butanediol, diglycidyl ether of cyclohexane dimethanol, diglycidyl ether of resorcinol, p-tert-butyl phenyl glycidyl ether, cresyl glycidyl ether, diglycidyl ether of neopentyl glycol, triglycidyl ether of trimethylolethane, triglycidyl ether of trimethylolpropane, triglycidyl p-amino phenol, N,N'-diglycidylaniline, N,N,N',N',-tetraglycidyl meta-xylylene diamine, and vegetable oil polyglycidyl ether. Reactive diluents are commercially available under the trade designation HELOXY 107 and CARDURA N10 from Momentive Specialty Chemicals, Inc.

In some embodiments, the first part of the two-part composition comprises at least one reactive diluent having at least one glycidyl ether terminal portion, and preferably, a saturated or unsaturated cyclic backbone.

In some embodiments, the first part comprises at least 1, 2, 3, 4, or 5 wt-% and typically no greater than 15 or 20 wt-% of reactive diluents such as aliphatic glycidyl epoxy resins and/or cycloaliphatic epoxides.

Blends of various epoxy-containing materials can also be utilized. Suitable blends can include two or more weight average molecular weight distributions of epoxy- containing compounds such as low molecular weight epoxides (e.g., having a weight average molecular weight below 200 g/mole), intermediate molecular weight epoxides (e.g., having a weight average molecular weight in the range of about 200 to 1000 g/mole), and higher molecular weight epoxides (e.g., having a weight average molecular weight above about 1000 g/mole). Alternatively or additionally, the epoxy resin can contain a blend of epoxy-containing materials having different chemical natures such as aliphatic and aromatic or different functionalities such as polar and nonpolar.

In some embodiments, the first part comprises a mixture of a bisphenol epoxy resin, a novolac epoxy resin, and an aromatic epoxy resin comprising at least two or three epoxide groups that is not a bisphenol (e.g. A) epoxy resin.

Epoxies are typically cured with stoichiometric or near-stoichiometric quantities of curative. In the case of two-part epoxy compositions, the second part comprises the curative, also referred to herein as the curing agent. The equivalent weight or epoxide number is used to calculate the amount of co-reactant (hardener) to use when curing epoxy resins. The epoxide number is the number of epoxide equivalents in 1 kg of resin (eq/kg); whereas the equivalent weight is the weight in grams of resin containing 1 mole equivalent of epoxide (g/mol).  $\text{Equivalent weight (g/mol)} = 1000 / \text{epoxide number (eq/kg)}$ . In favored embodiments, the concentration of (e.g. liquid) first curing agent is selected such that there are unreacted epoxy groups after curing at ambient temperature. Thus, the quantity of first curing agent is less than a stoichiometric quantity relative to the equivalent weight of epoxide. However, the epoxide groups are cured with stoichiometric or near-stoichiometric quantities relative to the total amount of curatives (e.g. first ambient temperature curing agent and second latent curing agent).

The concentration of first curing agent typically ranges from about 5 to 25 wt-% of the total composition but can vary depending on the number of epoxy-reactive groups of the first curing agent.

The second part of the two-part composition comprises at least two curing agents that (e.g. independently) react with epoxide groups of the epoxy resin. The first curing agent can be characterized as an ambient temperature curing agent since it reacts with the epoxide groups of the epoxy resin at ambient temperature. The second curing agent is a latent curing agent. Latent curing agent exhibit limited or no reactivity at ambient temperature, but react with epoxy resins at an activation temperature that is higher than ambient temperature.

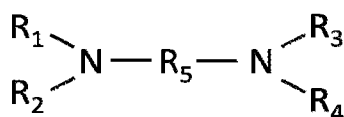
Common classes of curatives for epoxy resins include amines, amides, ureas, imidazoles, and thiols. In typical embodiments, the curing agent comprises reactive  $-NH$  groups or reactive  $-NR_1R_2$  groups wherein  $R_1$  and  $R_2$  are independently H or  $C_1$  to  $C_4$  alkyl, and most typically H or methyl.

The first curing agent that is highly reactive with the epoxide groups at ambient temperature. Such curing agents are typically a liquid at ambient temperature. However, the first curing agent can also be a solid provided it has an activation temperature at or below ambient temperature.

One class of curing agents are primary, secondary, and tertiary polyamines. The polyamine curing agent may be straight-chain, branched, or cyclic. In some favored embodiments, the polyamine crosslinker is aliphatic. Alternatively, aromatic polyamines can be utilized.

Useful polyamines are of the general formula  $R_5-(NR_1R_2)_x$  wherein  $R_1$  and  $R_2$  are independently H or alkyl,  $R_5$  is a polyvalent alkylene or arylene, and  $x$  is at least two. The alkyl groups of  $R_1$  and  $R_2$  are typically  $C_1$  to  $C_{18}$  alkyl, more typically  $C_1$  to  $C_4$  alkyl, and most typically methyl.  $R_1$  and  $R_2$  may be taken together to form a cyclic amine. In some embodiment  $x$  is two (i.e. diamine). In other embodiments,  $x$  is 3 (i.e. triamine). In yet other embodiments,  $x$  is 4.

Useful diamines may be represented by the general formula:



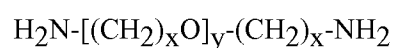
wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are independently H or alkyl, and  $R_5$  is a divalent alkylene or arylene. In some embodiments,  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are each H and the diamine is a primary amine. In other embodiments,  $R_1$  and  $R_4$  are each H and  $R_2$ , and  $R_3$  and  $R_4$  are each independently alkyl; and the diamine is a secondary amine. In yet other embodiments,  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are independently alkyl and the diamine is a tertiary amine. In some embodiments, primary amines are preferred.

Examples include hexamethylene diamine; 1,10-diaminodecane; 1,12-diaminododecane; 2-(4-aminophenyl)ethylamine; isophorone diamine; 4,4'-diaminodicyclohexylmethane; and 1,3-bis(aminomethyl)cyclohexane. Illustrative six member ring diamines include for example piperazine and 1,4-diazabicyclo[2.2.2]octane ("DABCO").

Other useful polyamines include polyamines having at least three amino groups, wherein the three amino groups are primary, secondary, or a combination thereof. Examples include 3,3'-diaminobenzidine and hexamethylene triamine.

In typical embodiments, the second part comprises a major amount of a first (e.g. primary amine) curing agent. In some embodiments, the amount of first (e.g. primary amine) curing agent is at least 20, 30 or 40 wt-% and typically no greater than 70, 60 or 50 wt-% of the second part. The ambient temperature cured epoxy resins typically comprises at least 5, 10 or 15 wt-% and no greater than 25 or 20 wt-% of reaction products derived from the first (e.g. primary amine) curing agent.

In some embodiments, the first curing agent is an unbranched polyetherdiamine as can be represented by the following formula:



where y is 1, 2, 3 or 4, more typically 2 or 3, and each x is independently selected from 2, 3, or 4, more typically 2 or 3. In some embodiments y is 2. In some embodiments y is 2 and each x is independently selected from 2 or 3. In some embodiments y is 3. In some embodiments y is 3 and each x is independently selected from 2 or 3. In some embodiments the primary amine is Jeffamine® D230 (wherein y is 1 and x is about 2.5).

Polymeric polyamines can also be utilized. One representative polymeric polyamine includes for example an epoxy-reactive (e.g. amine) terminated liquid rubber such as butadiene-acrylonitrile reactive liquid polymers, as available from Noveon under the trade designation Hycar™ ATBN". Such polymers can range in acrylonitrile content from 5 to about 30 wt-%. In some embodiments, the acrylonitrile content is less than 20 or 15 wt-%.

The second part may comprise more than one ambient temperature curing agent, i.e. a mixture of ambient temperature curing agents. Further, the ambient temperature epoxy curing reaction may be accelerated by addition of small quantities of accelerators. Tertiary amines, carboxylic acids and alcohols (especially phenols) are effective accelerators, as well as Bisphenol A.

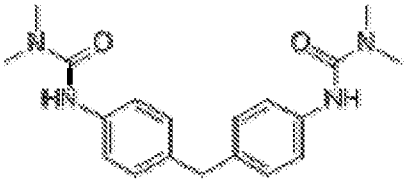
The second latent curing agent is also selected from classes of curatives for epoxy resins as previously described for the liquid curing agent. The latent curing agent comprises at least two epoxy-reactive groups that do not react with the epoxy resin at a temperature below the activation temperature of at least 50°C. In some embodiments, the latent curing agent comprises at least 3, 4, 5, and typically no greater than 6 epoxy-reactive groups. In typical embodiments, the latent curing agent comprises reactive -NH groups or reactive -NR<sub>1</sub>R<sub>2</sub> groups wherein R<sub>1</sub> and R<sub>2</sub> are independently H or C<sub>1</sub> to C<sub>4</sub> alkyl, and most typically H or methyl. The latent curing agent typically comprises epoxy-reactive groups such as an amine, amide (e.g. dicyandiamide or substituted dicyandiamide), urea (e.g. aromatic diurea), or imidazole.

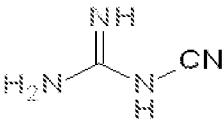
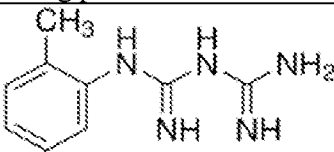
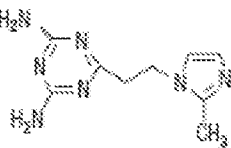
However, the second latent curing agent is a different compound than the liquid curing agent since the latent curing agent has an activation temperature greater than ambient temperature. Further, the

latent curing agent remains unactivated or in other words uncured after the two-part epoxy composition is cured at ambient temperature.

The activation temperature can be determined by combining the curing agent (at a concentration of 5 wt-%) with a standard epoxy resin (bisphenol A diglycidyl ether available as "EPON 828") and then determining the onset temperature of polymerization with Differential Scanning Calorimetry (DSC) from 25-300°C at a rate of 10°C/in. The activation temperature is generally selected based on the service temperature of the substrate or article being bonded. By service temperature, it is meant a temperature that the ambient temperature cured epoxy resin or substrate or article comprising such is typically exposed to or may be exposed to during normal usage of the substrate or article.

The activation temperature of the second latent curing agent is typically at least 5, 10, 15, 20, or 25 °C greater than the activation temperature of the ambient temperature curing agent. In some embodiments, the latent curing agent has an activation temperature of at least 50, 55, 60 °C. In other embodiments, the latent curing agent has an activation temperature of at least 65, 70, 75 or 80°C. In some embodiments, such as wherein the epoxy resin composition is used to bond a substrate for the aerospace industry, the latent curing agent has an activation temperature greater than 80°C, such as at least 85, 90, 100, 105, 110, 115 or 120°C. Further, the activation temperature is typically no greater than 150, 145, 140°C. However, for other embodiments, the activation temperature may be lower, for example no greater than 135, 130, 125, 120, 115, or 120 °C. In yet other embodiments, the activation temperature may be no greater than 115, 110, 105, 100, or 95°C. The following table lists various latent curing agents and their activation temperature.

| <u>Chemical Description</u>                                                                                                                                                          | <u>Minimum Activation Temp (°C)</u> | <u>Trade Designation Supplier</u>                               |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------|-----------------------------------------------------------------|
| 4,4 methylene bis(phenyl dimethyl urea)<br><br>melting point – 220-230°C                          | 120                                 | Omicure U52M<br>CVC Thermoset<br>Specialties,<br>Moorestown, NJ |
| <br>2,4-isocyanuric diamino-6[2'-methylimidazolyl]-(1') ethyl-s-triazine<br>melting point – 250°C | 120                                 | Curezol 2MA-OK<br>Shikoku Chemicals,<br>Japan                   |
|                                                                                                                                                                                      | 100                                 | Amicure CG1400                                                  |

|                                                                                                                                                                                   |     |                                                           |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|-----------------------------------------------------------|
| <br>dicyandiamide<br>melting point – 207-211°C                                                   |     | Air Products,<br>Allentown, PA                            |
| <br>1-o-tolylbiguanide<br>melting point – 143-145°C                                              | 80  | Aradur 2844<br>Huntsman<br>Chemical, The<br>Woodlands, TX |
| epoxy-amine adduct                                                                                                                                                                | 100 | Ancamine 2441<br>Air Products                             |
| 2-methylimidazole                                                                                                                                                                 | 130 | Imicure AMI-2<br>Air Products                             |
| <br>2,4-diamino-6-[2'-methyl imidazolyl-(1')]-ethyl-<br>s-triazine<br>Melting point – 247-251°C | 120 | Curezol 2MZ Azine<br>Shikoku Chemicals                    |
| <br>2-phenyl-4,5-dihydroxy methylimidazole<br>Melting point – 213-255°C                        | 120 | Curezol 2PHZ-S<br>Shikoku Chemicals                       |
| boron trichloride amine complex                                                                                                                                                   | 110 | Omicure BC120<br>CVC Thermoset<br>Specialties             |
| heterocyclic, substituted imidazole                                                                                                                                               | 80  | Aradur 3123<br>Air Products                               |

It is also contemplated to utilize a blend of latent curing agents having different activation temperatures. For example, the second part may comprise a latent curing agent with an activation temperature between 80°C and 120°C to improve the tensile strength at that particular temperature range and another latent curing agent with an activation temperature between 120 °C and 140°C to improve the tensile strength at that particular temperature range.

The second latent curing agent has an activation temperature that is no greater than its melting point. Typically the activation temperature is less than the melt point. Or in other words the latent curing agent has a melt point greater than the activation temperature. In some embodiments, the latent curing agent typically has a melt point of at least 30, 35, 40, 45, or 50°C. In some embodiments, the latent curing agent has a melt point of at least 55, 60, 65, 70, or 75°C. In some embodiments, the latent curing agent has a melt point of at least 80, 85, 90, 95 or 100°C. In other embodiments, the latent curing agent has a melt point of at least 105, 110, 115, 120 or 125°C. In some favored embodiments, the latent curing agent has a melt point of at least 105, 110, 115, 120 or 125°C. In other favored embodiments, the latent curing agent has a melt point of at least 130, 135, 140, 145 or 150°C. The melt point of the latent curing agent is typically no greater than 250-260°C.

The second part may comprise more than one ambient temperature curing agent and more than one latent curing agent. The concentration of latent curing agent is typically at least 0.005 or 0.01 wt-% ranging up to 5 wt-% of the total composition but can vary depending on the number of epoxy-reactive groups of the latent curing agent.

The second part may also comprise other epoxy-reactive components that are generally relatively higher molecular weight and hence are not considered curatives. For example, the second part may comprise an epoxy-reactive liquid rubber such as butadiene-acrylonitrile reactive liquid polymers. In some embodiments, the second part comprises at least 5, 10 or 15 wt-% and no greater than 35, 30 or 25 wt-% of epoxy-reactive liquid rubber such as butadiene-acrylonitrile reactive liquid polymers.

Alternatively, the first part may comprise an epoxy-functional liquid polymer at the concentrations just described. The total composition may comprise at least 2 or 3 wt-% and typically no greater than 15 or 20 wt-% reactive liquid rubber such as butadiene-acrylonitrile reactive liquid polymers.

The composition (i.e. the first or second part) may further comprise optional additives such as (e.g. silane-treated) fillers, anti-sag additives, thixotropes, processing aids, waxes, and UV stabilizers. Examples of typical fillers include glass bubbles, fumed silica, alumina, mica, feldspar, aluminum flake, and wollastonite.

In some embodiments, the curative typically comprises no particulate metal filler or additive. In some embodiments, the curative typically comprises no particulate aluminum or aluminum alloy filler or additive. In some embodiments the curative composition typically comprises no particulate iron, steel, or iron alloy filler or additive. In some embodiments the curative composition typically comprises no particulate copper or copper alloy filler or additive.

The two-part epoxy resin composition described herein is useful for method of bonding a substrate. Such method generally comprising providing an epoxy resin composition comprising a first liquid part; a second liquid part as described herein; applying the mixture such that it contacts at least one substrate; and curing the mixture below the activation temperature of the latent curing agent.

Although the (e.g. adhesive) composition may take many forms, the composition is typically provided as multipack or two-part adhesive systems where one package or part contains the epoxy resin

and a second package or part contains the curing agents. The two parts are mixed together at the time of use in order to initiate the reaction of the epoxy monomer with the curing agent having an activation temperature at or below ambient temperature. The typical means for dispensing the (e.g. adhesive) composition are two-chambered cartridges equipped with static mixers in the nozzle, and for larger scale application, meter mix dispensing equipment. After mixing the individual packages, one or both surfaces to be joined are coated with the mixed adhesive system and the surfaces are placed in contact with each other.

The mixture may be brushed, rolled, sprayed, dotted, knifed, cartridge-applied, especially from a dual cartridge; or otherwise applied to one substrate or both substrates to a desired thickness. The thickness can generally range from about 0.090 mm to 0.300 mm.

The epoxy resin gels at room temperature within 1-2 hours. The ambient temperature cure of the epoxy resin is typically complete in twenty-four to forty-eight hours and can be sanded or drilled 4 hours after application. In some embodiments, epoxy resin compositions as described herein will have about 3 hours pot life (time for positioning and adjusting) and may be cured at an accelerated rate with application of heat, typically curing 2 hours at temperature below the activation temperature of the latent curing agent. In contrast to the manner latent curing agents are typically utilized, the method of bonding described herein does not include heating the mixture to the activation temperature of the latent curing agent. Hence, the mixture comprises unreacted epoxy groups after curing at ambient temperature.

The adhesive generally provides effective initial bond strength at ambient temperature, thus heat is not required either for applying the adhesive systems to the substrates or for developing handling strength and dimensional stability. In some embodiments, the initial bond strength provided by the first ambient temperature curing agent is generally at least 3, 4, or 5 and in some embodiments at least 10 or 15 MPa. In some embodiments, the initial bond strength provided by the first ambient temperature curing agent is no greater than 35 or 30 MPa. The difference in bond strength that can be attributed to the inclusion of the latent curing agent can be on the order of magnitude of 2, 3, 4, 5, 6, 7, or 8 MPa.

The initial bond (i.e. tensile) strength can decrease at elevated temperatures, especially at elevated temperatures that are below the activation temperature of the second latent curing agent. Such decrease can be on the order of magnitude of 10, 20 or 30% of the initial bond strength at a temperature of about 80°C. However, the initial bond strength is typically in sufficient excess such that it can offset some decrease in bond strength, thereby continuing to provide effective bond strength at such an elevated temperature. When the bonded substrate lacks a latent curing agent, the initial bond strength can decrease by as much as 50, 55, or 60% at 120°C and in excess of 70% at 135°C. However, when the epoxy resin composition further comprises a latent curing agent as described herein, exposure to a temperature at the activation temperature of the latent curing agent can induce additional cross-linking. This secondary cross-linking contributed by the latent curing agent can offset the reduction in bond (i.e. tensile) strength.

The two-part epoxy resin composition described herein may be used to bond metal surfaces, such

as steel, aluminum and copper, to a variety of substrates, including metal (e.g. aluminum), polymers, fibers, composite materials glass, ceramics, wood, and the like. Composite material include for examples thermoplastic polymers and thermosetting resins further comprising high strength fibers such as carbon, graphite, boron, glass, aramid (available from Dupont under the trade designation Kevlar<sup>TM</sup>) or ceramic fibers. Thermosetting resins include for example polyester resin, vinyl ester resin, phenolic resin, epoxy resin, polybenzimidazole, and bismaleimide. In some embodiments, the composite material comprises bundles of individual fibers (i.e. filaments) referred to as tows, yarns, or rovings. Tightly woven fabrics are commonly utilized in composite materials of aerospace components.

In some embodiments, epoxy resin described herein is particularly suitable for aerospace (i.e. aircraft, spacecraft, satellites, and the like.) The primary uses in these industries include the bonding of structural metal and polymer-fiber composite materials. Epoxy resins have been used in the construction of aerospace components, the assembly of aerospace components as well as for the repair of such components. The epoxy resin described herein is particularly suitable for internal components of aircraft and may also be suitable for external components, depending on the requirements.

In the case of aircraft, the fuselage is the main structure or body of the aircraft to which all other units attach. A monocoque aircraft design relies largely on the strength of the skin or shell (covering) to carry the various loads. The reinforced shell has the shell reinforced by a complete framework of structural members. The cross sectional shape is derived from bulkheads, station webs, and rings. The longitudinal contour is developed with longerons, formers, and stringers. The skin (covering) which is mechanically fastened to all these members carries primarily the shear load and, together with the longitudinal members, the loads of tension and bending stresses. Station webs are built up assemblies located at intervals to carry concentrated loads and at points where fittings are used to attach external parts such as wings, landing gear, and engine mounts. Formers and stringers may be single pieces of built-up sections.

The semimonocoque fuselage is constructed primarily of aluminum alloy; however, on newer aircraft (e.g. graphite) epoxy composite materials are often used. Steel and titanium are found in areas subject to high temperatures. Primary bending loads are absorbed by the "longerons," which usually extend across several points of support. The longerons are supplemented by other longitudinal members, called "stringers." Stringers are lighter in weight and are used more extensively than longerons. The vertical structural members are referred to as "bulkheads, frames, and formers." These vertical members are grouped at intervals to carry concentrated loads and at points where fittings are used to attach other units, such as the wings, engines, and stabilizers.

The epoxy resin composition, described herein can also be used in the repair of various (e.g. aircraft or other aerospace) components. One repair technique that is commonly used involves adhesive bonding of a patch onto a damaged (e.g. metal or composite material) component. The patch typically comprises a composite material as previously. In this type of repair a first substrate, e.g. the aerospace component is bonded to a second substrate, e.g. the patch, with the epoxy resin described herein.

However, in other embodiments, the epoxy resin described herein may be applied to a damaged (e.g. aircraft) component to fill in and reinforce the damaged area. In this embodiment, the epoxy resin described herein may be applied to substrate, yet not bonded to a second substrate.

Although the present invention has been described with reference to particular embodiments, it should be recognized that these embodiments are merely illustrative of the principles of the present invention. Those of ordinary skill in the art will appreciate that the compositions, apparatus and methods of the present invention may be constructed and implemented in other ways and embodiments. The invention is further illustrated by the following examples.

## Examples:

### Test Methods

#### Forest Products Laboratory (FPL) Etched and Phosphoric Acid Anodized Aluminum Substrate

The aluminum substrates as described above were treated as follows before bonding:

- 1) soaking for 10 minutes in a caustic wash solution such as ISOPREP 44, available from Martin Aerospace, Los Angeles, CA, USA, at a temperature of  $160 \pm 10^\circ \text{F}$  ( $71^\circ \text{C}$ );
- 2) submerging the sheets (in a rack ) in tank of tap water for 10 minutes;
- 3) spray rinsing with tap water for 2-3 minutes;
- 4) soaking at  $150^\circ \text{F}$  ( $66^\circ \text{C}$ ) for 10 minutes in a tank of FPL etch (a hot solution of sulfuric acid, sodium dichromate, and aluminum, according to section 7 of the latest revision of ASTM D-2651, similar to the process described by Forest Products Laboratory of Madison, Wisconsin, USA; see *The Electrochemistry of the FPL (Forest Products Laboratory) Process and its Relationship to the Durability of Structural Adhesive Bonds*, A. V. Pocius, The Journal of Adhesion, Volume 39, Issue 2-3, 1992);
- 5) spray rinsing with tap water for 3-5 minutes;
- 6) drip drying for 10 minutes at ambient temperature and then for 30 minutes in a re-circulating air oven at  $150^\circ \text{F}$  ( $71^\circ \text{C}$ .)

In all cases, the panels were further treated as follows. The etched panels were anodized by immersion in phosphoric acid at  $22^\circ \text{C}$  with an applied voltage of 15 Volts for 20-25 minutes, followed by rinsing with tap water. With the wet sample surfaces approximately horizontal, the water film was observed to check for any “water breaks” where the surface developed unwetted regions, which would indicate surface contamination. This step was followed by air drying for 10 minutes at room temperature, then oven drying in a forced air oven at  $66^\circ \text{C}$  for 10 minutes. The resulting anodized aluminum panels were immediately primed within 24 hours of treatment. The anodized panels were primed with a corrosion inhibiting primer for aluminum (3M Scotch-Weld™ Structural Adhesive Primer EW-5000, available from 3M Company, St. Paul, Minnesota, USA) according to the manufacturer's instructions to give a dried primer thickness of between 0.00010 and 0.00020 inches (2.6 to 5.2 micrometers).

Generally, a strip of approximately 0.5 in (1.3 cm) x 0.15 mm of adhesive was applied to one edge of each of the two adherends (e.g. the panels) using a scraper. The bond was closed and taped on the edge. The bond was placed between sheets of aluminum foil and pieces of cardboard. Two 14 lb (6.4 kg) steel plates were used to apply pressure to provide for adhesive spreading. After the adhesive had been  
5 allowed to cure (as described in each Example), the large specimen was cut into 1 in (2.5 cm) wide smaller specimens, providing a 0.5 in<sup>2</sup> (3.2 cm<sup>2</sup>) bonded area. Five overlap shear specimens were obtained from each larger specimen. The bonds were tested to failure at various temperatures on a SINTECH Tensile Testing machine (MTS, Eden Prairie, Minnesota), using a crosshead displacement rate of 0.5 mm/min. The failure load was recorded. The lap width was measured with a Vernier caliper. The quoted  
10 lap shear strengths are calculated as (2 times the failure load)/(measured width). The average (mean) and standard deviation were calculated from the results of five tests. Adhesive peel was determined using the floating roller peel test (FRP) at room temperature. The samples were conditioned for a period at least 30 minutes at the specified elevated temperatures before testing.

**Components Utilized in the Examples**

|                                 |                                                                                                                                                                                                                                                      |
|---------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| MX-257                          | KANE ACE® MX-257 core-shell particle toughened diglycidyl ether of bisphenol-A epoxy resin containing 37.5 weight percent butadiene- acrylic co-polymer core shell rubber from Kaneka Texas Corporation, Pasadena, TX, USA.                          |
| DEN 431                         | a semi-solid epoxy novolac resin commercially available from Dow Chemicals, Midland, MI, as the trade designation “D.E.N. 431” (epoxide equivalent wt is 172-179 g/eq., viscosity 1100-1700 mPa/sec at 51.7°C)                                       |
| HELOXY 107                      | cyclohexane dimethanol diglycidyl ether available from Momentive, Columbus, Ohio.                                                                                                                                                                    |
| TACTIX 742                      | tris-(hydroxyl phenyl)methane-based epoxy available from Huntsman Chemicals, The Woodlands, TX, USA, as Tactix™ 742.                                                                                                                                 |
| HYCAR 1300X21                   | amine terminated butadiene-acrylonitrile liquid polymer available from Noveon (Wickliffe, Ohio) as “Hycar™ Reactive Liquid Polymer ATBN 100X21”                                                                                                      |
| AEROSIL R202                    | hydrophobic fumed silica available from Evonik (Parsippany, NJ)                                                                                                                                                                                      |
| QS-4                            | fused silica is available as SILICA ACE QS from MRC Unitec Inc. (Tokyo, Japan)                                                                                                                                                                       |
| ALUMINUM FLAKE                  | Aluminum 62450G flake Eckart America Corporation in Painesville, Ohio                                                                                                                                                                                |
| TITANIUM DIOXIDE                | primary particle diameter is greater than 100 nm, Kronos 2310 from Cranbury, NJ                                                                                                                                                                      |
| CARBON BLACK                    | Monarch 120 powder from Cabot, Billerica, MA                                                                                                                                                                                                         |
| EUROCELL                        | quartz free silica further comprising 17% alumina, 1% calcium, 5% potassium oxide and 3% sodium oxide (particle size is 5 – 140 µm) available from Europeri, Polten, Austria as the trade designation Eurocell™                                      |
| OMICURE U52                     | substituted urea accelerator comprised of 4,4' methylene bis(phenyl dimethyl urea) having melting point of 220-230°C obtained from CVC Thermoset Specialties (Moorestown, NJ)                                                                        |
| CUREZOL 2-MAOK                  | substituted imidazole accelerator comprised of diamino-6[2'-methylimidazolyl-(1'')]ethyl-s-triazine, 2,4-, isocyanurate having a molecular weight of 384 and a melting point of 250°C obtained from Air Products and Chemicals, Inc. (Allentown, PA) |
| Dicyanex™ 1400B<br>Curing Agent | curative comprised of micronized dicyandiamide containing 3% of inert flow control additive obtained from Air Products and Chemicals, Inc. (Allentown, PA) (having a melting point of 201-211°C and an activation temperature of about 120 °C)       |
| ARADUR 2844                     | a substituted dicyandiamide curing agent having a melting point of 139-143°C, 37 g/eq. (H), available from Huntsman, Chemicals, The Woodlands, TX, USA                                                                                               |
| JEFFAMINE D230                  | Jeffamine® D230, a polyetheramine from Huntsman Chemicals, The Woodlands, TX, USA                                                                                                                                                                    |
| ANCAMINE 2422                   | high functionality aliphatic amine (amine equivalent wt. (H) = 49, viscosity 2,000 mPa/sec at 25°C from Air Products (Allentown, PA)                                                                                                                 |
| GLASS BEADS<br>125 micron       | GL0191B4/125 were obtained from Mo-Sci Corporation (Rolla, MO), and were used to control the bond-line thickness of test specimens                                                                                                                   |

**Adhesive Preparation**

Part B was made by mixing the raw materials in order in the table above in a speed mixer and then degassed before adding to a 2:1 cartridge. For Part A, the amine-epoxy adducts were prepared by mixing 100 grams of EPON 828 + 180 g Ancamine D230 at 80°C for 1 h. To make the other adduct, we mixed 70 grams EPON 828 + 300 g Ancamine 2422 at 75°C for 1 h. The other materials were adding to the adducts in order and speed mixed. The mixture was degassed and then added into a 2:1 cartridge.

**First Part – Base**

| <b><u>Formula</u></b> | <b><u>Control<br/>(wt%)</u></b> | <b><u>% of<br/>total</u></b> |
|-----------------------|---------------------------------|------------------------------|
| MX257                 | 42.1                            | 28.1                         |
| DEN 431               | 10.2                            | 6.8                          |
| Heloxyl 107           | 7.1                             | 4.7                          |
| Aerosil R202          | 1.5                             | 1.0                          |
| Tactix 742            | 32.5                            | 21.7                         |
| QS-4 Fused Silica     | 6.1                             | 4.1                          |
| Titanium Dioxide      | 0.5                             | 0.3                          |

**Second Part – Curative**

| <b><u>Formula</u></b>  | <b><u>Control<br/>(wt%)</u></b> | <b><u>% of<br/>total</u></b> | <b><u>Ex. 1</u></b> | <b><u>Ex. 2</u></b> | <b><u>Ex. 3</u></b> | <b><u>Ex. 4</u></b> | <b><u>Ex. 5</u></b> | <b><u>Ex. 6</u></b> |
|------------------------|---------------------------------|------------------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| Ancamine 2422 adduct   | 16                              | 5.3                          | 16                  | 16                  | 16                  | 11                  | 16                  | 16                  |
| Jeffamine D230 adduct  | 48                              | 16.0                         | 48                  | 48                  | 48                  | 21                  | 48                  | 48                  |
| Hycar 1300X21          | 21                              | 7.0                          | 21                  | 21                  | 21                  | 10.5                | 21                  | 21                  |
| QS-4 Fused Silica      | 6                               | 2.0                          | 6                   | 6                   | 6                   | 3                   | 6                   | 6                   |
| Aerosil R202           | 1                               | 0.3                          | 1                   | 1                   | 1                   | 0.5                 | 1                   | 1                   |
| 125 micron glass beads | 1                               | 0.3                          | 1                   | 1                   | 1                   | 0.5                 | 1                   | 1                   |
| Eurocell               | 3                               | 1.0                          | 3                   | 3                   | 3                   | 0                   | 3                   | 3                   |
| Aluminum Flake         | 0                               | 0.0                          | 0                   | 0                   | 0                   | 0.5                 | 0                   | 0                   |
| Carbon Black           | 0.02                            | 0.0                          | 0.02                | 0.02                | 0.02                | 0.1                 | 0.02                | 0.02                |
| Omicure U52            | 0                               | 0.0                          | 0.5                 | 1                   | 0                   | 0                   | 0                   | 0                   |
| Aradur 2844            | 0                               | 0.0                          | 0                   | 0                   | 2                   | 1.5                 | 0                   | 0                   |
| Dicyanex™ 1400B        | 0                               | 0.0                          | 0                   | 0                   | 0                   | 0                   | 1                   | 0                   |
| Curezol 2MA-OK         | 0                               | 0.0                          | 0                   | 0                   | 0                   | 0                   | 0                   | 1                   |

The first part was combined with each of the second parts in a 2:1 ratio by volume of part 1 to part 2. The mixture was applied to the panels as previously described and cured for 2 hours at 80°C. The samples were then conditioned at various temperatures and the tensile strength was tested.

Average Strength on anodized aluminum (in psi)

| <b><u>Sample</u></b> | <b><u>OLS at 25°C</u></b> | <b><u>OLS at 80°C</u></b> | <b><u>OLS at 120°C</u></b> | <b><u>OLS at 135°C</u></b> |
|----------------------|---------------------------|---------------------------|----------------------------|----------------------------|
| Control              | 4395                      | 3140                      | 2033                       | 1225                       |
| U52M<br>Ex. 2        | 3950                      | 3225                      | 1983                       | 1874<br>(+649 psi, +53%)   |
| 2MA-OK<br>Ex. 6      | 4391                      | 3366                      | 2464<br>(+429 psi, +21%)   | 1672<br>(+447 psi, +36%)   |
| DICY<br>Ex. 5        | 4483                      | 3313                      | 2463<br>(+430 psi, +21%)   | 2298<br>(+1073 psi, +88%)  |

Average Strength on anodized aluminum (in MPa)

| <b><u>Sample</u></b> | <b><u>OLS at 25°C</u></b> | <b><u>OLS at 80°C</u></b> | <b><u>OLS at 120°C</u></b> | <b><u>OLS at 135°C</u></b> |
|----------------------|---------------------------|---------------------------|----------------------------|----------------------------|
| control 1            | 30                        | 22                        | 14                         | 8                          |
| U52M<br>Ex. 2        | 27                        | 22                        | 14                         | 13                         |
| 2MA-OK<br>Ex. 6      | 30                        | 23                        | 17                         | 12                         |
| DICY<br>Ex. 5        | 31                        | 23                        | 17                         | 16                         |

**Samples were cured for 7 days at 25°C**

Average Strength on anodized aluminum (in psi)

| <b><u>Sample</u></b> | <b><u>OLS at 25°C</u></b> | <b><u>OLS at 80°C</u></b> | <b><u>OLS at 120°C</u></b> | <b><u>OLS at 135°C</u></b> |
|----------------------|---------------------------|---------------------------|----------------------------|----------------------------|
| control 1            | 3829                      | 2826                      | 1549                       | 1253                       |
| U52M<br>Ex. 2        | 2535                      | 2576                      | 1767<br>(+218 psi, +14%)   | 1149                       |
| 2MA-OK<br>Ex. 6      | 3524                      | 2807                      | 2137<br>(+588 psi, +38%)   | 1791<br>(+538 psi, +43%)   |
| DICY<br>Ex. 5        | 4058                      | 2730                      | 2002<br>(+453 psi, +29%)   | 1727<br>(+474 psi, +38%)   |

Average Strength on anodized aluminum (in MPa)

| <b><u>Sample</u></b> | <b><u>OLS at 25°C</u></b> | <b><u>OLS at 80°C</u></b> | <b><u>OLS at 120°C</u></b> | <b><u>OLS at 135°C</u></b> |
|----------------------|---------------------------|---------------------------|----------------------------|----------------------------|
| control 1            | 26                        | 19                        | 11                         | 9                          |
| U52M<br>Ex.3         | 17                        | 18                        | 12                         | 8                          |
| 2MA-OK<br>Ex. 6      | 24                        | 19                        | 15                         | 12                         |
| DICY<br>Ex. 5        | 28                        | 19                        | 14                         | 12                         |

**What is claimed is:**

1. A method of bonding a substrate comprising

a) providing an epoxy resin composition comprising

a first liquid part comprising an epoxy resin; and

a second liquid part comprising a first curing agent having an activation temperature at or below 20-25°C and a second latent curing agent having an activation temperature greater than 25°C;

b) applying a mixture of the first and second parts such that it contacts at least one substrate; and

c) curing the mixture below the activation temperature of the latent curing agent.

2. The method of claim 1 wherein the latent curing agent has an activation temperature ranging from 50 °C to 150°C.

3. The method of claims 1-2 wherein the method does not include heating the mixture to the activation temperature of the latent curing agent.

4. The method of claims 1-3 wherein the mixture comprises unreacted epoxy groups after curing at 20-25°C.

5. The method of claims 1-4 wherein the latent curing agent comprises unreacted epoxy-reactive groups after curing at 20-25°C.

6. The method of claims 2-5 wherein the latent curing agent has a melt point of at least 60, 70, 80, 90, or 100 °C.

7. The method of claims 1-6 wherein the substrate is metal or a composite material, the composite material comprising a polymer and a fibrous material.

8. The method of claims 1-7 wherein the method is a method of repairing the substrate, a method of assembling a component comprising the substrate, or a method of constructing a component.

9. The method of claims 1-8 wherein the method comprises applying the mixture such that it contacts a first and second substrate.

10. The method of claims 1-9 wherein the substrate comprising the uncured latent curing agent is present in an aircraft or other aerospace article.

11. The method of claims 1-10 wherein the two-part epoxy resin is further characterized by claims 20-33.

12. An article comprising at least one first substrate bonded with an ambient temperature cured epoxy resin composition of claims 1-11.

5

13. An article comprising at least one first substrate bonded with a cured epoxy resin composition wherein the cured epoxy resin composition comprises an uncured latent curing agent having an activation temperature greater than 25°C.

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14. The article of claim 13 wherein the uncured latent curing agent has an activation temperature ranging from 80 °C to 150°C.

15. The article of claims 13-14 wherein cured epoxy resin composition comprises unreacted epoxy groups.

15

16. The article of claims 13-15 wherein the uncured latent curing agent has a melt point greater than the activation temperature.

20

17. The article of claims 13-16 wherein the substrate is metal or a composite material the composite material comprising a polymer and a fibrous material.

18. The article of claims 13-17 wherein the article comprising the uncured latent curing agent is present in an aircraft or other aerospace article.

25

19. The article of claims 13-18 wherein the article comprises a first substrate bonded to a second substrate with the cured epoxy resin.

20. The article of claims 13-19 wherein the epoxy resin composition is further characterized by claims 21-30.

30

21. A two-part epoxy resin composition comprising  
a first liquid part comprising an epoxy resin; and  
a second liquid part comprising first curing agent having an activation temperature at or below 20-25°C  
and a second latent curing agent having an activation temperature greater than 25°C.

35

22. The two-part epoxy resin composition of claim 21 wherein the latent curing agent has an activation temperature ranging from 50°C to 150°C.

23. The two-part epoxy resin composition of claims 21-22 wherein the latent curing agent has a melt point greater than the activation temperature.

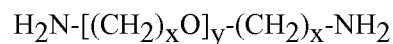
24. The two-part epoxy resin composition of claims 21-22 wherein the latent curing agent comprises at least two epoxy-reactive groups that do not react with the epoxy resin at a temperature below the activation temperature.

25. The two-part epoxy resin composition of claim 24 wherein the epoxy-reactive groups are selected from amine, amide, urea, imidazole, or a combination thereof.

26. The two-part epoxy resin composition of claims 21-25 wherein the latent curing agent is selected from dicyandiamide, substituted dicyandiamide, and an aromatic diurea.

27. The two-part epoxy resin composition of claims 21-26 wherein the first curing agent is a primary aliphatic amine.

28. The two-part epoxy resin composition of claim 27 wherein the first curing agent is a polyetherdiamine having the formula



where y is 1, 2, 3 or 4, and where each x is independently selected from 2, 3, or 4.

29. The two-part epoxy resin composition of claims 21-28 wherein the second part further comprises an epoxy-functional or the first part comprises an acid-functional rubber.

30. The two-part epoxy resin composition of claims 21-29 wherein the epoxy resin comprise a bisphenol epoxy resin, a novolac epoxy resin, or a mixture thereof.

## INTERNATIONAL SEARCH REPORT

International application No

PCT/US2014/067224

A. CLASSIFICATION OF SUBJECT MATTER  
 INV. C08G59/40 C08G59/56 C09J163/00  
 ADD.

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

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08G C09J

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         | US 4 146 700 A (WADDILL HAROLD G ET AL)<br>27 March 1979 (1979-03-27)<br>claims 1-20<br>example 3<br>column 6, lines 26-34         | 1-30                  |
| X         | US 4 147 857 A (WADDILL HAROLD G ET AL)<br>3 April 1979 (1979-04-03)<br>claims 1-19<br>example 2                                   | 1-30                  |
| Y         | EP 1 174 481 A2 (ILLINOIS TOOL WORKS [US])<br>23 January 2002 (2002-01-23)<br>claims 1-12<br>paragraphs [0021] - [0026]<br>table 1 | 2-30                  |
|           | -----<br>-/-                                                                                                                       |                       |



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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

13 February 2015

Date of mailing of the international search report

20/02/2015

Name and mailing address of the ISA/

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Authorized officer

Mensah, Laure

## INTERNATIONAL SEARCH REPORT

International application No

PCT/US2014/067224

| C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT |                                                                                                                     |                       |
|------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------|-----------------------|
| Category*                                            | Citation of document, with indication, where appropriate, of the relevant passages                                  | Relevant to claim No. |
| Y                                                    | EP 1 884 533 A2 (ZEPHYROS INC [US])<br>6 February 2008 (2008-02-06)<br>the whole document<br>-----                  | 2-30                  |
| A                                                    | US 4 766 186 A (SELLSTROM KATHY B [US] ET<br>AL) 23 August 1988 (1988-08-23)<br>claims 1-4<br>examples 1-6<br>----- | 1-30                  |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2014/067224

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s) | Publication<br>date                                                                                        |
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