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(54) **Title:** CURABLE COMPOSITIONS

(57) **Abstract:** A curable composition or system including (a) at least one divinylarene dioxide, (b) at least one polythiol compound curing agent; and (c) at least one catalyst; wherein the resulting curable composition may be cured at ambient conditions to provide durable cured material.



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CURABLE COMPOSITIONS

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to curable compositions and cured products made therefrom. More specifically, this invention relates to curable compositions utilizing a divinylarene dioxide such as divinylbenzene dioxide and a polythiol curing agent, wherein such curable compositions cure at a reasonable rate, and the cured products made from the curable compositions have good solvent resistance and good surface hardness properties. The compositions of the present invention may be useful, for example, for fabricating castings, composites, coatings and adhesives.

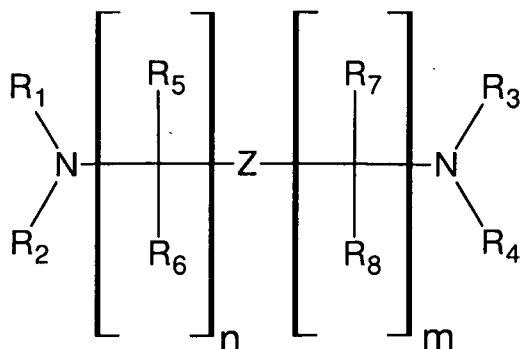
Description of Background and Related Art

Divinylarene dioxides are known to be cured with a variety of curing agents. For example, the curing of admixtures comprising divinylarene dioxides and polythiols is taught in U.S. Patent No. 2,927,580. As described in Chapter 15.5 of "Epoxy Resins" by Ha Q. Pham and Maurice J. Marks in *Ullmann's Encyclopedia of Industrial Chemistry*, the curing of epoxy resins with polythiols requires a tertiary amine catalyst. However, it has been found that the tertiary amine catalysts taught in U.S. Patent No. 2,927,580 are ineffective in divinylarene dioxide formulations.

Therefore, it would be desirable to prepare a curable composition comprising a divinylarene dioxide, a polythiol, and a catalyst which cures under ambient conditions (e.g., at a temperature of from about 20 °C to about 25 °C and at a pressure of about 1 bar) within about 24 hours of formulating the composition and applying composition to various substrates.

SUMMARY OF THE INVENTION

The present invention solves the problems of the prior art by providing a curable composition such as a curable epoxy resin composition comprising (a) at least one divinylarene dioxide, (b) at least one polythiol compound, and (c) at least one catalyst selected from catalysts containing a fragment corresponding to the following Formula I:

Formula I

wherein Z in the above structure may be selected from O, S, or a single bond; R₁ – R₄ may be selected from an alkyl or a cycloalkyl each individually having from 1 to about 20 carbon atoms; R₅ – R₈ may be selected from H, or an alkyl or a cycloalkyl, wherein the alkyl or cycloalkyl each individually having from 1 to about 20 carbon atoms; any of R₁ – R₈ may be bonded to form one or more rings; any of R₁ – R₈ may contain functional groups tolerant to tertiary amines such as an aryl, an alkenyl, or an alkynyl each individually having from 1 to about 20 carbon atoms, an ether, a thioether, a keto, an ester, a hydroxyl, a cyano, an imino, or a nitro; n may be an integer from 2 to 20; m may be an integer from 0 to 18; and m + n may be an integer of less than or equal to (≤) about 20. The remaining portion of the catalyst containing the above fragment of Formula I may be any organic radical having from 1 to about 20 carbon atoms and optionally bearing any one or more of the above functional groups tolerant to tertiary amines.

The composition of this invention advantageously cures under “ambient conditions” (defined herein below) within a predetermined period of time to give a non-tacky, solvent resistant cured article having good surface hardness.

One embodiment of the present invention is directed to a curable composition containing (a) at least one divinylarene dioxide, (b) at least one polythiol curing agent, and (c) at least one catalyst selected from catalysts compounds containing a fragment corresponding to Formula I above such that the resulting curable composition cures under ambient conditions within a predetermined amount of time such as for example within about 48 hours to provide materials having useful properties. The curable compositions of the present invention can be useful, for example, as shaped articles, coatings, composites, and adhesives.

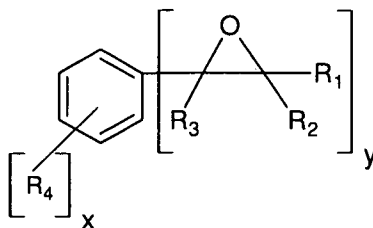
In one preferred embodiment of the present invention, a divinylarene dioxide such as for example divinylbenzene dioxide (DVBDO) may be used with a polythiol curing agent such as for example a polymercaptan or a polysulfide.

DETAILED DESCRIPTION OF THE INVENTION

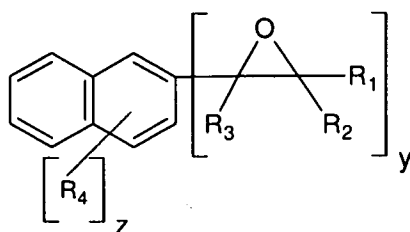
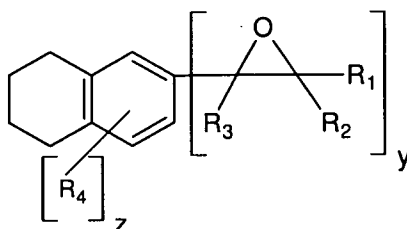
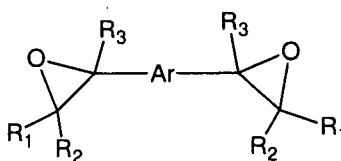
5 One broad aspect of the present invention includes a curable resin composition comprising (a) at least one divinylarene dioxide; (b) at least one polythiol curing agent; and (c) at least one catalyst selected from catalyst compounds containing a fragment corresponding to Formula I above; wherein the resulting curable composition is capable of being cured at ambient conditions to provide a cured product within a
10 predetermined amount of time for example within about 48 hours.

The divinylarene dioxide, component (a), useful in the present invention may comprise, for example, any substituted or unsubstituted arene nucleus bearing one or more vinyl groups in any ring position. For example, the arene portion of the divinylarene dioxide may consist of benzene, substituted benzenes, (substituted) ring-annulated benzenes
15 or homologically bonded (substituted) benzenes, or mixtures thereof. The divinylbenzene portion of the divinylarene dioxide may be *ortho*, *meta*, or *para* isomers or any mixture thereof. Additional substituents may consist of H₂O₂-resistant groups including for example a saturated alkyl or an aryl each individually having from 1 to about 20 carbon atoms, a halogen, a nitro, an isocyanate, or an RO- group wherein R may be a saturated alkyl or an
20 aryl each individually having from 1 to about 20 carbon atoms. Ring-annulated benzenes may consist of naphthalene, tetrahydronaphthalene, and the like. Homologously bonded (substituted) benzenes may consist of biphenyl, diphenylether, and the like.

The divinylarene dioxide used for preparing the composition of the present invention may be illustrated by general chemical Structures I-IV as follows:



Structure I

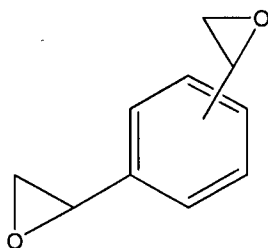
Structure IIStructure IIIStructure IV

- In the above Structures I, II, III, and IV of the divinylarene dioxide
- 10 comonomer of the present invention, each R_1 , R_2 , R_3 and R_4 individually may be hydrogen; an alkyl, a cycloalkyl, an aryl or an aralkyl group each individually having from 1 to about 20 carbon atoms; or a H_2O_2 -resistant group including for example a halogen, a nitro, an isocyanate, or an RO- group, wherein R may be an alkyl, an aryl or an aralkyl each individually having from 1 to about 20 carbon atoms; x may be an integer of 0 to 4; y may
- 15 be an integer greater than or equal to 2; x+y may be an integer less than or equal to 6; z may be an integer of 0 to 6; and z+y may be an integer less than or equal to 8; and Ar may be an arene fragment including for example, a 1,3-phenylene group. In addition, R_4 can be a reactive group(s) including for example an epoxide, an isocyanate, or any other reactive group; and Z can be an integer from 0 to 6 depending on the substitution pattern.

In one embodiment, the divinylarene dioxide used in the present invention may be for example a divinylarene dioxide produced, for example, by the process described in U.S. Patent Provisional Application Serial No. 61/141457, filed December 30, 2008, entitled "Process for Preparing Divinylarene Dioxides", by Marks et al., incorporated herein
5 by reference. Divinylarene dioxide compounds useful in the present invention are also disclosed, for example, in U.S. Patent No. 2,924,580, incorporated herein by reference.

In another embodiment, the divinylarene dioxide useful in the present invention may comprise, for example, divinylbenzene dioxide, divinyl-naphthalene dioxide, divinylbiphenyl dioxide, divinyl-diphenylether dioxide, or mixtures thereof.

10 In a preferred embodiment of the present invention, the divinylarene dioxide used in the epoxy resin formulation may be for example divinylbenzene dioxide (DVBDO). For example, divinylbenzene dioxide, as component (a), useful in the present invention may include a divinylbenzene dioxide as illustrated by the following chemical formula of Structure V:



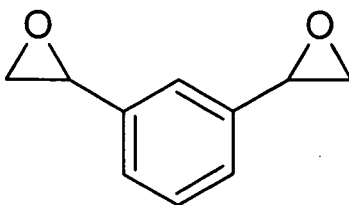
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Structure V

The chemical formula of the above DVBDO compound may be as follows: $C_{10}H_{10}O_2$; the molecular weight of the DVBDO is about 162.2; and the elemental analysis of the DVBDO is about: C, 74.06; H, 6.21; and O, 19.73 with an epoxide equivalent weight
20 of about 81 g/mol.

Divinylarene dioxides, particularly those derived from divinylbenzene such as for example DVBDO, are class of diepoxides which have a relatively low liquid viscosity but a higher rigidity and crosslink density than conventional epoxy resins.

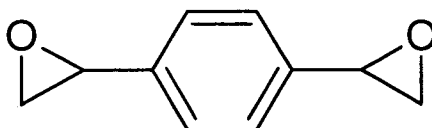
Structure VI below illustrates an embodiment of a preferred chemical
25 structure of the DVBDO useful in the present invention:



Structure VI

Structure VII below illustrates another embodiment of a preferred chemical structure of the DVBD0 useful in the present invention:

5



Structure VII

When DVBD0 is prepared by the processes known in the art, it may be possible to obtain one of three possible isomers: *ortho*, *meta*, and *para*. Accordingly, the present invention includes a DVBD0 illustrated by any one of the above Structures individually or as a mixture thereof. Structures VI and VII above show the *meta* (1,3-DVBD0) and *para* isomers of DVBD0, respectively. The *ortho* isomer is rare; and usually DVBD0 is mostly produced generally in a range of from about 9:1 to about 1:9 ratio of *meta* (Structure VI) to *para* (Structure VII) isomers. The present invention preferably includes as one embodiment a range of from about 6:1 to about 1:6 ratio of Structure VI to Structure VII, and in other embodiments the ratio of Structure VI to Structure VII may be from about 4:1 to about 1:4 or from about 2:1 to about 1:2.

In yet another embodiment of the present invention, the divinylarene dioxide may contain quantities [such as for example less than about 20 weight percent (wt %)] of substituted arenes. The amount and structure of the substituted arenes depend on the process used in the preparation of the divinylarene precursor to the divinylarene dioxide. For example, divinylbenzene prepared by the dehydrogenation of diethylbenzene (DEB) may contain quantities of ethylvinylbenzene (EVB) and DEB. Upon reaction with hydrogen peroxide, EVB produces ethylvinylbenzene monoxide while DEB remains unchanged. The presence of these compounds can increase the epoxide equivalent weight

of the divinylarene dioxide to a value greater than that of the pure compound but can be utilized at levels of 0 to 99 percent (%) of the epoxy resin portion.

In one embodiment, the divinylarene dioxide useful in the present invention comprises, for example, DVBDO, a low viscosity liquid epoxy resin. The viscosity of the divinylarene dioxide used in the process of the present invention ranges generally from
5 about 0.001 Pa s to about 0.1 Pa s in one embodiment, from about 0.01 Pa s to about 0.05 Pa s in another embodiment, and from about 0.01 Pa s to about 0.025 Pa s in yet another embodiment, at 25 °C.

The concentration of the divinylarene oxide used in the present invention as
10 the epoxy resin portion of the formulation may range generally from about 0.5 wt % to about 100 wt % in one embodiment, from about 1 wt % to about 99 wt % in another embodiment, from about 2 wt % to about 98 wt % in yet another embodiment, and from about 5 wt % to about 95 wt % in still another embodiment, depending on the fractions of the other formulation ingredients.

15 The divinylarene dioxide used in the present invention may be used as the sole epoxy resin component in the curable composition of the present invention; or the divinylarene dioxide may be used in combination with other epoxy resins known in the art such as epoxy resins described in Lee, H. and Neville, K., *Handbook of Epoxy Resins*, McGraw-Hill Book Company, New York, 1967, Chapter 2, pages 2-1 to 2-27, incorporated
20 herein by reference. Particularly suitable epoxy resins other than the divinylarene dioxide may include for example epoxy resins based on reaction products of polyfunctional alcohols, phenols, cycloaliphatic carboxylic acids, aromatic amines, or aminophenols with epichlorohydrin. A few non-limiting embodiments include, for example, bisphenol A diglycidyl ether, bisphenol F diglycidyl ether, resorcinol diglycidyl ether, and triglycidyl
25 ethers of para-aminophenols. Other suitable epoxy resins known in the art include for example reaction products of epichlorohydrin with o-cresol and, respectively, phenol novolacs. It is also possible to use a mixture of two or more other epoxy resins with the divinylarene dioxide. The other epoxy resin may also be selected from commercially available products such as for example, D.E.R. 331®, D.E.R.332, D.E.R. 334, D.E.R. 580,
30 D.E.N. 431, D.E.N. 438, D.E.R. 736, or D.E.R. 732 epoxy resins available from The Dow Chemical Company.

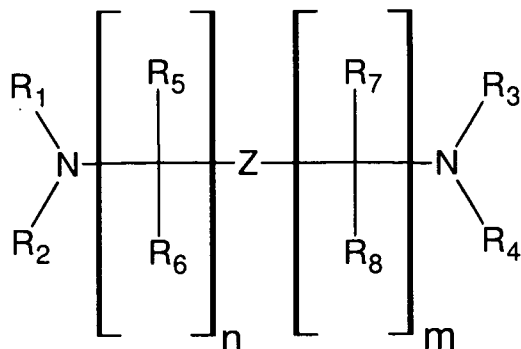
The concentration of total epoxy resin used in the formulation of the present invention may range from about 1 wt % to about 99 wt % in one embodiment, from about

2 wt % to about 98 wt % in another embodiment, from about 5 wt % to about 95 wt % in yet another embodiment, and from about 10 wt % to about 90 wt % in still another embodiment, depending on the fractions of the other formulation ingredients.

In the broadest scope of the present invention, any polythiol compound
5 containing at least one thiol (-SH) moiety can be used in the curable composition of the present invention. For example, in one embodiment of the polythiol compound, component (b), useful in the present invention may comprise, for example any organic compound bearing two or more thiol (-SH) groups. In one embodiment, the polythiol compound, component (b), useful in the present invention may comprise, for example any substituted or
10 unsubstituted alkyl or aromatic group each having from 1 to about 20 carbon atoms, bearing two or more thiol (-SH) moieties. Examples of polythiols useful in the present invention include polymercaptans such as Capcure 3-800, 40 SEC HV, and LOF commercially available from BASF, Inc.; polysulfides such as Thiokol LP-2, LP-3, LP-12, LP-31, LP-32, LP-33, LP-977, and LP-980 commercially available from Toray Fine Chemicals Co., Ltd.;
15 Thiocure PETMP, TMPMP, GDMP, and TMPMA commercially available from Bruno Bock Chemische Fabrik GmbH & Co. KG; Polymercaptan 358, 407, and 805C commercially available from Chevron Phillips Chemical Co. LLP; and mixtures thereof.

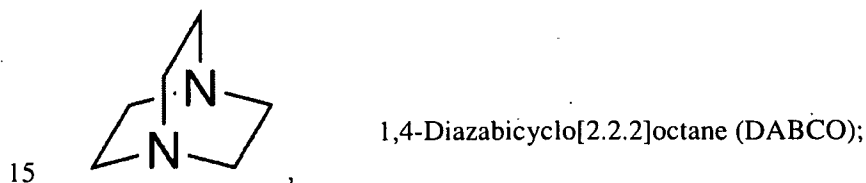
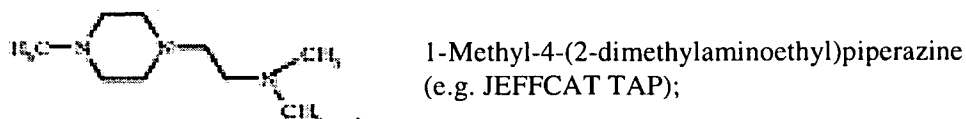
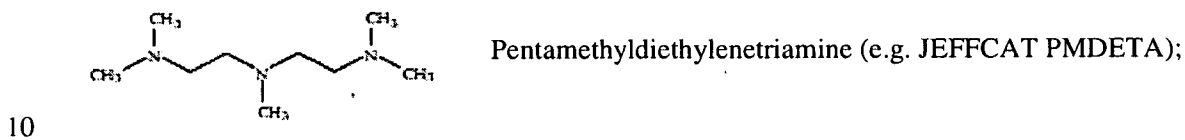
In general, the concentration of the polythiol compound used in the present invention as component (b) of the curable composition may range generally from about
20 1 wt % to about 99 wt % in one embodiment, from about 2 wt % to about 98 wt % in another embodiment, from about 5 wt % to about 95 wt % in yet another embodiment, and from about 10 wt % to about 90 wt % in still another embodiment.

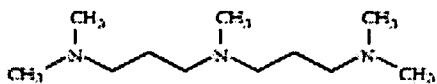
In the broadest scope of the present invention, the catalyst of the present invention may comprise any amine compound containing at least two nitrogen atoms
25 separated by two or more substituted or unsubstituted carbon atoms. For example, the catalyst useful in the present invention may include any compound which contains a fragment represented by the following chemical Formula I:

Formula I

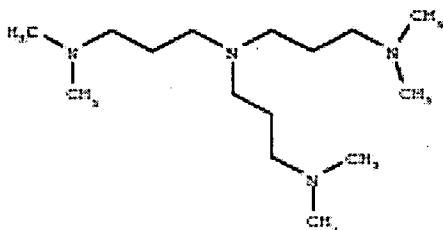
wherein Z, R₁ – R₈, n, m, and m + n are as defined above. The remaining portion of the catalyst containing the above fragment of Formula I may be any organic radical having
 5 from 1 to about 20 carbon atoms and optionally bearing any of the above defined functional groups tolerant to tertiary amines.

Suitable catalysts useful in the present invention may include for example one or more of the following catalysts:

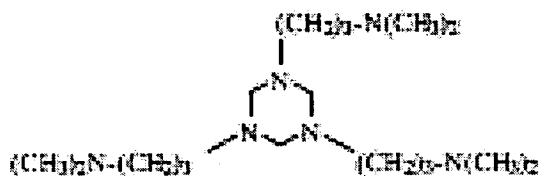




N,N,N',N'',N'''-Pentamethyldipropylenetriamine (e.g. JEFFCAT ZR-40);

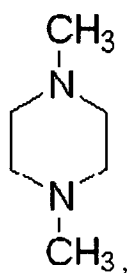


5 N,N,N'-Tris(3-dimethylaminopropyl)amine (e.g. JEFFCAT Z-80);



1,3,5-Tris(3-(dimethylamino)propyl)hexahydro-s-triazine (e.g. JEFFCAT TR-90);

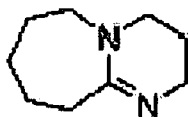
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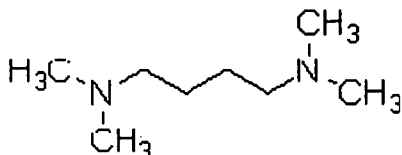
1,4-Dimethylpiperazine (e.g. JEFFCAT DMP);



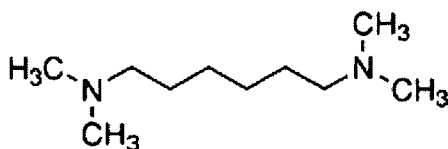
Bis(2-dimethylaminoethyl)ether (e.g. JEFFCAT ZF-20);



1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU);

*N,N,N',N'*-Tetramethyl-1,4-butanediamine (TMBD);

5

*N,N,N',N'*-Tetramethyl-1,6-hexanediamine;

and mixtures thereof.

The catalyst used in the present invention may be used for example as a single component or in combination with other catalysts known in the art. The concentration of catalyst used in the formulation of the present invention may range from about 0.01 wt % to about 20 wt % in one embodiment, from about 0.1 wt % to about 10 wt % in another embodiment, from about 1 wt % to about 10 wt % in yet another embodiment, and from about 2 wt % to about 10 wt % in still another embodiment depending, on the fractions of the other formulation ingredients.

Other optional components may be used in the curable composition of the present invention including for example curing agents (used as co-curing agents) other than the thiol compounds such as amines bearing active hydrogens; other thermoset resins such as epoxy resins described in the aforementioned *Handbook of Epoxy Resins* by Lee et al.; fillers such as clay, talc, silica, or calcium carbonate; solvents such as ethers or alcohols; toughening agents such as elastomers or liquid block copolymers; pigments such as carbon black or iron oxide; surfactants such as silicones; fibers such as fiberglass or carbon fiber; and mixtures two or more of the above optional components.

In general, the concentration of any one of the optional compounds used in the present invention composition may range generally from 0 wt % to about 90 wt % in

one embodiment, from about 0.01 wt % to about 80 wt % in another embodiment, from about 1 wt % to about 65 wt % in yet another embodiment, and from about 10 wt % to about 50 wt % in still another embodiment.

The preparation of the curable resin composition of the present invention is achieved for example by admixing in a vessel the components of the present invention including a divinylarene dioxide, a polythiol curing agent, a catalyst, and any other optional components such as one or more of the aforementioned optional additives and/or a solvent; and then allowing the components to formulate into a curable resin composition. There is no criticality to the order of mixture, i.e., the components of the formulation or composition of the present invention may be admixed in any order to provide the thermosettable or curable composition of the present invention. Any of the above-mentioned optional assorted formulation additives, for example fillers, may also be added to the composition during the mixing or prior to the mixing to form the composition. In some instances it may be preferable to dissolve the catalyst into either the epoxy resin component or into the polythiol component prior to combining with the other formulation components. By this approach solutions of catalysts in either the epoxy or the polythiol component can be prepared using elevated temperatures without concern of premature reaction of the formulation.

The components for preparing the curable composition are typically mixed and homogeneously dispersed at a temperature enabling the preparation of an effective resin composition having a viscosity for the desired application. In one embodiment, the temperature during the mixing of the components may be generally from about 0 °C to about 100 °C and from about 20 °C to about 50 °C in another embodiment. In one preferred embodiment, the divinylarene dioxide, the polythiol compound, the catalyst, and optional components may be mixed at a temperature of from about 20 °C to about 50 °C. At temperatures below the aforementioned ranges, the viscosity of the formulation can become excessive, while at temperatures above the aforementioned ranges, the formulation can react prematurely.

The curable resin composition of the present invention described above, have improved cure rates compared to known compositions in the art. For example, the cure rate of the compositions of the present invention provides non-liquid, tack-free, and solvent resistant cured materials within a predetermined period of time such as for example within about 48 hours in one embodiment, within about 24 hours in another embodiment, and

within about 18 hours in yet another embodiment; wherein the predetermined period of time is the time of preparing the formulation, applying the formulation to a substrate, and exposing the formulation to ambient conditions.

5 The divinylarene dioxide such as DVBDO, component (a) of the present invention, may be used as the sole epoxy resin to form the resin matrix in the final formulation; or the divinylarene dioxide resin may be used in combination with another thermoset resin such as an additional conventional epoxy resin as one of the components in the final formulation.

10 One of the advantages of the curable composition of the present invention includes the ability to cure the composition at ambient conditions. By "ambient conditions" as used herein with reference to a composition of the present invention, it is meant that the composition can be cured at a temperature of from about 0 °C to about 50 °C and at a pressure of about 1 bar. In one preferred embodiment, the composition may be cured at room temperature (about 25 °C).

15 In one embodiment, the curable resin composition may be cured at a predetermined temperature and for a predetermined period of time sufficient to partially cure or completely cure the composition. For example, the temperature of curing the formulation may be generally from about 0 °C to about 50 °C in one embodiment; from about 10 °C to about 40 °C in another embodiment; and from about 20 °C to about 30 °C in yet another embodiment; and the curing time may be chosen between about 0.01 hour to about 48 hours in one embodiment, between about 1 hour to about 24 hours in another embodiment, and between about 1 hour to about 18 hours in yet another embodiment. Below a period of time of about 0.01 hour, the time may be too short to ensure sufficient reaction under conventional processing conditions; and above about 48 hours, the time may be too long to be practical or economical.

25 The curing process of the present invention may be a batch or a continuous process. The reactor used in the process may be any reactor and ancillary equipment well known to those skilled in the art.

30 The process to produce a thermoset product from the curable composition of the present invention may include for example gravity casting, vacuum casting, automatic pressure gelation (APG), vacuum pressure gelation (VPG), infusion, filament winding, lay up injection, transfer molding, prepregging, dipping, coating, spraying, brushing, and the like.

The resulting cured composition upon curing the curable composition displays excellent properties, such as resistance to organic solvents and surface hardness. The properties of the cured compositions of the present invention may depend on the nature of the components of the curable formulation. In one preferred embodiment, the cured compositions of the present invention show no marring after about 100 double-rubs of a cotton-tipped applicator soaked in methylethyl ketone. Also, in one preferred embodiment, the cured compositions of the present invention exhibit a Shore A hardness value of from about 5 to about 100, from about 10 to about 100 in another embodiment, and from about 20 to about 100 in yet another embodiment.

The curable composition of the present invention may be used in applications where conventional epoxy resins are used such as in the field of coatings, films, adhesives, encapsulations, castings, composites, laminates, electronics, electrical laminates, insulation, civil engineering and construction; and the like. In one embodiment, for example, the cured composition of the present invention may be useful for ambient cured coatings and adhesives.

EXAMPLES

The following examples and comparative examples further illustrate the present invention in detail but are not to be construed to limit the scope thereof.

In the following Examples, various terms and designations used such as: “DVBDO” stands for divinylbenzene dioxide. The DVBDO used in the Examples is a divinylbenzene dioxide having an epoxide equivalent weight of 81 g/eq.

Polymercaptan 358 is a mercaptanized soybean oil (MSO) having a thiol equivalent weight of 354 g/eq.

Jeffcat™ products are amine catalysts which are commercially available from Huntsman Performance Products; and Jeffcat™ is a trademark of Huntsman.

In the following Examples, standard analytical equipment and methods are used such as for example:

Shore A hardness was determined using ASTM D2240 with a Shore A durometer from Shore-Instron, Inc.

“Tack-free” means that the cured formulation is non-tacky as determined by the absence of sticking or removal of material from the surface of the cured formulation by manual pressing with a wooden stick.

Examples 1–11: Ambient Cure Catalysts for DVBDO and Polymercaptan 358

5 To a 20 mL vial were added 1.0 g of DVBDO, 4.0 g of Polymercaptan 358 (epoxide/thiol equivalent ratio of 1.1) and 0.1 g of amine catalyst. The resulting formulation mixture was mixed for 1 minute, poured into a 5.1 cm aluminum dish, and allowed to cure for 18 hours at ambient temperature (20 – 25 °C) to form a tack-free, flexible solid. The amine catalyst used in Examples 1-11 are listed in Table I. In addition,
10 the Shore A hardness values of the resultant cured materials are also listed in Table I.

 In Examples 1-11, the DVBDO-catalyst mixture was heated to 50 °C for 5 minutes to dissolve the catalyst and then the mixture was allowed to cool to about 30 °C. The cooled DVBDO-catalyst mixture was added to MSO (a thiol compound) and the two were mixed together. The resultant formulation mixture was poured into the aluminum dish
15 as described above to cure. Each cured sample material of Examples 1-11 was tack-free and showed no marring after 100 double-rubs with a cotton-typed applicator soaked in methylethyl ketone.

Table I – Catalysts for Shore A Hardness of DVBDO-MSO Cured Compositions.

Example	Amine Catalyst	Shore A Hardness
1	1,4-diazabicyclo[2.2.2]octane (DABCO)	62
2	N,N,N',N'',N'''-pentamethyldiethylenetriamine (Jeffcat PMDETA)	50
3	1,4-dimethylpiperazine (Jeffcat DMP)	35
4	1-methyl-4-(2-dimethylaminoethyl)piperazine (Jeffcat TAP)	48
5	bis-(2-dimethylaminoethyl)ether (Jeffcat ZF-20)	54
6	N,N,N',N'',N'''-pentamethyldipropylenetriamine (Jeffcat ZR-40)	53
7	N,N,N,-tris-(3-dimethylaminopropyl)amine (Jeffcat Z-80)	57
8	1,3,5-tris(3-(dimethylamino)propyl)hexahydro-s-triazine (Jeffcat TR-90)	57
9	1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)	48
10	N,N,N',N'-tetramethyl-1,4-butanediamine (TMBD)	47
11	N,N,N',N'-tetramethyl-1,6-hexanediamine (TMHD)	54

5

Comparative Examples A – I Ambient Cure Non-Catalysts for DVBDO and Polymercaptan
358

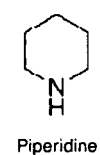
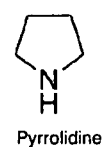
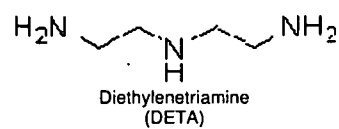
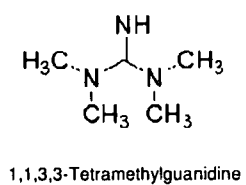
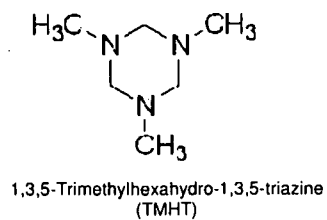
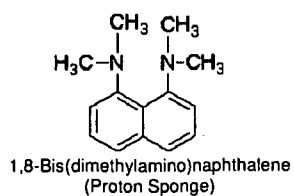
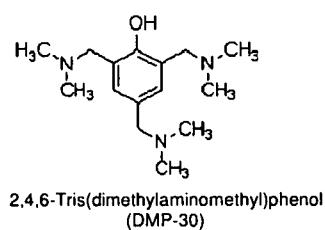
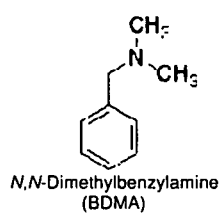
The amines listed in Table II were evaluated as described for

- 10 Examples 1 – 11. After 18 hours at ambient temperature, the formulations of Comparative Examples A – I remained liquids and did not cure.

Table II – Non-Catalysts for DVBDO-MSO Formulations

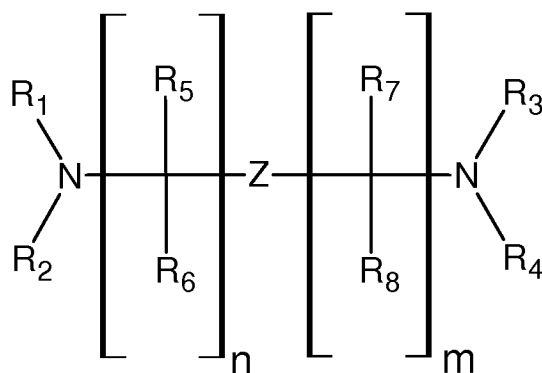
Comparative Example	Amine Non-Catalyst
A	triethylamine
B	N,N-dimethylbenzylamine (BDMA)
C	2,4,6-tris(dimethylaminomethyl)phenol (DMP-30)
D	1,8-bis(dimethylamino)naphthalene
E	1,1,3,3-tetramethylguanidine
F	1,3,5-trimethylhexahydro-1,3,5-triazine
G	diethylenetriamine
H	pyrrolidine
I	piperidine

5 The chemical structures and the chemical names of the non-catalysts used in the above Comparative Examples A – I shown in Table II are as follows:



WHAT IS CLAIMED IS:

1. A curable composition comprising (a) at least one divinylarene dioxide; (b) at least one polythiol compound curing agent; and (c) at least one catalyst; wherein the curable composition is capable of being cured at ambient conditions.
- 5 2. The curable composition of claim 1, wherein the at least one divinylarene dioxide comprises divinylbenzene dioxide.
3. The curable composition of claim 1, wherein the concentration of the at least one divinylarene dioxide comprises from about 1 weight percent to about 99 weight percent.
- 10 4. The curable composition of claim 1, wherein the at least one polythiol compound curing agent comprises a compound containing at least one thiol moiety.
5. The curable composition of claim 1, wherein the concentration of the at least one polythiol compound curing agent comprises from about 99 weight percent to
15 about 1 weight percent.
6. The curable composition of claim 1, wherein the at least one catalyst comprises one or more compounds containing a fragment of the following Formula I:



20

Formula I

wherein Z in the above structure of Formula I comprises O, S, or a single bond; R₁ – R₄ comprises an alkyl or a cycloalkyl each individually having from 1 to about 20 carbon atoms; R₅ – R₈ each individually comprises H, or an alkyl or a cycloalkyl, wherein the alkyl or cycloalkyl each individually having from 1 to about 20 carbon atoms; n comprises an

integer from 2 to 20; m comprises an integer from 0 to 18; and m + n comprises an integer of less than or equal to about 20; and wherein the remaining portion of the catalyst containing the above fragment of Formula I comprises an organic radical having from 1 to about 20 carbon atoms.

5 7. The curable composition of claim 6, wherein n comprises an integer of 2 up to less than or equal to 10; m comprises an integer of 0 up to about 8; and wherein m + n comprises an integer of less than or equal to about 18.

 8. The curable composition of claim 6, wherein n comprises an integer of 2 up to less than or equal to 6; m comprises an integer of 0 up to about 4; and m + n
10 comprises an integer of less than or equal to about 6.

 9. The curable composition of claim 6, wherein the curing catalyst comprises 1,4-diazabicyclo[2.2.2]octane; N,N,N',N'',N'''-pentamethyldiethylenetriamine; 1,4-dimethylpiperazine; 1-methyl-4-(2-dimethylaminoethyl)piperazine; bis-(2-dimethylaminoethyl)ether; N,N,N',N'',N'''-pentamethyldipropylenetriamine;
15 N,N,N',-tris-(3-dimethylaminopropyl)amine; 1,3,5-tris(3-(dimethylamino)propyl)hexahydro-s-triazine; 1,8-diazabicyclo[5.4.0]undec-7-ene; N,N,N',N'-tetramethyl-1,4-butanediamine; N,N,N',N'-tetramethyl-1,6-hexanediamine; or mixtures thereof.

 10. The curable composition of claim 6, wherein the concentration of the curing catalyst comprises from about 0.01 weight percent to about 20 weight percent.

20 11. The curable composition of claim 1, including an epoxy resin other than the at least one divinylarene dioxide, an active hydrogen curing agent other than the at least one polythiol compound curing agent, a filler, a toughening agent, an adhesion promoter, or mixtures thereof.

 12. The curable composition of claim 1, wherein the composition is
25 capable of curing to a tack-free cured composition within about 48 hours at ambient conditions.

 13. The curable composition of claim 1, wherein the composition is capable of curing to a tack-free cured composition within about 24 hours at ambient conditions.

30 14. The curable composition of claim 1, wherein the composition is capable of curing to a tack-free cured composition within about 18 hours at ambient conditions.

15. A process for preparing a curable composition or system comprising admixing (a) at least one divinylarene dioxide; (b) at least one polythiol compound curing agent; and (c) at least one catalyst; wherein the curable composition or system is capable of being cured at ambient conditions.
- 5 16. A process for preparing a curable composition or system comprising the steps of:
- (I) admixing at least one divinylarene dioxide and at least one catalyst to form a first solution; and
- (II) admixing the first solution of step (I) with at least one polythiol curing agent.
- 10 17. A process for preparing a curable composition or system comprising the steps of:
- (A) admixing at least one polythiol curing agent; and at least one catalyst to form a first solution; and
- (B) admixing the first solution of step (A) with at least one divinylarene dioxide.
- 15 18. A cured product comprising a cured composition of claim 1, wherein the cured product comprises a tack-free surface.
19. A cured product comprising a cured composition of claim 1, wherein the cured product comprises an un-marred surface after rubbing the surface with an organic solvent.
- 20 20. A cured product comprising a cured composition of claim 1, wherein the cured product comprises a Shore A hardness as determined by ASTM D2240 of from about 5 to about 100.
- 25 21. A process for preparing a thermoset product comprising the steps of:
- (i) preparing a curable composition comprising admixing (a) at least one divinylarene dioxide; (b) at least one polythiol compound curing agent; and (c) at least one catalyst; wherein the curable composition is capable of being cured at ambient conditions; and
- 30 (ii) curing the curable composition at ambient conditions.

22. The process of claim 21, wherein the ambient conditions include a temperature of from about 0 °C to about 50 °C.

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2011/056858

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08G59/66 C08L63/00 C08G59/02
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08G C08L

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 practical, search terms used)

EP0-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2 982 752 A (BENJAMIN PHILLIPS ET AL) 2 May 1961 (1961-05-02) column 9, lines 2-3,29 -----	1-22
Y	WO 2010/043638 A2 (BASF SE [DE]; TRAUT ALEXANDER [DE]; WAGNER NORBERT [DE]; FECHTENKOETTE) 22 April 2010 (2010-04-22) pages 11-13; claims 8,11 -----	1-22
Y	US 2 924 580 A (BENJAMIN PHILLIPS ET AL) 9 February 1960 (1960-02-09) cited in the application column 6, line 22; claims -----	1-22
A	WO 2010/077485 A1 (DOW GLOBAL TECHNOLOGIES INC [US]; MARKS MAURICE J [US]; HUNTER GARY A) 8 July 2010 (2010-07-08) claims; examples ----- -/--	1-22

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

☒ See patent family annex.

* Special categories of cited documents :

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

12 January 2012

Date of mailing of the international search report

31/01/2012

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INTERNATIONAL SEARCH REPORT

International application No

PCT/US2011/056858

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	EP 2 402 395 A2 (DOW GLOBAL TECHNOLOGIES LLC [US]) 4 January 2012 (2012-01-04) paragraph [0039]; claims 10,11 -----	1-22

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2011/056858

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W0 2010077485	A1	08-07-2010	CA 2744063 A1 08-07-2010
			CN 102209741 A 05-10-2011
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			US 2011315916 A1 29-12-2011
