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(54) **Title**: CURABLE EPOXY RESIN COMPOSITIONS

(57) **Abstract**: A curable resin composition comprising an epoxy resin, an epoxy diluent, and a hardener compound; a process for preparing the curable resin composition; and the use of the above curable epoxy resin composition in coating applications.

# Curable Epoxy Resin Compositions

## FIELD OF THE INVENTION

The present invention relates to a curable resin composition and a process of preparing the same.

## INTRODUCTION

Epoxy resins have been widely used in coating applications such as corrosion resistant coatings. Due to the viscosity of epoxy resins, coating applicators have to deal with applicability (that is, sprayability or paintability) problems of epoxy coating compositions by adding one or more organic solvents. The organic solvents such as xylene significantly reduce the viscosity, but cause environmental concerns in the industries worldwide.

Attempts to lower the viscosity of the epoxy resins with less environmental concerns include the addition of non-reactive diluents including high boiling point alcohols and phenols with active hydrogens and reactive diluents with epoxy functionalities including glycidyl ethers or esters of mono or multifunctional alcohols such as cresol glycidyl ether and $C_{12}$-$C_{14}$ alkyl glycidyl ether to epoxy resin compositions. Unfortunately, adding these diluents usually increases the cost of coating compositions and compromises one or more properties of coatings made therefrom including, for example, glass transition temperature ($T_g$), adhesion, corrosion resistance, and hardness.

To solve the issue of decreased corrosion resistance associated with these conventional reactive diluents, mono-functional cardanol epoxy diluents made from the reaction of cardanol and epichlorohydrin have been used. Owing to their long alkyl chain on the meta-position of the phenolic ring, these mono-functional cardanol epoxy diluents may provide increased corrosion resistance compared to conventional reactive diluents. Due to the mono-functionality of such cardanol epoxy diluents, the loading of such diluents in coating formulations is limited. Otherwise, the glass transition temperature ($T_g$) of the obtained coatings will significantly decrease.

Therefore, it is desirable to provide a curable resin composition suitable for coating applications that is free from the challenges associated with conventional diluents. It is also desirable to provide a curable resin composition upon curing with better corrosion resistance than compositions comprising conventional diluents without significantly compromising $T_g$ of the cured composition.

## SUMMARY OF THE INVENTION

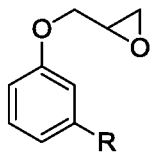
The present invention provides a novel curable resin composition that offers a solution to the problems described above. The curable resin composition has comparable viscosity as compared to resin compositions comprising the same dosage of conventional reactive diluents. The curable resin composition upon curing shows comparable or even higher $T_g$ and better corrosion resistance as compared to resin compositions containing the same dosage of conventional epoxy diluents upon curing.

In a first aspect, the present invention includes a curable resin composition comprising:

(a) an epoxy resin;

(b) an epoxy diluent, different from the epoxy resin of component (a); wherein the epoxy diluent has an epoxy functionality of from 1.1 to 1.6, and wherein the epoxy diluent comprises:

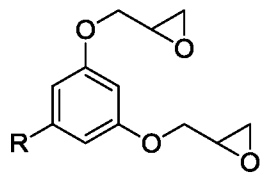
(b1) a first compound having the structure represented by Formula (I):




Formula (I),

wherein R is a straight-chain alkyl with 15 carbons containing 0 to 3 C=C bond(s) selected from $-C_{15}H_{31}$, $-C_{15}H_{29}$, $-C_{15}H_{27}$, and $-C_{15}H_{25}$; and

(b2) a second compound, different from the first compound of component (b1); wherein the second compound has the structure represented by Formula (II):




Formula (II),

wherein R is a straight-chain alkyl with 15 carbons containing 0 to 3 C=C bond(s) selected from $-C_{15}H_{31}$, $-C_{15}H_{29}$, $-C_{15}H_{27}$, and $-C_{15}H_{25}$; and

(c) a hardener compound.

In a second aspect, the present invention includes a curable resin composition comprising:

(a) an epoxy resin;

(b) an epoxy diluent, different from the epoxy resin of component (a); wherein the epoxy diluent has an epoxy functionality of from 1.1 to 1.6, and wherein the epoxy diluent is prepared by reacting an epihalohydrin with a cashew nutshell liquid comprising cardanol and cardol, and wherein the molar ratio of cardanol to cardol in the cashew nutshell liquid is from 9:1 to 4:6; and

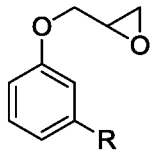
(c) a hardener compound.

In a third aspect, the present invention includes a process for preparing a curable epoxy resin composition of the first aspect. The process comprises admixing:

(a) an epoxy resin;

(b) an epoxy diluent, different from the epoxy resin of component (a); wherein the epoxy diluent has an epoxy functionality of from 1.1 to 1.6, and wherein the epoxy diluent comprises:

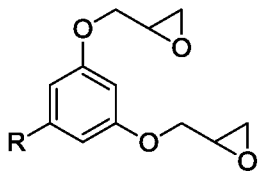
(b1) a first compound having the structure represented by Formula (I):



Formula (I),

wherein R is a straight-chain alkyl with 15 carbons containing 0 to 3 C=C bond(s) selected from $-C_{15}H_{31}$, $-C_{15}H_{29}$, $-C_{15}H_{27}$, and $-C_{15}H_{25}$; and

(b2) a second compound, different from the first compound of component (b1); wherein the second compound has the structure represented by Formula (II):



Formula (II),

wherein R is a straight-chain alkyl with 15 carbons containing 0 to 3 C=C bond(s) selected from $-C_{15}H_{31}$, $-C_{15}H_{29}$, $-C_{15}H_{27}$, and $-C_{15}H_{25}$; and

(c) a hardener compound.

In a fourth aspect, the present invention includes a method of preparing a coating, wherein the method comprises:

applying a curable resin composition of the first or second aspect to a substrate, and curing the curable resin composition to form a coating.

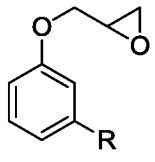
## DETAILED DESCRIPTION OF THE INVENTION

The curable resin composition of the present invention comprises (a) one or more epoxy resins. The epoxy resins, component (a), refer to epoxy compounds containing, on the average, one or more reactive oxirane groups and having a viscosity of 2,000 centipoises (cps) or higher, 5,000 cps or higher, or even 10,000 cps or higher, as measured at 25 °C by a Brookfield viscometer. The epoxy resins used in the curable resin composition can include a wide variety of epoxy compounds. For example, the epoxy compounds can be aliphatic, cycloaliphatic, aromatic, hetero-cyclic and mixtures thereof. Epoxy resins useful in the present invention may include, for example, mono-functional epoxy resins, multi- or poly-functional epoxy resins, and combinations thereof.

The epoxy resins useful in the present invention and the preparation of such epoxy resins are disclosed, for example, 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 herein by reference. Suitable epoxy resins may include, for example, bisphenol A or F epoxy resins, phenolic epoxy resins, polyphenolic epoxy resins, novolac epoxy resins, cresol epoxy resins, or mixtures thereof. In one embodiment, the epoxy resin used in the curable resin composition is a bisphenol A diglycydyl ether. Examples of commercially available epoxy resins that can be used in the present invention may include for example D.E.R.™ 331, D.E.N.™ 438, D.E.R. 671, and D.E.R. 852 epoxy resins, available from The Dow Chemical Company, and mixtures thereof (D.E.R. and D.E.N. are trademarks of The Dow Chemical Company).

Generally, the amount of the epoxy resin used in the present invention may be 50 weight percent (wt%) or more, 70 wt% or more, 80 wt% or more, or even 85 wt% or more, and at the same time, 95 wt% or less, 92.5 wt% or less, 90 wt% or less, or even 90 wt% or less, based on the total weight of the epoxy resin and the epoxy diluent in the curable resin composition.

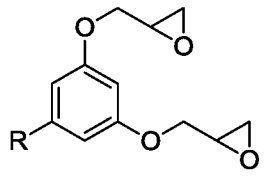
The curable resin composition of the present invention also comprises (b) an epoxy diluent, different from the epoxy resin of component (a). “Epoxy diluent” refers to a compound containing one or more reactive oxirane groups and having a viscosity of less than 1,000 cps as measured at 25 °C by a Brookfield viscometer. The epoxy diluent useful in the present invention comprises (b1) a first compound and (b2) a second compound. The first compound, component (b1), useful in the present invention may have the structure represented by Formula (I):



Formula (I),

wherein R is a straight-chain alkyl with 15 carbons containing 0 to 3 C=C bond(s) selected from $-C_{15}H_{31}$, $-C_{15}H_{29}$, $-C_{15}H_{27}$, and $-C_{15}H_{25}$.

The second compound, component (b2), different from the first compound of component (b1), useful in the present invention may have the structure represented by Formula (II):



Formula (II),

wherein R is a straight-chain alkyl with 15 carbons containing 0 to 3 C=C bond(s) selected from $-C_{15}H_{31}$, $-C_{15}H_{29}$, $-C_{15}H_{27}$, and $-C_{15}H_{25}$.

The total concentration of the first compound of Formula (I) and the second compound of Formula (II) is, based on the total weight of the epoxy diluent, from 90 wt% to 100 wt%, from 92 wt% to 99 wt%, from 95 wt% to 98 wt%, or from 96 wt% to 97 wt%.

The first compound of Formula (I) and the second compound of Formula (II) are present in a certain ratio to provide a desired epoxy functionality of the epoxy diluent. For example, the epoxy diluent used in the curable resin composition of the present invention may have an epoxy functionality of 1.1 or higher, 1.15 or higher, 1.2 or higher, or even 1.3 or higher, and at the same time, 1.6 or lower, 1.55 or lower, 1.5 or lower, or even 1.4 or lower.

The epoxy diluent in the curable resin composition of the present invention may further comprise from 0 to 10 wt% of glydicyl ethers of cardanol oligomers, glydicyl ethers of cardol oligomers, or mixtures thereof, from 1 wt% to 8 wt%, from 2 wt% to 5wt%, or from 3 wt% to 4 wt%, based on the total weight of the epoxy diluent.

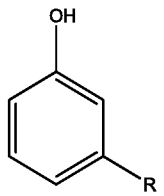
The total concentration of the epoxy diluent in the curable resin composition may be, based on the total weight of the epoxy diluent and the epoxy resin, from 5 wt% to 50 wt%, from 7.5 wt% to 30 wt%, from 10 wt% to 20 wt%, or from 10 wt% to 15 wt%.

The epoxy diluent useful in the present invention may be prepared by reacting an epihalohydrin with a cashew nutshell liquid (CNSL) comprising cardanol and cardol, for

example, through an epoxidation reaction. The epoxidation reaction may be conducted under conditions known in the art. The ratio of epihalohydrin equivalents to the total hydroxyl equivalents of the CNSL may range from 1:1 to 20:1, or from 3:1 to 8:1. One or more basic acting substances, for example, sodium hydroxide, may be employed in the reaction. One or more catalysts, for example, quaternary ammonium or phosphonium salts, may optionally be employed. One or more solvents, for example, isopropanol, may optionally be employed. The reaction may optionally be an azeotropic epoxidation wherein an epihalohydrin and water azeotrope is removed under vacuum during the reaction. The CNSL used in the reaction may comprise, based on the weight of the CNSL, from 90% to 100 wt% of cardol and cardanol, from 90 wt% to 100 wt%, from 92 wt% to 99 wt%, from 95 wt% to 98 wt%, or from 96 wt% to 97 wt%. The epihalohydrin used in reacting with the CNSL is preferably epichlorohydrin. In one embodiment, the epoxy diluent useful in the present invention comprises a reaction product of an epihalohydrin with the CNSL described above. The obtained epoxy diluent has the epoxy functionality as described above. In one preferred embodiment, the epoxy diluent is prepared by epoxidation the CNSL with the epihalohydrin, while no further distillation of the obtained reaction product is required to remove some or all of the first compound of Formula (I) and low boiling point impurities.

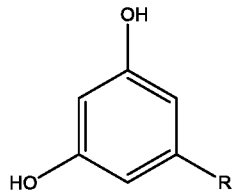
In one embodiment, the CNSL used in preparing the epoxy diluent comprise cardanol and cardol at a molar ratio of cardanol to cardol from 9:1 to 4:6, from 8:2 to 5:5, from 8.5:1.5 to 4.5: 5.5, or from 7:3 to 6:4.

The CNSL useful in the present invention comprises cardanol. Cardanol is a monohydroxyl phenol having a long hydrocarbon chain in the meta position. Cardanol useful in the present invention is one component of the CNSL, an oil isolated from the shell of the cashew nut. In general, the chemical structure of cardanol is a phenol containing one hydroxyl group in the para-position, and an aliphatic side chain of from 15 carbon atoms in the meta-position. Cardanol can be illustrated, for example, by the following structure:




wherein R is a straight-chain alkyl with 15 carbons containing 0 to 3 C=C bond(s) selected from $-C_{15}H_{31}$, $-C_{15}H_{29}$, $-C_{15}H_{27}$, and $-C_{15}H_{25}$.

The CNSL useful in the present invention also comprises cardol. Cardol can be illustrated, for example, by the following structure:




wherein R is a straight-chain alkyl with 15 carbons containing 0 to 3 C=C bond(s) selected from $-C_{15}H_{31}$, $-C_{15}H_{29}$, $-C_{15}H_{27}$, and $-C_{15}H_{25}$.

The CNSL useful in the present invention may further include minor amounts of other materials such as anacardic acid, oligomers of cardanol, oligomers of cardol, and mixtures thereof. Typically, the total concentration of the other materials present in the CNSL is < 10 wt %, less than 6 wt%, less than 5 wt%, less than 4 wt%, less than 3 wt%, less than 2 wt%, or even less than 1 wt%, based on the total weight of the CNSL.

The curable resin composition of the present invention also comprises one or more hardener compounds. The hardener compounds may be any conventional hardeners for epoxy resins. Conventional hardeners may be, for example, any amine or mercaptan with at least two epoxy reactive hydrogen atoms per molecule, anhydrides, phenolic compounds, or mixtures thereof. In one embodiment, the hardener compound is an amine where the nitrogen atoms are linked by divalent hydrocarbon groups that contain at least 2 carbon atoms per subunit, for example, aliphatic, cycloaliphatic or aromatic groups.

In one embodiment, the hardener compound is a polyamine containing from 2 to 6 amine nitrogen atoms per molecule, from 2 to 8 amine hydrogen atoms per molecule, and 2 to 50 carbon atoms. Suitable polyamines may include aliphatic polyamines including, for example, ethylene diamine, diethylenetriamine, triethylenetetramine; cycloaliphatic polyamines including, for example, isophoronediamine, 1,3-bis(aminomethyl)cyclohexane, isomeric mixtures of bis(4-aminocyclohexyl)methanes; bicyclic imines including, for example, 3-azabicyclo[3.3.1]non-2-ene; bicyclic diamines including, for example, 3-azabicyclo[3.3.1]nonan-2-amine; heterocyclic diamines including, for example, 3,4-diaminofuran, aminoethylpiperazine, and piperazine; polyamines containing amide linkages derived from “dimer acids” (dimerized fatty acids) which may be produced by condensing the dimer acids with ammonia and then optionally hydrogenating; adducts of suitable amines with epoxy resins, epichlorohydrin, acrylonitrile, acrylic monomers, ethylene oxide, and the like, including, for example, an adduct of isophoronediamine with a diglycidyl ether of a dihydric phenol; polyether amines; aromatic polyamines including, for example, 4,4’-methylenedianiline, 1,3-phenylenediamine and 3,5- diethyl-2,4-toluenediamine;

amidoamines including, for example, condensates of fatty acids with diethylenetriamine or triethylenetetramine; polyamides including, for example, condensates of dimer acids with diethylenetriamine, triethylenetetramine, or oligo(propylene oxide)diamine; and Mannich bases including, for example, the condensation products of a phenol, formaldehyde, and a polyamine or phenalkamines; or mixtures thereof. Mixtures of more than one diamine and/or polyamine can also be used. Primary monoamines may be included as chain extending agents. In one embodiment, polyamides are used as the hardener compound.

Generally, the stoichiometric ratio of total epoxy resins to the hardener compound in the curable resin composition may range from 0.5:1 to 1:0.5, from 0.7:1 to 1:0.7, from 0.8:1 to 1:0.8, or from 0.9:1 to 1:0.9.

A curing catalyst may be optionally added to the curable resin composition of the present invention to speed up the curing process of the resin composition. The curing catalyst may include quaternary ammonium and phosphonium salts such as tetraethylammonium chloride; phosphines; nitrate salts including, for example, calcium nitrate; and phosphites including, for example, triphenylphosphite or combinations thereof as described in U.S. Pat. Nos. 5,208,317, 5,109,099 and 4,981,926, phenolic compounds such as t-butylphenol, bisphenol A, salicylic acid and aminophenols such as 2,4,6-tris(dimethylamionomethyl) phenol and bis(dimethylaminomethyl) phenol; and mixtures thereof.

Generally, the amount of the curing catalyst used in the present invention may be, based on the total weight of the epoxy resin, the epoxy diluent, and the hardener compound, in the range of from 0 to 10 wt%, from 0.01 wt% to 5 wt%, or from 0.1 wt% to 3 wt%.

The curable resin composition of the present invention may optionally contain organic or inorganic pigments. The pigments may be ceramic materials; metallic materials metalloid materials; organic pigments including, for example, phthalocyanines or hollow core or void containing polymer pigments; or mixtures thereof. Suitable ceramic materials may include, for example, metal oxides including zinc oxide and titanium dioxide; metal nitrides including boron nitride; metal carbides; metal sulfides including molybdenum disulfide, tantalum disulfide, tungsten disulfide, and zinc sulfide; metal silicates including aluminum silicates and magnesium silicates such as vermiculite; metal borides; metal carbonates; and mixtures thereof. Generally, when pigments are included in the curable resin composition, the weight ratio of the pigments to the total weight of the epoxy resin, the epoxy diluent, and the hardener compound may range from 0.1:1 to 5:1, or up to 3:1. In

one embodiment, the concentration of the pigments may be in range of from zero to 10 wt%, based on the total weight of the curable resin composition.

The curable resin composition of the present invention may optionally include from 0 to 15 wt%, up to 10 wt%, or up to 5 wt% of solvents. Examples of suitable solvents include methylethylketone (MEK); xylene; n-butanol; toluene; glycols such as ethylene glycol, propylene glycol and butyl glycol; glycol ethers such as propylene glycol monomethyl ether and ethylene glycol dimethyl ether; or mixtures thereof.

The curable resin composition may further comprise one or more additional diluents. The additional diluents may include, for example, high boiling point alcohols and phenols with active hydrogens, additional reactive diluents with epoxy functionalities ("additional reactive diluent") that are different from the epoxy diluent described above, or mixtures thereof. Examples of suitable high boiling point alcohols and phenols include benzyl alcohol, furfuryl alcohol, nonyl phenol or mixtures thereof. The additional reactive diluents may be glycidyl ethers or esters of mono or multifunctional alcohols. Examples of the additional reactive diluents include cresol glycidyl ether; butyl glycidyl ether and $C_{12}$-$C_{14}$ aliphatic glycidyl ether; diglycidyl ethers such as butanediol diglycidyl ether, hexanediol diglycidyl ether, cyclohexanedimethanol diglycidyl ether, and polypropylene glycol diglycidyl ether; and triglycidyl ethers such as trimethylolpropane triglycidyl ether and glycerol triglycidyl ether; and mixtures thereof. The additional diluent may be present in an amount of from 0 to 10 wt%, from 0.5 wt% to 5 wt%, or from 1 wt% to 4 wt%, based on the total weight of the epoxy resins, the epoxy diluent, and the additional reactive diluent.

In one preferred embodiment, the curable resin composition is substantially free of the additional reactive diluent. "Substantially free of the additional reactive diluent" means that the concentration of the additional reactive diluent is zero wt % in one preferred embodiment and can be less than 1 wt% in another embodiment, less than 0.5 wt% in still another embodiment or even less than 0.1 wt% in yet another embodiment, based on the total weight of the epoxy resins, the epoxy diluent, and the additional reactive diluent.

In addition to the components described above, the curable resin composition of the present invention may be substantially free of, or further comprise any one or combination of the following additives: wetting agents, buffers, neutralizers, dispersants, humectants, mildewcides, biocides, anti-skinning agents, colorants, flowing agents, anti-oxidants, plasticizers, leveling agents, thixotropic agents, toughening agents, and adhesion promoters. These additives may be present in a combined amount of from 0 to 10 wt%, from 0.1 wt%

to 5 wt%, or from 0.5 wt% to 2 wt%, based on the total weight of the curable resin composition.

A process of preparing the curable resin composition of the present invention may comprise admixing the epoxy resin, the epoxy diluent, and the hardener compound. Other optional components may also be added as described above. Components in the curable resin composition may be mixed in any order to provide the curable resin composition of the present invention. Any of the above-mentioned optional components may also be added to the composition during the mixing or prior to the mixing to form the composition.

The curable resin composition of the present invention can be applied to, and adhered to, various substrates. Examples of substrates over which the curable resin composition may be applied include wood, concrete, metals such as steel and aluminum, composites, plastics, foams, elastomeric substrates, or substrates that are found on motor vehicles.

The curable resin composition of the present invention may be used in various applications, including for example, coatings, adhesives, electrical laminates, structural laminates, structural composites, filament windings, moldings, castings, encapsulations, pultrusion.

In one embodiment, the curable resin composition is a curable coating composition. The curable resin composition can be applied by conventional means including brushing, dipping, rolling and spraying to form a coating layer. The curable resin composition is preferably applied by spraying. The standard spray techniques and equipment for air spraying and electrostatic spraying, such as electrostatic bell application, and either manual or automatic methods can be used. The curable resin composition is suitable for various coating applications, such as marine coatings, protective coatings, automotive coatings, wood coatings, coil coatings, plastic coating, anticorrosive applications, and flooring and maintenance coating applications. The curable resin composition is suitable for use in factory and field applications such as coatings for use on substrates such as concrete, metal such as water towers or bridges, pipes, tanks, ships, machinery, heavy mass parts, ships, buildings under construction, bridges, and tanks. The curable resin composition may be used as a primer.

The curable resin composition of the present invention may have a comparable viscosity as compositions comprising the mono-functional cardanol epoxy diluent. For example, the viscosity of the curable resin composition of the present invention can be from

100 mPa·s to 20,000 mPa·s, from 200 mPa·s to 10,000 mPa·s, or from 400 mPa·s to 8,000 mPa·s. The viscosity may be measured by a Brookfield viscometer at 25ºC.

The curable resin composition of the present invention upon curing forms a cured product. The curable resin composition can be cured under conventional processing conditions to form a film, a coating, or a solid. Curing the resin composition of the present invention may be carried out at curing reaction conditions including a predetermined temperature and for a predetermined period of time sufficient to cure the composition. The curing conditions may be dependent on the various components used in the curable resin composition such as the hardener compound used in the formulation. The curing reaction conditions include, for example, carrying out the reaction under a temperature, generally in the range of from 0 °C to 200 °C, from 50 °C to 180 °C, or from 100 °C to 150 °C. The present invention also provides a method of preparing a coating, wherein the method comprises: applying the curable resin composition to a substrate, and curing the curable resin composition to form a coating.

The cured product made from the curable resin composition, can exhibit a combination and balance of advantageous properties including, for example, $T_g$ and corrosion resistance. For example, the cured product may advantageously have a $T_g$ in the range of between 50 °C and 150 °C, between 80 °C and 140 °C, or between 90 °C and 120 °C. The $T_g$ of the cured product can be measured for example by Differential Scanning Calorimetry. The cured product also shows better corrosion resistance than cured products made from compositions containing conventional reactive diluents, for example, mono-functional cardanol epoxy diluents. The corrosion resistance may be measured according to the test method described in the Example section below.

## 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. All parts and percentages are by weight unless otherwise indicated.

CNSL ("S6036"), available from Huada Saigao (Yantai) Technology Company Ltd., comprises 60 wt% of cardanol, 36 wt% of cardol and the rest (4 wt%) being oligomers as determined by Gas Chromatography (GC), based on the total weight of S6036.

D.E.R. 331 epoxy resin, available from The Dow Chemical Company, is a diglycidyl ether of bisphenol A (DGEBA) and has an epoxide equivalent weight (EEW) of from 182 to 192 grams per equivalent (g/eq).

D.E.H.™ 140 hardener, available from The Dow Chemical Company, is a polyamide hardener having an active hydrogen equivalent weight (HEW) of around 125 g/eq (D.E.H. is a trademark of The Dow Chemical Company).

CARDOLITE™ NC-513 ("NC-513"), available from Cardolite Company, is a mono-functional cardanol epoxy diluent and has an EEW of 395 g/eq.

The following standard analytical equipment and methods are used in the Examples.

Viscosity

Viscosity of an epoxy resin composition is tested at 25 °C by a Brookfield viscometer.

Glass Transition Temperature ($T_g$)

$T_g$ is measured by differential scanning calorimetry (DSC). Around 20 milligram (mg) sample is analyzed in an open aluminum pan on a TA Instrument DSC Q2000 fitted with an auto-sampler under nitrogen atmosphere. $T_g$ measurement by DSC is with 30-250 °C, 20 degree Celsius per minute (°C/min) (1st cycle), and 30-250 °C, 20 °C/min (2nd cycle). $T_g$ is obtained from the 2nd cycle. The $T_g$ values are determined by the method of half height.

Epoxide Equivalent Weight (EEW)

A standard titration method is used to determine percent epoxide in the various epoxy resins. A sample is weighed (ranging from about 0.1 g to about 0.2 g) and dissolved in dichloromethane (10 mL). Tetraethylammonium bromide solution in acetic acid (30 mL) is added to the sample. The resultant solution is treated with 3 drops of crystal violet solution (0.1 % w/v in acetic acid) and was titrated with 0.1N perchloric acid in acetic acid on a Metrohm 665 Dosimat titrator (Brinkmann). Titration of a blank sample comprising dichloromethane (10 mL) and tetraethylammonium bromide solution in acetic acid (30 mL) provided correction for solvent background. General methods for this titration are found in the scientific literature, for example, in Jay, R.R., "Direct Titration of Epoxy Compounds and Aziridines", Analytical Chemistry, 36, 3, pp 667-668 (March, 1964).

Gas Chromatography Analysis

By using 3-pentadecylphenol (PDP) as calibration standard, the quantification analysis of the concentration of components in CNSL samples is conducted by GC-FID. A standard solution is prepared as follows: about 0.2 grams of PDP is dissolved in about 8 grams of THF to give the PDP standard solution with a concentration of about 2.5 wt%. The resulting standard solution is filtered with 0.45 μm syringe filter before the GC injection.

About 0.2 grams of CNSL sample are diluted with about 8 grams of THF. 1 µl of the resulting CNSL solution is injected into the GC after filtered. The analysis is then conducted on Agilent 7890A equipped with FID. GC conditions are given below:

| | |
|---|---|
| Injection volume | 1.0 µL liquid |
| Instrument | Agilent 7890A with FID |
| Column | Rxi-50 (30m x 0.32 mm x 0.5 um) |
| Carrier gas | Helium |
| Inlet temperature | 280 °C |
| ratio | 20:1 |
| Column flow (constant) | 3.0 mL/min |
| Oven temperature | hold at 200 °C for 2 minutes, then heated at a rate of 5°C/min to 275 °C, and hold for 10 minutes. |
| Detector temperature | 280 °C |
| FID flow | $H_2$ = 40 mL/min; Air = 450 mL/min; $N_2$ = 45 mL/min |

Electrochemical Impedance Spectroscopy (EIS) Test

EIS test is used to measure the corrosion resistance of coatings. The coatings are prepared by spin coating an epoxy resin composition (25 wt% in methyl ethyl ketone) onto polished steel panels, which are then fully cured at 60 °C for 5 hours. The obtained coated steel panels have a dry film thickness of about 60 to 70 microns. The EIS test is then performed at room temperature (20-25 °C) in 3.5 wt% of NaCl solution using CHI604B electrochemical workstation (Shanghai Chenhua Instruments Inc., China) connected to a three-electrode cell including a working electrode, a reference electrode, and a counter electrode in a plastic cylinder. The plastic cylinder has a round hole with an area of 9.07 $cm^2$ in the center of the cylinder bottom. The hole is covered by the coated steel panel (used as the working electrode) by gluing and attaching the coated steel panel outside the cylinder bottom. The cylinder is then filled with NaCl solution. A saturated calomel electrode (SCE) and a platinum electrode are used as the reference electrode and the counter electrode, respectively. The EIS spectra are obtained at the Open Circuit Potential (OCP), with a perturbation amplitude of 10 mV and in the frequency range of from 100 kHz to 0.01 Hz. $C_c$ and $R_t$ values are then obtained. $C_c$ refers to the capacitance of a coating. $R_t$ refers to the charge-transfer resistance of a coating. The higher the value of $C_c$ and the lower the value of $R_t$, the better the corrosion resistance of the coating.

Synthesis of Epoxidized CNSL

A 5 L, 4-neck, round bottom glass reactor was charged with S-6036 CNSL (827.0

gram (g), 3.7 hydroxyl equivalent [eq.]), epichlorohydrin (1710.60 g, 18.48 moles, 5:1 epichlorohydrin:hydroxyl eq.), isopropanol (921.1 g, 35 wt % of epichlorohydrin used), and deionized (DI) water (148.8 g, 6 wt % of epichlorohydrin used) in the indicated order. The reactor was additionally equipped with a condenser (maintained at 0 °C), a thermometer, a Claisen adaptor, an overhead nitrogen inlet, and a stirrer. Sodium hydroxide solution (133.05 g, 3.33 moles dissolved in 532.2 g of DI water) was added to a side arm vented addition funnel. Stirring and heating commenced to give a 52 °C solution followed by dropwise addition of the sodium hydroxide solution. The reaction temperature was maintained at 52 °C during the 2.25 hours of aqueous sodium hydroxide addition time. After 20 minutes of post reaction at 52 °C, stirring and heating ceased, and the reactor contents were added to a pair of 2 L separatory funnels. The aqueous phase and a minor amount of dark colored insoluble material were drained off and discarded as waste and the remaining organic layer added back into the reactor.

Stirring and heating of the 44 °C solution resumed. Sodium hydroxide solution (59.13 g, 1.478 moles dissolved in 236.5 g of DI water) was added to a side arm vented addition funnel. Stirring and heating commenced to reestablish a 52 °C solution followed by commencement of dropwise addition of the sodium hydroxide solution. The reaction temperature was maintained at 52 °C during the 1 hr aqueous sodium hydroxide addition time. After 20 min of post reaction at 52 °C, stirring and heating ceased, and the reactor contents were added to a pair of 2 L separatory funnels. The aqueous phase and a minor amount of dark colored insoluble material were drained off and discarded as waste and the remaining organic layer added back into the reactor.

Stirring and heating of the 40 °C solution resumed. Sodium hydroxide solution (14.78 g, 0.37 moles dissolved in 59.1 g of DI water) was added to a side arm vented addition funnel. Stirring and heating commenced to reestablish a 52 °C solution followed by dropwise addition of the sodium hydroxide solution. The reaction temperature was maintained at 52 °C during the 15 min aqueous sodium hydroxide addition time. After 20 min of post reaction at 52 °C, stirring and heating ceased, and the reactor contents were equally split into a pair of 2 L separatory funnels. The aqueous phase was drained off and discarded as waste. The contents of each separatory funnel were washed by vigorously shaking with 400 mL of DI water. The washed product was allowed to settle for < 30 min to resolve the aqueous and organic phases then the aqueous phase was removed and discarded as waste. Second and third washes were completed using the aforementioned method.

Rotary evaporation of the organic phase using a maximum oil bath temperature of 110 °C to a final vacuum of 4.7 mm of Hg removed the bulk of the volatiles. A total of 971.96 g of amber colored, slightly hazy liquid was recovered after completion of the rotary evaporation. Normalized GC analysis revealed 56.67 area % monoglycidyl ethers of cardanol, 37.09 area % diglycidyl ethers of cardol, 1.89 area % as four minor components with retention times lower than that of the monoglycidyl ethers of cardanol, and 4.35 area % as four minor components with retention times between the monoglycidyl ethers of cardanol and the diglycidyl ethers of cardol ("S-6036 Epoxy"). Epoxide titration indicated an EEW of 290 g/eq.

Examples 1-2 and Comparative Examples A-B

Epoxy resin compositions of Examples 1 and 2 and Comparative Examples A and B were prepared by mixing the ingredients described in Table I, respectively. An epoxy diluent (S-6036 Epoxy or NC-513) was first mixed with DGEBA, and then mixed with a stoichiometric amount of a hardener to obtain an epoxy resin composition. Viscosities of the epoxy resin compositions are given in Table I. $T_g$s of the epoxy resin compositions upon curing and corrosion resistance of coatings obtained from the epoxy resin compositions were evaluated according to the test methods described above and results are given in Table II.

As shown in Table I, the epoxy resin compositions of Examples 1 and 2 showed similar viscosities as those of Comparative Examples A and B, respectively. $T_g$s and corrosion resistance properties were summarized in Table II. $T_g$s of the inventive epoxy resin compositions upon curing (Examples 1 and 2) showed comparable or even higher $T_g$s compared to the comparative epoxy resin compositions upon curing (Comparative Examples A and B), respectively. Coatings prepared from compositions comprising S-6036 Epoxy diluent (Examples 1 and 2) exhibited lower $C_c$ and higher $R_t$ values compared to coatings prepared from compositions comprising the same dosage of the mono-functional cardanol epoxy diluent (Comparative Examples A and B). Therefore, the epoxy resin compositions of the present invention provide coatings with better corrosion resistance than compositions comprising the same dosage of the mono-functional cardanol epoxy diluent. Surprisingly, coatings made from the epoxy resin composition comprising 10 wt% S-6036 Epoxy diluent showed the best corrosion resistance among all the coatings.

Table I

| Component, weight part | | Comparative Example A | Comparative Example B | Example 1 | Example 2 |
|---|---|---|---|---|---|
| DGEBA | D.E.R. 331 | 90 | 50 | 90 | 50 |
| Epoxy Diluent | NC-513 | 10 | 50 | | |
| | S-6036 Epoxy | | | 10 | 50 |
| Hardener | D.E.H.140 | 48.1 | 37.4 | 49.0 | 41.8 |
| Viscosity of epoxy resin compositions (mPa·s) | | 3800 | 550 | 4200 | 580 |

Table II

| Test results | Immersion time (hour) | Comparative Example A | Comparative Example B | Example 1 | Example 2 |
|---|---|---|---|---|---|
| $C_c$ (nF·cm$^2$) | 0 | 1.5 | 3.5 | 0.019 | 0.48 |
| | 27 | 1.4 | 16 | 0.065 | 2.3 |
| | 39 | 1.3 | 14 | 0.1 | 2.4 |
| $R_t$ (MΩ·cm$^2$) | 0 | 3.5 | 1.5 | 25 | 8.3 |
| | 27 | 0.0054 | 0.000083 | 8.3 | 0.0026 |
| | 39 | 0.01 | 0.00024 | 0.62 | 0.0035 |
| $T_g$ ($^o$C) | | 76 | 57 | 81 | 68 |

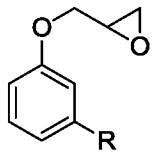
CLAIMS

1. A curable resin composition comprising:

(a) an epoxy resin;

(b) an epoxy diluent, different from the epoxy resin of component (a); wherein the epoxy diluent has an epoxy functionality of from 1.1 to 1.6, and wherein the epoxy diluent comprises:

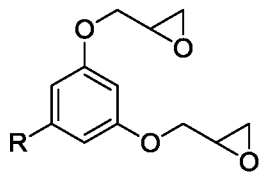
(b1) a first compound having the structure represented by Formula (I):




Formula (I),

wherein R is a straight-chain alkyl with 15 carbons containing 0 to 3 C=C bond(s) selected from $-C_{15}H_{31}$, $-C_{15}H_{29}$, $-C_{15}H_{27}$, and $-C_{15}H_{25}$; and

(b2) a second compound, different from the first compound of component (b1); wherein the second compound has the structure represented by Formula (II):




Formula (II),

wherein R is a straight-chain alkyl with 15 carbons containing 0 to 3 C=C bond(s) selected from $-C_{15}H_{31}$, $-C_{15}H_{29}$, $-C_{15}H_{27}$, and $-C_{15}H_{25}$; and

(c) a hardener compound.

2. The curable resin composition of claim 1, wherein the epoxy functionality of the epoxy diluent is from 1.2 to 1.4.

3. The curable resin composition of claim 1, wherein the total concentration of the first compound of Formula (I) and the second compound of Formula (II) is from 90 wt% to 100 wt%, based on the weight of the epoxy diluent.

4. The curable resin composition of claim 1, wherein the concentration of the epoxy diluent is from 5 wt% to 50 wt%, based on the total weight of the epoxy diluent and the epoxy resin.

5. The curable resin composition of claim 4, wherein the concentration of the epoxy diluent is from 10 wt% to 30 wt%, based on the total weight of the epoxy diluent and the

epoxy resin.

6. The curable resin composition of claim 1, wherein the epoxy resin is bisphenol A diglycidyl ether.

7. The curable resin composition of claim 1, wherein the hardener compound is a polyamine.

8. The curable resin composition of claim 1, wherein the curable resin composition is substantially free of additional reactive diluents.

9. A curable resin composition comprising:

(a) an epoxy resin;

(b) an epoxy diluent, different from the epoxy resin of component (a); wherein the epoxy diluent has an epoxy functionality of from 1.1 to 1.6, and wherein the epoxy diluent is prepared by reacting an epihalohydrin with a cashew nutshell liquid comprising cardanol and cardol, and wherein the molar ratio of cardanol to cardol in the cashew nutshell liquid is from 9:1 to 4:6; and

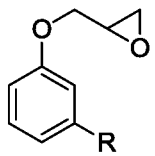
(c) a hardener compound.

10. A process for preparing a curable epoxy resin composition of any one of claims 1-8, comprising admixing:

(a) an epoxy resin;

(b) an epoxy diluent, different from the epoxy resin of component (a); wherein the epoxy diluent has an epoxy functionality of from 1.1 to 1.6, and wherein the epoxy diluent comprises:

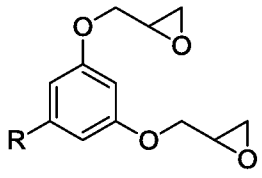
(b1) a first compound having the structure represented by Formula (I):




Formula (I),

wherein R is a straight-chain alkyl with 15 carbons containing 0 to 3 C=C bond(s) selected from $-C_{15}H_{31}$, $-C_{15}H_{29}$, $-C_{15}H_{27}$, and $-C_{15}H_{25}$; and

(b2) a second compound, different from the first compound of component (b1); wherein the second compound has the structure represented by Formula (II):



Formula (II),

wherein R is a straight-chain alkyl with 15 carbons containing 0 to 3 C=C bond(s) selected from $-C_{15}H_{31}$, $-C_{15}H_{29}$, $-C_{15}H_{27}$, and $-C_{15}H_{25}$; and

(c) a hardener compound.

11. A method of preparing a coating, wherein the method comprises:

applying a curable resin composition of any one of claims 1-9 to a substrate, and

curing the curable resin composition to form a coating.

# INTERNATIONAL SEARCH REPORT

International application No.
**PCT/CN2015/079257**

## A. CLASSIFICATION OF SUBJECT MATTER

C08G 59/00(2006.01)i; C08L 63/00(2006.01)i; C08K 5/15(2006.01)n; C08K 5/1515(2006.01)n

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)

C08G59; C08L63

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)

CNABS, WPI, EPODOC, CNKI; epoxy, epoxide, +glycidyl, reactive diluent, hardener, curing agent,

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | JP 2007284518 A (DAINIPPON INK&CHEM INC) 01 November 2007 (2007-11-01)<br>the whole document | 1-11 |
| A | JP H0532868 A (SAKAMOTO YAKUHIN KK) 09 February 1993 (1993-02-09)<br>the whole document | 1-11 |
| A | JP H06172336 A (SAKAMOTO YAKUHIN KOGYO KK) 21 June 1994 (1994-06-21)<br>the whole document | 1-11 |
| A | JP S536400 A (MITSUBISHI PETROCHEMICAL CO LTD) 20 January 1978 (1978-01-20)<br>the whole document | 1-11 |
| A | JP 1161075 A (SUMITOMO BAKELITE CO LTD) 05 March 1999 (1999-03-05)<br>the whole document | 1-11 |

☐ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

* Special categories of cited documents:

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"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 | Date of mailing of the international search report |
|---|---|
| **16 February 2016** | **24 February 2016** |
| Name and mailing address of the ISA/CN<br>**STATE INTELLECTUAL PROPERTY OFFICE OF THE P.R.CHINA**<br>**6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing 100088, China**<br>Facsimile No. **(86-10)62019451** | Authorized officer<br>**TANG,Shaohua**<br>Telephone No. **(86-10)62084439** |

**INTERNATIONAL SEARCH REPORT**
**Information on patent family members**

International application No.
**PCT/CN2015/079257**

| Patent document cited in search report | Publication date (day/month/year) | Patent family member(s) | Publication date (day/month/year) |
|---|---|---|---|
| JP 2007284518 A | 01 November 2007 | JP 5028844 B | 19 September 2012 |
| JP H0532868 A | 09 February 1993 | none | |
| JP H06172336 A | 21 June 1994 | JP 2676459 B | 17 November 1997 |
| JP S536400 A | 20 January 1978 | none | |
| JP 1161075 A | 05 March 1999 | none | |