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(54) Title: PARTIALLY HYDROLYZED EPOXY RESIN COMPOSITIONS

(57) Abstract: A partially hydrolyzed aliphatic or cycloaliphatic epoxy resin composition including a partially hydrolyzed aliphatic or cycloaliphatic epoxy resin composition having an γ -glycol moiety content of from about 2.3 area % to about 25 area % of the total components comprising the epoxy resin composition as measured by gas chromatographic analysis; and a process for preparing the above partially hydrolyzed aliphatic or cycloaliphatic epoxy resin composition.



PARTIALLY HYDROLYZED EPOXY RESIN COMPOSITIONS

FIELD

The present invention is related to epoxy resin compositions and more particularly to partially hydrolyzed aliphatic and cycloaliphatic epoxy resin compositions.

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BACKGROUND

Several methods for the partial hydrolysis of epoxy resins are known in the prior art; particularly hydrolyzing aromatic epoxy resins such as epoxy resins of bisphenol A. None of the prior art discloses a partially hydrolyzed aliphatic and cycloaliphatic epoxy resin composition, for example, the partially hydrolyzed epoxy resin of
10 cyclohexanedimethanols (CHDM), additionally having improved properties such as low CHDM monoglycidyl ether (MGE) and/or low hydrolyzable chloride.

For example, U.S. Patent No. 3,632,836 describes the complete hydrolysis of aromatic epoxy resins in a solvent solution using an aqueous solution of an acidic catalyst in an autoclave under at least autogeneous pressure at a temperature of 50 °C to 374 °C.
15 U.S. Patent No. 4,404,335 teaches partial hydrolysis of epoxy resins without an organic solvent using water, a catalyst that contains a dicarboxylic acid (such as oxalic acid) and a phosphonium catalyst, at a temperature of 50 °C to 200 °C. Totally hydrolyzed aromatic epoxy resins resulting from the process of U.S. Patent No. 3,632,836 may be blended with non-hydrolyzed epoxy resins.

20 The known hydrolysis processes described above have several drawbacks which make them undesirable for use in an industrial process for mass producing large quantities of epoxy resin containing α -glycol. For instance, the known processes use catalysts, and in some instances solvents, that must be removed from the epoxy resin product before the resin can be used in a subsequent operation. In addition, the known
25 processes produce large quantities of bis- α -glycol species in the epoxy resin in addition to the mono- α -glycol species. Such bis- α -glycol species present in the epoxy resin have no curable epoxide groups, and thus, the bis- α -glycol species may: (1) depress glass transition temperature of articles (thermosets) made from the epoxy resin containing such species; (2) migrate to the surface of the thermoset causing softness or tackiness; and (3) depress
30 mechanical properties such as modulus.

WO1995011266A1 seeks to increase the level of mono- α -glycol species in an epoxy resin without using catalyst or solvent in a process in which a mixture of liquid

epoxy resin and water (0.5 and 10 parts water per 100 parts resin by weight) is reacted at elevated temperatures in order to hydrolyze epoxy groups into α -glycol groups. One drawback of the process described in WO1995011266A1 is the process requires a relatively high reaction temperature (e.g., 130 °C to 200 °C) for the hydrolysis to take place.

5 In addition to the above prior art, various aliphatic or cycloaliphatic epoxy resin products are known including: (1) high purity diglycidyl ethers of aliphatic or cycloaliphatic epoxy resins, (2) aliphatic or cycloaliphatic epoxy resins produced using non-Lewis acid catalyzed processes, (3) low (MGE) aliphatic or cycloaliphatic epoxy resins, (4) advanced diglycidyl ethers of aliphatic or cycloaliphatic epoxy resins (containing
10 residual glycidyl ether functionality available for hydrolysis), and (5) blends of one or more of (1) - (4) with one or more partially or totally hydrolyzed epoxy resins. However, nothing in the prior art discloses partially hydrolyzing any of the above aliphatic or cycloaliphatic diglycidyl ethers or epoxy resins of (1) - (4), particularly, a partially hydrolyzed diglycidyl ether or epoxy resin of CHDM. A partially hydrolyzed aliphatic or cycloaliphatic epoxy
15 resin is not the same, and does not have the same, properties as the above currently known CHDM diglycidyl ethers or epoxy resins.

Processes for preparing the aforementioned aliphatic and cycloaliphatic epoxy resin products of (1)-(4) are disclosed for example in co-pending U.S. Provisional Patent Application Serial No. 61/969,290, filed of even date herein by Robert E. Hefner, Jr.
20 et al.; WO 2012/044442A1; WO 2012/044443A1; WO 2012/044455A1; WO 2012/044458A1; WO 2012/044490A1; WO 2012/047420A2; WO 2012/050688A2; and WO 2012/050777A1; all of which are incorporated herein by reference.

SUMMARY

To alleviate the aforementioned deficiencies of the prior art, it would be
25 highly desirable to be able to produce a novel partially hydrolyzed aliphatic or cycloaliphatic diglycidyl ether or epoxy resin composition. Accordingly, one aspect of the present invention is directed to a novel partially hydrolyzed aliphatic and cycloaliphatic epoxy resin composition having an α -glycol moiety content of from about 2.3 area percent (area %) to about 25 area % of the total components comprising the epoxy resin
30 composition as measured by gas chromatographic (GC) analysis; and another aspect of the present invention is directed to a process for preparing such epoxy resin composition.

Other aspects of the present invention include a curable composition utilizing the above epoxy resin composition; and a cured product utilizing the above curable

composition. The epoxy resin composition includes α -glycol moieties resulting from hydrolysis of glycidyl ether moieties.

In one embodiment, the present invention includes a partially hydrolyzed cycloaliphatic epoxy resin, particularly a CHDM epoxy resin. For example, the partially hydrolyzed cycloaliphatic epoxy resin can include partially hydrolyzed versions of:

- (1) high purity diglycidyl ethers of aliphatic or cycloaliphatic epoxy resins; (2) aliphatic or cycloaliphatic epoxy resins produced using non-Lewis acid catalyzed processes;
- (3) low MGE aliphatic or cycloaliphatic epoxy resins; (4) advanced diglycidyl ethers of aliphatic or cycloaliphatic epoxy resins (containing residual glycidyl ether functionality available for hydrolysis); or (5) blends of one or more of (1) - (4) with one or more partially or totally hydrolyzed epoxy resins.

For example, the present invention includes novel aliphatic and cycloaliphatic epoxy resin compositions of matter containing elevated α -glycol content resulting from hydrolysis of a minor amount of the glycidyl ether groups. By GC analysis, an effective minor amount of one or more components containing an α -glycol moiety is preferably from about 2.3 area % to about 25 area %, more preferably from about 3.5 area % to about 15 area %, and most preferably from about 5 area % to about 10 area % of the total components comprising the epoxy resin composition product.

Some other advantages of the aliphatic and cycloaliphatic epoxy resin composition of the present invention include lower viscosity, high boiling point of the α -glycol containing compounds which prevents them from being removed during processing to recover the epoxy resin product, and stability of the α -glycol containing components of the epoxy resin. Particularly preferred aliphatic and cycloaliphatic epoxy resin compositions of the present invention are those low in MGE which retain the aforementioned benefits and additionally possess higher average (curable) epoxide and improved shelf life. With respect to shelf life, the isolated aliphatic and cycloaliphatic MGE are prone to slow polymerization at room temperature causing increase in viscosity, reduction in epoxide functionality available for cure and ultimately even gelation.

In another embodiment, the present invention includes a process for producing a partially hydrolyzed aliphatic or cycloaliphatic epoxy resin, particularly a CHDM epoxy resin including for example, the partially hydrolyzed CHDM diglycidyl ether or epoxy resin versions of (1)-(5) above.

Some other advantages of the process for preparing the aliphatic and cycloaliphatic epoxy resin composition of the present invention include no change in the unit operations of the process used to produce and recover the epoxy resin product containing α -glycol moieties. To produce the α -glycol containing epoxy resin, the neutralization step employed in the isolation and recovery of the epoxy resin product becomes an over neutralization (to a pH below about 7). There is no change in process equipment or neutralizing agent used, with no additional catalyst(s), solvent(s) or other additive(s) required. The partial hydrolysis is generally performed under mild conditions, most preferably at from about 25 °C to about 30 °C.

In still another embodiment, the present invention includes a process for controlling the amounts of α -glycol during the production of the aliphatic and cycloaliphatic epoxy resin by adjusting the stoichiometry of a neutralizing agent normally employed in the production of the aliphatic and cycloaliphatic epoxy resin while simultaneously removing any residual alkalinity from the epoxy resin product. To achieve the desired stoichiometry of the neutralizing agent, pH of the reaction mixture is typically measured. GC analysis may be employed to directly measure formation of the α -glycol compounds.

In yet another embodiment, the present invention is related to curable compositions using the above novel aliphatic and cycloaliphatic epoxy resin compositions. Some advantages of the curable composition of the present invention include acceleration of curing (decreased curing onset temperature), especially with a polyalkylene polyamine curing agent which can be used for room temperature (about 25 °C) curing. Improved reactivity is achieved demonstrated by increased enthalpy of curing. These advantages are achieved while maintaining crucial mechanical properties of cured articles such as glass transition temperature (T_g) and curable composition properties such as low viscosity. Particularly preferred curable compositions of the present invention are those α -glycol containing aliphatic and cycloaliphatic epoxy resin compositions low in MGE which retain the aforementioned benefits and additionally possess higher average epoxide functionality and reduction in epoxide monofunctional MGE. The higher average epoxide functionality provides increased crosslink density upon curing while the reduction in epoxide monofunctional MGE reduces deleterious chain terminating species present in the curable composition.

In even still another embodiment, the present invention is related to cured compositions of the above curable compositions. Curing of the partially hydrolyzed

aliphatic and cycloaliphatic epoxy resin compositions to prepare, for example, coatings, adhesives, films, foams, composites and laminates, is favorably accelerated due to the presence of the α -glycol moieties, while Tg is maintained, that is, not adversely impacted. Some other advantages of the cured aliphatic and cycloaliphatic thermoset epoxy resin matrices of the present invention include reduced yellowing upon weathering and none of the chalking upon weathering typically observed with aromatic thermoset epoxy resin matrices. Particularly preferred cured compositions of the present invention are those prepared using α -glycol containing aliphatic and cycloaliphatic epoxy resin compositions low in MGE which retain the aforementioned benefits and additionally include improved acid resistance in coatings concomitant with maintenance or improvement in other chemical resistant properties, including moisture resistance. Reduction in chain termination reaction caused by the epoxide mono-functionality of the MGE reduces defects in the cured epoxy resin composition which may in turn result in improved mechanical properties and increased Tg.

15 DETAILED DESCRIPTION

One broad embodiment of the present invention comprises a partially hydrolyzed aliphatic or cycloaliphatic epoxy (PHACE) resin composition.

An “aliphatic hydroxyl- or a cycloaliphatic hydroxyl-containing material or compound” herein means a material of higher hydroxyl functionality such as diols, triols and the like.

“Partially hydrolyzed”, with reference to an epoxy resin composition, herein means, as measured by GC analysis, one or more components containing an α -glycol moiety comprising from about 2.3 area % to about 25 area % of the total components comprising the epoxy resin composition.

25 “Totally hydrolyzed” or “completely hydrolyzed”, with reference to an epoxy resin composition, herein means approximately 100 percent (%) of the glycidyl ether groups have been converted to α -glycol groups.

In one embodiment, suitable aliphatic or cycloaliphatic epoxy (ACE) resin compositions to be partially hydrolyzed in accordance with the present invention can include most any ACE resin including: (1) high purity diglycidyl ethers of aliphatic or cycloaliphatic epoxy resins, (2) aliphatic or cycloaliphatic epoxy resins produced using non-Lewis acid catalyzed processes, (3) low MGE aliphatic or cycloaliphatic epoxy resins, and (4) advanced diglycidyl ethers of aliphatic or cycloaliphatic epoxy resins (containing

residual glycidyl ether functionality available for hydrolysis). The ACE resin compounds used in the present invention can be formed by non-Lewis acid catalyzed epoxidation of aliphatic or cycloaliphatic hydroxyl-containing compounds.

5 The non-Lewis acid catalyzed epoxidation process for epoxidizing the aliphatic hydroxyl-containing compounds or the cycloaliphatic hydroxyl-containing compounds generally includes the steps of: (1) coupling of an epihalohydrin with an aliphatic or cycloaliphatic hydroxyl-containing material; and (2) dehydrohalogenating an intermediate halohydrin component formed in step (1). The two-step epoxidation process may include, for example, a phase transfer catalyzed aqueous epoxidation process, a slurry
10 epoxidation process, or an anhydrous epoxidation process.

In one embodiment, a phase transfer catalyzed aqueous epoxidation process is used in the present invention. The aqueous epoxidation process may optionally be run partially under vacuum or totally under vacuum in a manner that removes all or a part of the water, for example via azeotropic distillation. The aqueous epoxidation process may be
15 carried, for example, by admixing: (a) an aliphatic or cycloaliphatic hydroxyl containing material, (b) an epihalohydrin, (c) a non-Lewis acid catalyst, and (d) optionally, a solvent; and then, reacting the above mixture by the addition of (e) a basic acting substance to form an epoxy resin product. The epoxy resin product formed by epoxidizing an aliphatic or cycloaliphatic hydroxyl containing material, particularly an aliphatic or cycloaliphatic diol
20 is described, for example, in WO2009/142901. After the epoxidation reaction, the product is subjected to a partial hydrolysis procedure via over neutralization (to a pH below about 7) to produce α -glycol moieties.

A general process for manufacturing an ACE resin composition via the aqueous epoxidation process typically involves a series of two or more stages of addition of
25 an aqueous basic-acting substance, followed by separation of the aqueous phase after addition then post reaction for each respective stage is complete. It should be understood that the number of epoxidation stages used the aqueous epoxidation process may comprise one, two or more stages of addition of aqueous basic acting substance and post reaction. Preparation of the ACE resin via the aqueous epoxidation process is not limited to the
30 embodiment described herein which uses three epoxidation stages. In other embodiments, two or more stages or steps may be combined and carried out by one apparatus or by two or more separate apparatuses.

In the aqueous epoxidation process an aliphatic or cycloaliphatic hydroxyl containing material, an epihalohydrin, a non-Lewis acid catalyst, optionally a solvent, and an inert gas such as a nitrogen stream are charged to the reactor. An aqueous basic-acting substance feed stream is then added to the stirred reaction mixture of this first
5 epoxidation reaction stage. After completion of any post reaction, the first epoxidation reaction stage product is separated from the aqueous phase, optionally washed with water, and the aqueous waste stream is the directed to a waste recovery operation or to another operation for further processing. The first stage epoxidation product is recovered for processing in a second epoxidation reaction stage. The epoxidation product from the first
10 stage, fresh non-Lewis acid catalyst and an inert gas stream (nitrogen) are treated with a second aqueous basic-acting substance feed stream to carry out further epoxidation of the epoxidation product from the first stage to form a second epoxidation reaction stage product. In an optional embodiment, a second epihalohydrin stream and a second solvent stream may be fed into the second epoxidation stage if desired. After completion of any
15 post reaction, the second epoxidation reaction stage product is separated from the aqueous phase, optionally washed with water, and the aqueous waste stream is the directed to a waste recovery operation or to another operation for further processing. The second stage epoxidation product is recovered for processing in a third epoxidation reaction stage. The epoxidation product from the second stage, fresh non-Lewis acid catalyst and an inert gas
20 stream (nitrogen) are treated with a third aqueous basic-acting substance feed stream to carry out further epoxidation of the epoxidation product from the second stage to form a third epoxidation reaction stage product. In an optional embodiment, a third epihalohydrin stream and a third solvent stream may be fed into the third epoxidation stage if desired. After completion of any post reaction, the third epoxidation reaction stage product is
25 separated from the aqueous phase, optionally washed with water, and the aqueous waste stream is the directed to a waste recovery operation or to another operation for further processing.

The epoxidation product stream from the third stage is treated with a neutralizing agent, such as sodium dihydrogen phosphate, in an amount and at reaction
30 conditions sufficient to produce the desired amount of hydrolysis of glycidyl ether groups to α -glycol groups. The neutralizing agent may be employed either before or after water washing of the epoxidation product stream, optionally to which one or more solvents has been added. Additionally, the neutralizing agent may be used with the water washed or unwashed epoxidation product stream which has been stripped to remove a part or all of the

unreacted epichlorohydrin. The neutralizing agent may further be used with water washed or unwashed epoxidation product streams which have been stripped to remove all or a part of the unreacted epichlorohydrin and then combined with a solvent, such as toluene.

5 The product from the third epoxidation stage is typically subjected to a devolatilization process to remove any lights including unreacted epihalohydrin. The devolatilization process may additionally provide selective fractionation to remove a part or all of the MGE from the total epoxy resin composition without substantial removal of diglycidyl ether or oligomers. Alternatively, the devolatilized epoxidation product may be forwarded to a fractionation operation wherein any residual lights are removed and a part or
10 all of the MGE is removed from the total epoxy resin composition without substantial removal of diglycidyl ethers or oligomers. The above epoxidation process produces a product, an ACE resin, containing less than (<) from about 0.01 weight percent (wt %) to about 15 wt % MGE, from about 40 wt % to about 75 wt % diglycidyl ether, with the balance comprising α -glycol group containing compounds and oligomers.

15 In another embodiment of the present invention, an ACE resin may also be prepared by an azeotropic (anhydrous) epoxidation process. In the process, a mixture of (a) an aliphatic or cycloaliphatic hydroxyl containing material, (b) an epihalohydrin, (c) a non-Lewis acid catalyst, and optionally, (d) a solvent are prepared. Controlled addition of (e) a basic acting substance as an aqueous solution to the stirred mixture of (a) an aliphatic
20 or cycloaliphatic hydroxyl containing material, (b) an epihalohydrin, and (c) a non-Lewis acid catalyst is performed with continuous vacuum distillation of an epichlorohydrin-water azeotrope, removing of the water fraction from the distilled azeotrope, and recycling of the recovered epichlorohydrin back into the reaction, forming an epoxy resin composition. A solvent other than, or in addition to, the excess stoichiometric epihalohydrin which may
25 serve as a solvent, may also be used in the azeotropic epoxidation process.

Product from the azeotropic epoxidation reaction may be treated with a neutralizing agent, such as sodium dihydrogen phosphate, in an amount and at reaction conditions sufficient to produce the desired amount of hydrolysis of glycidyl ether groups to α -glycol groups. The neutralizing agent may be employed either before or after water
30 washing of the epoxidation product, optionally to which one or more solvents has been added. Alternately, after completion of addition of the aqueous basic acting substance and any post reaction, the epoxidation product mixture may be subjected to further distillation conditions to substantially remove the unreacted epihalohydrin along with

co-produced lights. The resultant slurry of salts and epoxy resin may then be processed further to remove salts. One such process involves centrifugation and/or filtration to remove the solid salts and recover the liquid aliphatic or cycloaliphatic epoxy resin. Partial hydrolysis of the liquid ACE resin, optionally to which one or more solvents has been added, is then completed by treating with a neutralizing agent in an amount and using reaction conditions which produce the desired amount of hydrolysis of glycidyl ether groups to α -glycol groups.

In another process, the slurry of salts and epoxy resin substantially free of unreacted epihalohydrin is diluted with a solvent, such as toluene, followed by addition of water to dissolve said salts. After separation of the aqueous salt solution, the resultant solvent solution of ACE resin may be washed further with water. The neutralizing agent may be employed either before or after water washing of the ACE resin and solvent solution. Treatment with neutralizing agent is done using an amount and reaction conditions which produce the desired amount of hydrolysis of glycidyl ether groups to α -glycol groups.

The washed product may be subjected to a devolatilization process to remove any lights or solvent(s). The devolatilization process may additionally provide selective fractionation to remove MGE to < about 2 wt % of the total epoxy resin composition without substantial removal of diglycidyl ether, α -glycol group containing compounds or oligomers. Alternatively, the devolatilized epoxidation product may be forwarded to a fractionation operation wherein any residual lights are removed and MGE is removed to < about 2 wt % of the total partially hydrolyzed epoxy resin composition without substantial removal of diglycidyl ether α -glycol group containing compounds or oligomers such that diglycidyl ether is greater than (>) about 60 wt % of the total epoxy resin.

It should be understood that any conventional equipment known to those skilled artisans can be used to carry out the manufacturing process of the present invention. For example, the equipment can include epoxidation reactor vessels; evaporation vessels such as rotary evaporators; and separation vessels such as distillation apparatus; which are known in the art. For example, generally, a separation vessel, such as a fractional vacuum distillation apparatus may be used to produce fractionation cuts including a "lights" stream, a MGE stream or mixed MGE and diglycidyl ether stream, and a "bottoms" stream comprising < about 2 wt % MGE, > about 60 wt % diglycidyl ether, α -glycol group

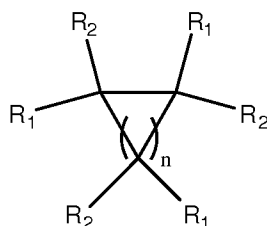
containing compounds and oligomers. The bottoms stream is separated and isolated from the other streams leaving the distillation apparatus may be forwarded to a subsequent process to form curable compositions and thermosets therefrom. For example, these partially hydrolyzed epoxy resin products can be mixed with a curing agent and/or a curing catalyst for making a thermosettable resin containing < about 2 wt % MGE; and the thermosettable resin can be partially cured to form a B-stage material or completely cured to form a thermoset article.

The epoxidation process step of the present invention may be carried out under various process conditions. For example, the temperature used in the epoxidation process is generally from about 20 °C to about 120 °C, preferably from about 25 °C to about 60 °C, and more preferably from about 30 °C to about 50 °C. The pressure used in the epoxidation process is generally from about 10 mm Hg vacuum to about 100 psi, preferably from about 30 mm Hg vacuum to about 50 psi, and more preferably from about 40 mm Hg vacuum to about atmospheric pressure (e.g., 760 mm Hg). The time for completion of the epoxidation step of the process is generally from about 1 hour to about 120 hours, more preferably from about 2 hours to about 72 hours, and most preferably from about 3 hours to about 24 hours.

Any aliphatic or cycloaliphatic hydroxyl-containing reactant may be employed in the epoxidation process to produce the ACE resin which is further processed to provide the PHACE resin. Some representative classes of aliphatic and/or cycloaliphatic hydroxyl-containing materials which may be employed in the epoxidation process can include for example any one or more of the following compounds described for example in WO2012/044443, pages 8 to 15, incorporated herein by reference:

- (A) cyclohexanedialkanols and cyclohexenedialkanols such as for example UNOXOLTM Diol (mixture of cis- and trans-1,3- and 1,4-cyclohexanedimethanol) and 1,4-cyclohexanedimethanol; (B) cyclohexanolmonoalkanols and cyclohexenolmonoalkanols such as for example 1-phenyl-cis-2-hydroxymethyl-r-1-cyclohexanol; (C) decahydronaphthalenedialkanols, octahydronaphthalenedialkanols and 1,2,3,4-tetrahydronaphthalenedialkanols such as for example 1,2-decahydronaphthalene-dimethanol and 1-hydroxy-2-hydroxymethyldecahydronaphthalene; (D) bicyclohexanedialkanols and bicyclohexanolmonoalkanols such as for example bicyclohexane-4,4'-dimethanol and bicyclohexene-1,1'-dimethanol; (E) bridged cyclohexanols such as for example bisphenol A (4,4'-isopropylidenediphenol); (F) other cycloaliphatic and polycycloaliphatic diols, monol monoalkanols, or dialkanols such as for

example norbornane-2,3-trans-dimethanol; (G) aliphatic hydroxyl-containing materials such as for example ethoxylated catechol, ethoxylated hydrogenated bisphenol A, and neopentyl glycol; and (H) cyclopropane, cyclobutane and cyclopentane diols. Suitable cyclopropane, cyclobutane and cyclopentane diols include:



5 wherein n is 1, 2, or 3; each R₁ is independently hydrogen, C₁₋₁₂ alkyl, C₃₋₁₂ cycloalkyl, or C₆₋₂₄ aryl; each R₂ is independently hydrogen, C₁₋₁₂ alkyl, hydroxyl, C₁₋₁₂ hydroxyalkyl, or C₆₋₂₄ hydroxyaryl, with the proviso that the diol has two hydroxyl, C₁₋₁₂ hydroxyalkyl, or C₆₋₂₄ hydroxyaryl groups. Examples of the diol are cyclobutane-1,3-diol, cyclobutane-1,2-
 10 diol, mono-C₁₋₄ alkyl-cyclobutane-1,3-diols, mono-C₁₋₄ alkyl-cyclobutane-1,2-diols, di-C₁₋₄ alkyl-cyclobutane-1,3-diols, di-C₁₋₄ alkyl-cyclobutane-1,2-diols, tri-C₁₋₄ alkyl-cyclobutane-1,3-diols, tetra-C₁₋₄ alkyl-cyclobutane diols, cyclopropane-1,2-diol, mono-C₁₋₄ alkyl-cyclopropane-1,2-diols, di-C₁₋₄ alkyl-cyclopropane-1,2-diols, cyclopentane-1,2-diol, cyclopentane-1,3-diol, mono-C₁₋₄ alkyl-cyclopentane-1,2-diols,
 15 mono-C₁₋₄ alkyl-cyclopentane-1,3-diols, di-C₁₋₄ alkyl-cyclopentane-1,2-diols, di-C₁₋₄ alkyl-cyclopentane-1,3-diols, tri-C₁₋₄ alkyl-cyclopentane-1,2-diols, tri-C₁₋₄ alkyl-cyclopentane-1,3-diols, tetra-C₁₋₄ alkyl-cyclopentane-1,2-diols, tetra-C₁₋₄ alkyl-cyclopentane-1,3-diols, penta-C₁₋₄ alkyl-cyclopentane-1,2-diols, penta-C₁₋₄ alkyl-cyclopentane-1,3-diols, hexa-C₁₋₄ alkyl-cyclopentane-1,2-diols, hexa-C₁₋₄ alkyl-cyclopentane-1,3-diols, or a combination
 20 comprising one or more of the foregoing. A preferred diol is cis- and trans-2,2,4,4-tetramethylcyclobutane-1,3-diol.

The epihalohydrin, the basic acting substance, the non-Lewis acid catalyst, component and the optional solvent useful in the epoxidation process may be selected from one or more of the same components as described in U.S. Patent Application Publication
 25 No. 2013/0237642A1, pages 6 and 7, paragraphs [0056] to [0063], incorporated herein by reference.

Most any process or series of processes for isolating the PHACE resin may be employed. Thus, methods such as, for example, vacuum distillation including rotary evaporation, fractional vacuum distillation, short path distillation, packed column
 30 distillation, spinning band column distillation, falling film distillation, wiped film

distillation, steam distillation, filtration including vacuum filtration, gravity filtration, nanofiltration, microfiltration and ultrafiltration, membrane separations including pervaporation and vapor permeation, centrifugation, water washing or extraction, solvent extraction, supercritical fluid extraction, decantation, column chromatography, electrostatic
5 coalescence, adsorption, and other known fractionation and separation processing methods and the like may be employed. Fractional vacuum distillation is a preferred method for the fractionation or separation.

Chemistry and processes for the manufacture of ACE resins via epoxidation of aliphatic and cycloaliphatic hydroxyl containing materials using an epichlorohydrin
10 typically involve a neutralization step during processing of the crude epoxy resin product. Typically, the neutralizing agent is employed either before or after water washing of the crude epoxy resin product to remove inorganic salts. However, the neutralizing agent may be used with crude epoxy resin product which has been stripped to remove a part or all of the unreacted epichlorohydrin, water washed crude epoxy resin which has been stripped to
15 remove all or a part of the unreacted epichlorohydrin, or water washed crude epoxy resin which has been stripped to remove all or a part of the unreacted epichlorohydrin and then combined with a solvent, such as toluene. Sodium dihydrogen phosphate (monobasic sodium phosphate), potassium dihydrogen phosphate, and phosphoric acid are examples of the neutralizing agent which is employed to remove excess alkaline agent, such as sodium
20 hydroxide, in the epoxidation process. Sodium dihydrogen phosphate is conveniently prepared and used as an aqueous solution, typically about 13 wt %.

In the partial hydrolysis process of the present invention, once the ACE resin, particularly a CHDM epoxy resin, is produced in an epoxidation process, the ACE can be partially hydrolyzed using a stoichiometric excess (e.g., a stoichiometric excess over
25 that required for neutralization) of a neutralizing agent, such as for example, sodium dihydrogen phosphate, which is a neutralizing agent that is typically employed with a crude epoxy resin product to neutralize alkaline salts.

In the process of the present invention, a stoichiometric excess of a neutralizing agent is used for controlled hydrolysis of glycidyl ether groups to produce the
30 corresponding α -glycol groups while simultaneously removing undesirable alkalinity from the epoxy resin product. The amount of the neutralizing agent used varies depending on the structure of the neutralizing agent, the amount of excess basic acting substance used in the epoxidation, the amount of residual alkalinity present in the epoxy resin product, the

amount of hydrolysis desired, the planned reaction time for the neutralizing agent and the epoxy resin, and the like.

In the process of the present invention, the neutralizing agent may be added in increments followed by analysis of pH of the epoxy resin product and neutralizing agent mixture. Typically practiced neutralization is complete once a pH of no lower than about 7 is achieved. Frequently, only partial neutralization is practiced, for example by addition of neutralizing agent until a pH of about 7.5 to about 8 is achieved. For the over neutralization of the present invention, neutralizing agent is added to achieve a pH below about 7. Generally, once a pH of about 6 to about 6.5 is achieved an effective amount of α -glycol groups is produced. Excess neutralizing agent and reaction product of the neutralizing agent can be removed from the PHACE resin, for example, by water washing. GC analysis may be employed to monitor formation of the α -glycol containing compounds.

As measured by GC analysis, the PHACE resin composition of the present invention includes an effective amount of one or more components containing an α -glycol moiety of generally less than 50 area %, preferably from about 2.3 area % to about 25 area %, more preferably from about 3.5 area % to about 15 area %, and most preferably from about 5 area % to about 10 area % of the total components comprising the epoxy resin composition product. Below about 2.3 area % of compound(s) containing a α -glycol moiety, no beneficial effect, such as acceleration of cure when used in a curable composition, is obtained. At concentrations exceeding about 25 area % of compound(s) containing a α -glycol moiety, deleterious effects, such as depression of Tg when used to form a cured product, may result due to a lack of sufficient glycidyl ether groups in the PHACE resin.

Another broad embodiment of the present invention is directed to providing a curable resin formulation or composition including: (I) the PHACE resin composition described above; and (II) a curing agent. Other optional additives known to the skilled artisan can be included in the curable composition such as for example a curing catalyst and other additives for various applications.

The PHACE resin composition useful in the curable composition of the present invention is as described above. Generally, the molar equivalence of active hydrogen groups (i.e., N-H) in the curing agent to molar equivalence of epoxy groups in the PHACE resin are preferably from about 0.5 molar equivalents to about 1.5 molar equivalents, more preferably from about 0.6 molar equivalents to about 1.3 molar

equivalents, and most preferably from about 0.7 molar equivalents to about 1.2 molar equivalents. If the concentration of the curing agent is outside the above listed ranges, the curing agent will either be present in significant excess or depletion, which creates cured products, for example coatings, that will not be fully cured and / or will have poor final
5 coating properties.

In general, the curing agent (also referred to as a hardener or crosslinking agent), component (II), is blended with the PHACE resin, component (I), to prepare the curable composition of the present invention. The curing agent of the present invention may include for example, any conventional curing agent known in the art useful for
10 including in a curable composition. The curing agent compound useful in the curable composition, may be selected, for example, but are not limited to, anhydride compounds, carboxylic acid compounds, amine compounds, phenolic compounds, sulfhydryl compounds, or mixtures thereof.

Examples of the curing agents useful in the present invention may include
15 co-reactive or catalytic curing agents known to be useful for curing epoxy resin compositions. Such co-reactive curing agent may include, for example, a polyamine, a polyamide, a polyaminoamide, a dicyandiamide, a polymeric thiol, a polycarboxylic acid and a polycarboxylic anhydride, and any combination thereof. Other specific examples of co-reactive curing agents useful in the present invention may include diaminediphenyl--
20 sulfone, styrene-maleic acid anhydride (SMA) copolymers; and any combination thereof. Among conventional co-reactive epoxy resin curing agents useful in the present invention, amines and amino or amido containing resins and phenolics are preferred. Suitable catalytic curing agents may include, for example, a tertiary amine, a quaternary ammonium halide, a Lewis acid such as boron trifluoride, and any combination thereof.

25 Generally, the amount of the curing agent used in the curable composition of the present invention will depend on the end use of the curable composition. For example, as an illustrative embodiment, the concentration of a co-reactive curing agent useful in the curable composition, can generally range from a molar equivalence of active hydrogen groups (i.e., N-H) in the curing agent to molar equivalence of epoxy groups of from about
30 0.5 molar equivalents to about 1.5 molar equivalents in one embodiment, from about 0.6 molar equivalents to about 1.3 molar equivalents in another embodiment, from about 0.7 molar equivalents to about 1.2 molar equivalents in still another embodiment. If the concentration of the curing agent is outside the above listed ranges, the curing agent will

either be present in significant excess or depletion, which creates coatings that will not be fully cured and/or will have poor final coating properties.

In addition to the PHACE resin, component (I), and the curing agent (II), the curable composition of the present invention may include other optional compounds. The optional compounds that may be added to the curable composition of the present invention may include compounds that are normally used in resin formulations known to those skilled in the art for preparing curable compositions and thermosets. For example, the optional components may comprise compounds that can be added to the composition to enhance application properties (e.g., surface tension modifiers or flow aids), reliability properties (e.g., adhesion promoters), the reaction rate, the selectivity of the reaction, and/or the catalyst lifetime.

Other optional compounds that may be added to the curable composition of the present invention and that may be used as optional additional elements of the present invention include, for example, additives generally known to be useful for the preparation, storage, application, and curing of epoxy resins. For example, the optional compounds may include accelerators, catalysts, stabilizers, defoamers, wetting agents, de-molding agents, curing catalysts, pigments, extenders, dyes, flow modifiers, adhesion promoters, toughening agents, processing aids, solvents, other resins, fillers, plasticizers, catalyst de-activators, lubricants, slip agents, anti-cratering agents, dispersants with acid functional/non ionic surfactants in water, diluents, flame retardants, and mixtures thereof.

Other optional components that may be added to the curable composition of the present invention may include, for example polymeric materials such as an acrylic resin or polyester resin; resins such as polyesters, acrylic resins, polyolefins, urethane resins, alkyd resins, polyvinylacetates, epoxy resins other than the aliphatic or cycloaliphatic epoxy resin of the present invention, phenolic resins, vinyl resins; and mixtures thereof and the like.

Generally, the amount of one or more optional components, when used in the present invention, may be for example, from 0 wt % to about 90 wt % in one embodiment, from about 0.001 wt % to about 80 wt % in another embodiment; from about 0.01 wt % to about 70 wt % in still another embodiment; from about 0.1 wt % to about 60 wt % in yet another embodiment; and from about 1 wt % to about 50 wt % in even still another embodiment.

The curable composition of the present invention may include at least one other additional epoxy resin compound different from the PHACE resin to form the epoxy matrix in a final curable formulation. For example, the additional or second epoxy resin compound useful in the present invention may include any conventional epoxy resin
5 compound.

One embodiment of the second epoxy resin compound used in the curable composition of the present invention, may be for example a single epoxy resin compound used alone; or a combination of two or more epoxy resin compounds known in the art such as any of the epoxy resin compounds described in Lee, H. and Neville, K., *Handbook of*
10 *Epoxy Resins*, McGraw-Hill Book Company, New York, 1967, Chapter 2, pages 2-1 to 2-27, incorporated herein by reference. In a preferred embodiment, the epoxy resin compound 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
15 example, epoxy resins of bisphenol A, bisphenol F, resorcinol, and para-aminophenols.

Other suitable epoxy resins known in the art include for example reaction products of epichlorohydrin with o-cresol novolacs, hydrocarbon novolacs, and, phenol novolacs.

20 The epoxy compound may also be selected from commercially available epoxy resin products such as for example, D.E.R. 331[®], D.E.R.332, D.E.R. 354, D.E.R. 580, D.E.N. 425, 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.

In another embodiment, an example of another optional compound useful in
25 the curable composition can be a curing catalyst. The curing catalyst useful in the present invention may include for example complexes of Lewis acids such as boron trifluoride, salicylic acid, nonylphenol, tris-2,3,6-(dimethylaminomethyl)phenol, calcium nitrate, and mixtures thereof.

The process for preparing the curable composition of the present invention
30 includes admixing: (I) PHACE resin composition described above; (II) a curing agent; and (III) any other optional ingredient(s) as desired. For example, the preparation of the curable resin formulation of the present invention is achieved by blending, in known mixing equipment, the PHACE resin, the curing agent, and optionally any other desirable additives.

Any of the above-mentioned optional additives, for example a catalyst, may be added to the curable composition during the mixing or prior to the mixing to form the curable composition.

5 All of the components of the curable formulation are typically mixed and dispersed at a temperature enabling the preparation of an effective curable PHACE resin composition having the desired balance of properties for a particular application. For example, the temperature during the mixing of all components may be generally from about -10 °C to about 40 °C in one embodiment, and from about 0 °C to about 30 °C in another embodiment. Lower mixing temperatures help to minimize reaction of the epoxide and
10 hardener in the composition to maximize the pot life of the composition.

The preparation of the curable formulation of the present invention, and/or any of the steps thereof, may be a batch or a continuous process. The mixing equipment used in the process may be any vessel and ancillary equipment well known to those skilled in the art.

15 Another aspect of the present invention is a process for curing the curable resin composition described above to form a thermoset or cured composition. For example, the curable low MGE PHACE resin composition or formulation of the present invention can be cured under conventional processing conditions to form a film, a coating, a foam or a solid. For example, the process to produce the cured PHACE resin products may be
20 performed by gravity casting, vacuum casting, automatic pressure gelation (APG), vacuum pressure gelation (VPG), infusion, filament winding, lay up injection, transfer molding, prepregging, coating, such as roller coating, dip coating, spray coating and brush coating, and the like.

The process of curing of the curable composition may be carried out at
25 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 composition such as the hardener used in the formulation. The process of curing the thermosettable PHACE resin composition of the present invention may be conducted at atmospheric (e.g., 760 mm Hg), superatmospheric or
30 subatmospheric pressures and at a temperature from about -10 °C to about 300 °C, preferably from about -5 °C to about 250 °C, and more preferably from about 0 °C to about 200 °C.

The curing of the curable epoxy resin composition may be carried out, for example, for a predetermined period of time and at a predetermined temperature sufficient to cure or partially cure (B-stage) the composition. For example, generally the curing time may be chosen between about 30 seconds to about 7 days, preferably between about 5 1 minute to about 24 hours, more preferably between about 2 minutes to about 6 hours, and even more preferably between about 2 minutes to about 30 minutes. A B-staged composition of the present invention may then be completely cured at a later time using the aforementioned conditions. Higher temperatures generally require a shorter period of time whereas lower temperatures generally require longer periods of time. Below the curing 10 period of time of about 30 seconds, the time may be too short to ensure sufficient reaction under conventional processing conditions; and above the curing time of about 7 days, the time may be too long to be practical or economical.

The cured product (i.e., the thermoset or cross-linked product made from the curable composition) of the present invention shows several improved properties over 15 conventional cured epoxy resins. For example, for the cured product or composite of the present invention, the curable composition may exhibit favorable acceleration of curing due to the presence of the α -glycol moieties, while T_g is maintained, that is, not adversely impacted in the resultant cured product. Some other advantages of the cured PHACE resin matrices of the present invention include reduced yellowing upon weathering and none of 20 the chalking upon weathering typically observed with aromatic thermoset epoxy resin matrices. PHACE resins of the present invention low in MGE retain the aforementioned benefits and additionally provide improved acid resistance in coatings concomitant with maintenance or improvement in other chemical resistant properties, including moisture resistance. Reduction in chain termination reaction caused by the epoxide 25 monofunctionality of the MGE reduces defects in the cured epoxy resin composition which may in turn result in improved mechanical properties and increased T_g.

The curable composition of the present invention includes a combination of compounds that advantageously deliver unique properties to the resulting cured product. The PHACE resin curable composition of the present invention may be used to prepare 30 coatings, adhesives, laminates, prepregs and composites that exhibit a combination and balance of advantageous properties including for example processability, T_g, mechanical performance and physical properties.

For example, the compositions of the present invention are especially desirable for preparing a thin film composition, such as a coating, capable of accelerated curing at room temperature (about 25 °C). Additional benefits anticipated for the compositions of the present invention include enhanced adhesion, increased flexibility, increased impact resistance, and better acceptance of additives such as fillers, pigments, thixotropic agents, flow modifiers, and mixtures of such additives.

Another advantage of the present invention is that the PHACE resin composition of the present invention can be used in an industrial scale plant to produce commercial products for coating applications such as maintenance and protective coatings; marine coatings; agriculture coatings; construction coatings; and for metal, concrete, plastic, wood substrates; and the like. In other words, the present invention process makes it advantageously viable to produce the PHACE resins on a commercial manufacturing capability.

The examples of the present invention demonstrate the preparation and performance of an improved low CHDM MGE PHACE resin. Low CHDM MGE epoxy resins (non-hydrolyzed) are target materials useful for coating applications involving, for example, low viscosity epoxy resins and weatherable epoxy resins. The low CHDM MGE PHACE resins of the present invention, on the other hand, are a significant improvement over the prior art. The examples of the present invention specifically provide a low CHDM MGE PHACE resin product capable of being produced on a commercial scale with the aforementioned advantages.

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.

The following standard abbreviations are used in the Examples and Comparative Examples: "CHDM" stands for cyclohexanedimethanol, "MGE" stands for monoglycidyl ethers, DGE stands for "diglycidyl ethers", DETA stands for diethylenetriamine, "GC" stands for gas chromatography (chromatographic); "EEW" stands for epoxide equivalent weight; "DI" stands for deionized; "eq" stands for equivalent(s); "wt" stands for weight(s); "vol" stands for volume(s); "min" stands for minute(s); "hr" stands for hour(s); "g" stands for gram(s); "mL" stands for milliliter(s); "L" stands for liter(s); "LPM" stands for liter(s) per minute; "μm" stands for micrometer(s); "mm" stands

for millimeter(s); “m” stands for meter(s); “cc” stands for cubic centimeter(s); “g/m³” stands for gram(s) per cubic centimeter; and “mPa-s” stands for millipascals-seconds.

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

5 Viscosity and Density

Viscosity and density were determined on a Stabinger Viscometer (Model SVM 3000, Anton Paar) at 25°C.

Percent Epoxide / Epoxide Equivalent Weight Analysis

A standard titration method was used to determine percent epoxide in the various epoxy resins [Jay, R.R., “Direct Titration of Epoxy Compounds and Aziridines”, Analytical Chemistry, 36, 3, 667-668 (March, 1964).] In the present adaptation of the above standard titration method, the carefully weighed sample (sample weight ranges from 0.17 g - 0.25 g) was dissolved in dichloromethane (15 mL) followed by the addition of tetraethylammonium bromide solution in acetic acid (15 mL). The resultant solution treated with 3 drops of crystal violet indicator (0.1 % wt/vol in acetic acid) was titrated with 0.1 N perchloric acid in acetic acid on a Metrohm 665 Dosimat titrator (Brinkmann). Titration of a blank consisting of dichloromethane (15 mL) and tetraethylammonium bromide solution in acetic acid (15 mL) provided correction for solvent background. Percent epoxide and EEW were calculated using the following equations:

$$\begin{aligned} \% \text{ Epoxide} &= \frac{[(\text{mL titrated sample}) - (\text{mL titrated blank})] (0.4303)}{(\text{g sample titrated})} \\ \text{EEW} &= \frac{4303}{\% \text{ epoxide}} \end{aligned}$$

Gas Chromatographic Analysis

In the general method, a Hewlett Packard 5890 Series II Plus gas chromatograph was employed using a DB-1 capillary column (61.4 m by 0.25 mm with a 0.25 µm film thickness, Agilent). The column was maintained in the chromatograph oven at a 50 °C initial temperature. Both the injector inlet and flame ionization detector were maintained at 300 °C. Helium carrier gas flow through the column was maintained at 1.1 mL per min. For the analyses of the epoxy resins and distillation cuts from the epoxy resins, an initial 50 °C oven temperature with heating at 12 °C per min to a final temperature of 300 °C was employed. A GC analysis provides a measure of components in area %.

Samples for GC analysis were prepared by collection of a 0.5 mL aliquot of the slurry product from the epoxidation and addition to a vial containing 1 mL of acetonitrile. After shaking to mix, a portion of the slurry in acetonitrile was loaded into a 1 mL syringe (Norm-Ject, all polypropylene / polyethylene, Henke Sass Wolf GmbH) and
5 passed through a syringe filter (Acrodisc CR 13 with 0.2 μ m PTFE membrane, Pall Corporation, Gelman Laboratories) to remove inorganic any insoluble debris. Samples of the distillation cuts were dissolved in acetonitrile directly analyzed without filtration of the sample.

Differential Scanning Calorimetry

10 For analysis of curing of the thermosettable blends of an epoxy resin with a curing agent and of the T_g of a cured sample, a DSC 2910 Modulated DSC (TA Instruments) was employed. A heating rate of 7 °C/min from 0 °C to 250 °C was used under a stream of nitrogen flowing at 35 cc/min. Each sample analyzed for curing was contained in an aluminum pan and loosely covered (not sealed) with an aluminum lid. Each
15 cured sample for analysis of T_g was contained in an open aluminum pan using the aforementioned parameters. The respective sample weight tested is given with the results obtained.

Comparative Example A - Preparation of CHDM Epoxy Resin from Azeotropic Epoxidation Process and Fractional Vacuum Distillation

20 A series of azeotropic epoxidations of cis- and trans-1,4-CHDM were performed and the epoxy resin products combined to provide a master batch. A 5 L, 5 neck, glass, round bottom reactor was employed for all azeotropic epoxidations. The reactor was equipped with a high efficiency condenser attached to a water separator which in turn was attached to the reactor. A ground glass stopper on the side of the water
25 separator was used for filling with epichlorohydrin. The condenser was maintained at 0 °C via re-circulating ethylene glycol-water coolant from a refrigeration unit. The condenser was capped with a fitting for attachment to the vacuum line. A needle valve was placed in the vacuum line to the condenser to regulate the vacuum to the reactor. A vacuum pump was employed along with a liquid nitrogen trap and an in-line digital thermal
30 conductivity vacuum gauge. A nitrogen line was attached to the reactor via a fitting with a needle valve in the line to regulate nitrogen feed. The reactor was additionally equipped with a thermometer and controller which monitored internal reactor temperature and provided heating via a heating mantle placed under the reactor. The stirrer assembly

consisted of a glass shaft tipped with a 6 inch (15 cm) long poly(tetrafluoroethylene) paddle driven by a variable speed motor and a glass bearing with an internal poly(tetrafluoroethylene) sleeve and saddle. A side arm vented addition funnel was filled with the aqueous sodium hydroxide used in the respective epoxidations, sealed with a
5 ground glass stopped and then attached to the reactor.

In a representative azeotropic epoxidation, the reactor was charged with molten cis- and trans-1,4-CHDM (432.63 g, 3.0 moles, 6.0 hydroxyl eq), epichlorohydrin (1110.24 g, 12.0 moles, 2:1 epichlorohydrin: cis- and trans-1,4-CHDM hydroxyl eq ratio) and 60 % aqueous benzyltriethylammonium chloride (54.53 g, 32.72 g active,
10 0.1436 mole) in the indicated order. Additional epichlorohydrin (583.7 g) was used to fill the water separator. Sodium hydroxide (336 g, 8.4 moles) dissolved in DI water (336 g) was added to a side arm vented addition funnel, sealed with a ground glass stopper, then attached to the reactor. The stirred reactor contents were heated to 50 °C under dynamic overhead nitrogen followed by cessation of nitrogen flow with application of
15 vacuum to the reactor. Once distillation of epichlorohydrin-water azeotrope into the water separator and return feed of epichlorohydrin to the reactor were established, dropwise addition of aqueous sodium hydroxide commenced. The aqueous sodium hydroxide was added over 5 hr at a rate of 2.24 g per min while maintaining the 50 °C temperature in the reactor. During this time, the vacuum in the reactor ranged from -26.45 to -27.48 in Hg.
20 Water present in the organic phase during the azeotropic epoxidation ranged from 1.25 wt % to 1.78 wt %. Post reaction for 30 min was completed under vacuum while maintaining 50 °C. At the completion of the post reaction, the water separator contained epichlorohydrin (156.97 g) containing 1.48 wt % water and water (395.93 g) containing 6.81 wt % epichlorohydrin.

25 The azeotropic epoxidation was sequentially followed by cooling the product slurry to 25 °C, partial neutralization to pH 7.5-8 using 13 wt % aqueous NaH_2PO_4 (58.1 g), mixing with DI water (1.6 L) and removal of the aqueous phase. The organic phase which remained was vacuum distilled to remove unreacted epichlorohydrin. At the completion of the azeotropic epoxidation and epichlorohydrin distillation, the liquid nitrogen vacuum trap
30 contained epichlorohydrin (118.61 g) containing 1.16 wt % water and water (31.59 g) containing 6.55 wt % epichlorohydrin. The resultant crude epoxy resin was diluted with toluene (1 L) and poured from the reactor into a pair of separatory funnels. Washing with DI water (400 mL) was completed 2 times. The washed epoxy resin solution was rotary

evaporated to final conditions of 100 °C and 0.3 mm Hg removing toluene and substantially removing other lights.

GC analysis of the master batch of cycloaliphatic epoxy resin after normalization to remove solvent (acetonitrile) revealed the presence of the individual
 5 compounds in the indicated area % amounts as described in Table I below (all structures are based on molecular weight data obtained from chemical ionization GC-mass spectroscopic analysis).

Table I

<u>COMPONENT</u>	<u>GC Area %</u>
lights (retention times below that of cyclohexanedimethanols)	0.46
cis- and trans-1,4-CHDM	0.90
unknown (retention time between cis- and trans-1,4-CHDM and MGE of cis- and trans-1,4-CHDM)	0.10
MGE of cis- and trans-1,4-CHDM	17.73
unknowns associated with DGE of cis- and trans-1,4-CHDM	0.91
DGE of cis- and trans-1,4-CHDM	65.22
2-propanol, 1-(oxiranylmethoxy)-3-[[4-[(oxiranylmethoxy)methyl]cyclohexyl]methoxy]- and oxirane, 2-[[2-chloro-1-[[[4-[(oxiranylmethoxy)methyl]cyclohexyl]methoxy]methyl]ethoxy]methyl]-	1.61
α -glycol glycidyl ether from partial hydrolysis	0.94
oxirane, 2-[[[4-[[2,3-bis(oxiranylmethoxy)propoxy]methyl]cyclohexyl]methoxy]methyl]- (plus minor amount of monochloro isomeric compounds)	4.37
cyclohexanemethanol, 4-[[2-hydroxy-3-[[4-[(oxiranylmethoxy)methyl]cyclohexyl]methoxy]propoxy]methyl]-	0.63
2-propanol, 1,3-bis[[4-[(oxiranylmethoxy)methyl]cyclohexyl]methoxy]-	3.05
unknowns (retention time between 2-propanol, 1,3-bis[[4-[(oxiranylmethoxy)methyl]cyclohexyl]methoxy]- and oxirane, 2-[[2-[[4-[(oxiranylmethoxy)methyl]cyclohexyl]methoxy]-1-[[[4-[(oxiranylmethoxy)methyl]cyclohexyl]methoxy]methyl]ethoxy]methyl]-)	0.34
oxirane, 2-[[2-[[4-[(oxiranylmethoxy)methyl]cyclohexyl]methoxy]-1-[[[4-[(oxiranylmethoxy)methyl]cyclohexyl]methoxy]methyl]ethoxy]methyl]-	3.74

The α -glycol glycidyl ether from partial hydrolysis of the corresponding glycidyl ether (0.94 area %) consisted of a single component at a 25.29 min retention time.

A portion (1000.34 grams) of the devolatilized epoxy resin was added to a 1 L, 3 neck, glass, round bottom reactor equipped with magnetic stirring and a thermometer
5 for monitoring the pot temperature. A heating mantle placed under the reactor was controlled via a thermocouple placed in the center surface of the heating mantle and interfaced to a digital temperature controller. A one piece integral vacuum jacketed Vigreux distillation column with distillation head was attached to a second section of vacuum jacketed Vigreux distillation column through the respective 24/40 joints on both
10 columns. The coupled pair of distillation columns was then attached to the center port of the reactor. According to the manufacturer, each of the distillation columns nominally provided 9 to 18 theoretical plates depending on the mode of operation. The distillation head was equipped with an overhead thermometer, air cooled condenser, a receiver and a vacuum takeoff. A vacuum pump was employed along with a liquid nitrogen trap and an
15 in-line digital thermal conductivity vacuum gauge. Stirring commenced followed by application of full vacuum then progressively increased heating using a thermostatically controlled heating mantle. A clean receiver was used to collect a distillation cut taken to remove all residual lights and the bulk of the cis- and trans-1,4-CHDM MGE while minimizing removal of significant cis- and trans-1,4-CHDM DGE.

20 A total of 313.27 grams was distilled into the receiver. A total of 661.8 g of cycloaliphatic epoxy resin product remained in the distillation pot. GC analysis after normalization to remove solvent (acetonitrile) revealed the presence of the individual compounds in the indicated area % amounts as described in Table II as follows:

25

30

35

Table II

<u>COMPONENT</u>	<u>GC Area</u> <u>%</u>
MGE of cis- and trans-1,4-CHDM	0.23
unknowns associated with DGE of cis- and trans-1,4-CHDM	0.89
DGE of cis- and trans-1,4-CHDM	76.66
2-propanol, 1-(oxiranylmethoxy)-3-[[4- [(oxiranylmethoxy)methyl]cyclohexyl]methoxy]- and oxirane, 2-[[2-chloro-1-[[4- [(oxiranylmethoxy)methyl]cyclohexyl]methoxy]methyl]ethoxy]methyl]-	2.23
α -glycol glycidyl ether from partial hydrolysis	1.75
oxirane, 2-[[[4-[[2,3- bis(oxiranylmethoxy)propoxy]methyl]cyclohexyl]methoxy]methyl]- (plus minor amount of monochloro isomeric compounds)	6.47
cyclohexanemethanol, 4-[[2-hydroxy-3-[[4- [(oxiranylmethoxy)methyl]cyclohexyl]methoxy]propoxy]methyl]-	0.47
2-propanol, 1,3-bis[[4-[(oxiranylmethoxy)methyl]cyclohexyl]methoxy]-	4.46
oxirane, 2-[[2-[[4-[(oxiranylmethoxy)methyl]cyclohexyl]methoxy]-1-[[[4- [(oxiranylmethoxy)methyl]cyclohexyl]methoxy]methyl]ethoxy]methyl]-	6.84

The α -glycol glycidyl ether from partial hydrolysis of the corresponding glycidyl ether (1.75 area %) consisted of a single component at a 25.28 min retention time.

Titration demonstrated that the epoxy resin had an EEW of 152. The
5 viscosity and density of the epoxy resin were 133.4 mPa-s and 1.087 g/m³, respectively, at 25 °C.

Example 1 - Preparation of Partially Hydrolyzed CHDM Epoxy Resin from Azeotropic Epoxidation Process and Fractional Vacuum Distillation

An azeotropic epoxidation of cis- and trans-1,4-CHDM was performed using
10 the equipment delineated in Comparative Example A. In the azeotropic epoxidation, the reactor was charged with molten cis- and trans-1,4-CHDM (432.63 g, 3.0 moles, 6.0 hydroxyl eq), epichlorohydrin (1110.24 g, 12.0 moles, 2:1 epichlorohydrin: cis- and trans-1,4-CHDM hydroxyl eq ratio) and 60 % aqueous benzyltriethylammonium chloride (54.53 g, 32.72 g active, 0.1436 mole) in the indicated order. Additional epichlorohydrin
15 (588.2 g) was used to fill the water separator. Sodium hydroxide (288 g, 7.2 moles) dissolved in DI water (288 g) was added to a side arm vented addition funnel, sealed with a

ground glass stopper, then attached to the reactor. The stirred reactor contents were heated to 55 °C under dynamic overhead nitrogen followed by cessation of nitrogen flow with application of vacuum to the reactor. Once distillation of epichlorohydrin-water azeotrope into the water separator and return feed of epichlorohydrin to the reactor were established, dropwise addition of aqueous sodium hydroxide commenced. The aqueous sodium hydroxide was added over 5 hr at a rate of 1.92 g per min while maintaining the 55 °C temperature in the reactor. During this time, the vacuum in the reactor ranged from -25.52 in Hg to -27.45 in Hg. Water present in the organic phase during the azeotropic epoxidation ranged from 0.51 wt % to 1.79 wt %. Post reaction for 30 min was completed under vacuum while maintaining 55 °C. At the completion of the post reaction, the water separator contained epichlorohydrin (166.6 g) containing 1.29 wt % water and water (395.1 g) containing 6.58 wt % epichlorohydrin.

The azeotropic epoxidation was sequentially followed by cooling the product slurry to 25 °C, over neutralization to pH 6 using excess 13 wt % aqueous NaH_2PO_4 (277.0 g), mixing with DI water (1.2 L) and removal of the aqueous phase. The organic phase which remained was vacuum distilled to remove unreacted epichlorohydrin. At the completion of the azeotropic epoxidation and epichlorohydrin distillation, the liquid nitrogen vacuum trap contained epichlorohydrin saturated with water (107.4 g) and water saturated with epichlorohydrin (29.4 g). The resultant crude epoxy resin was diluted with toluene (1 L) and poured from the reactor into a pair of separatory funnels. Washing with DI water (400 mL) was completed 2 times. The washed epoxy resin solution was rotary evaporated to final conditions of 100 °C and 0.5 mm Hg removing toluene and substantially removing other lights.

GC analysis of the cycloaliphatic epoxy resin after normalization to remove solvent (acetonitrile) revealed the presence of the individual compounds in the indicated area % amounts as described in Table III as follows:

Table III

<u>COMPONENT</u>	<u>GC Area %</u>
lights (retention times below that of cyclohexanedimethanols)	1.21
cis- and trans-1,4-CHDM	0.91
unknown (retention time between cis- and trans-1,4-CHDM and MGE of cis- and trans-1,4-CHDM)	0.14
MGE of cis- and trans-1,4-CHDM	17.48
unknowns associated with DGE of cis- and trans-1,4-CHDM	1.31
DGE of cis- and trans-1,4-CHDM	63.64
2-propanol, 1-(oxiranylmethoxy)-3-[[4-[(oxiranylmethoxy)methyl]cyclohexyl]methoxy]- and oxirane, 2-[[2-chloro-1-[[4-[(oxiranylmethoxy)methyl]cyclohexyl]methoxy]methyl]ethoxy]methyl]-	1.53
alpha-glycol glycidyl ethers from partial hydrolysis	3.10
oxirane, 2-[[[4-[[2,3-bis(oxiranylmethoxy)propoxy]methyl]cyclohexyl]methoxy]methyl]- (plus minor amount of monochloro isomeric compounds)	4.09
cyclohexanemethanol, 4-[[2-hydroxy-3-[[4-[(oxiranylmethoxy)methyl]cyclohexyl]methoxy]propoxy]methyl]-	0.31
2-propanol, 1,3-bis[[4-[(oxiranylmethoxy)methyl]cyclohexyl]methoxy]-	2.60
unknowns (retention time between 2-propanol, 1,3-bis[[4-[(oxiranylmethoxy)methyl]cyclohexyl]methoxy]-and oxirane, 2-[[2-[[4-[(oxiranylmethoxy)methyl]cyclohexyl]methoxy]-1-[[[4-[(oxiranylmethoxy)methyl]cyclohexyl]methoxy]methyl]ethoxy]methyl]-)	0.41
oxirane, 2-[[2-[[4-[(oxiranylmethoxy)methyl]cyclohexyl]methoxy]-1-[[[4-[(oxiranylmethoxy)methyl]cyclohexyl]methoxy]methyl]ethoxy]methyl]-	3.27

The α -glycol glycidyl ethers from partial hydrolysis of the corresponding glycidyl ethers (3.10 area %) consisted of 3 major components at the following retention

times and amounts: 25.05 min at 0.71 area %, 25.30 min at 1.76 area %, and 25.54 min at 0.17 area %.

A portion (654.78 grams) of the devolatilized epoxy resin was added to a 1 L, 3 neck, glass, round bottom reactor and distilled to remove all residual lights and the bulk of the cis- and trans-1,4-CHDM MGE while minimizing removal of significant cis- and trans-1,4-CHDM DGE. A total of 206.39 grams was distilled into the receiver. A total of 406.07 g of cycloaliphatic epoxy resin product remained in the distillation pot. GC analysis after normalization to remove solvent (acetonitrile) revealed the presence of the individual compounds in the indicated area % amounts as described in Table IV as follows:

Table IV

COMPONENT	GC Area %
MGE of cis- and trans-1,4-CHDM	0.21
unknowns associated with DGE of cis- and trans-1,4-CHDM	0.16
DGE of cis- and trans-1,4-CHDM	74.89
2-propanol, 1-(oxiranylmethoxy)-3-[[4-[(oxiranylmethoxy)methyl]cyclohexyl]methoxy]- and oxirane, 2-[[2-chloro-1-[[4-[(oxiranylmethoxy)methyl]cyclohexyl]methoxy]methyl]ethoxy]methyl]-	1.90
α -glycol glycidyl ethers from partial hydrolysis	5.11
oxirane, 2-[[4-[[2,3-bis(oxiranylmethoxy)propoxy]methyl]cyclohexyl]methoxy]methyl]- (plus minor amount of monochloro isomeric compounds)	5.77
cyclohexanemethanol, 4-[[2-hydroxy-3-[[4-[(oxiranylmethoxy)methyl]cyclohexyl]methoxy]propoxy]methyl]-	0.52
2-propanol, 1,3-bis[[4-[(oxiranylmethoxy)methyl]cyclohexyl]methoxy]-	4.60
unknowns (retention time between 2-propanol, 1,3-bis[[4-[(oxiranylmethoxy)methyl]cyclohexyl]methoxy]- and oxirane, 2-[[2-[[4-[(oxiranylmethoxy)methyl]cyclohexyl]methoxy]-1-[[4-[(oxiranylmethoxy)methyl]cyclohexyl]methoxy]methyl]ethoxy]methyl]-)	0.70
oxirane, 2-[[2-[[4-[(oxiranylmethoxy)methyl]cyclohexyl]methoxy]-1-[[4-[(oxiranylmethoxy)methyl]cyclohexyl]methoxy]methyl]ethoxy]methyl]-	6.14

The α -glycol glycidyl ethers from partial hydrolysis of the corresponding glycidyl ethers (5.11 area %) consisted of 3 major components at the following retention times and amounts: 25.07 min at 1.09 area %, 25.34 min at 2.80 area %, and 25.56 min at 0.66 area %. Eight minor components made up the remaining area.

Titration demonstrated an EEW of 146. Viscosity and density were 73.5 mPa-s and 1.082 g/m³, respectively, at 25 °C.

Comparative Example B – Curing of CHDM Epoxy Resin with DETA

A portion (8.0351 g, 0.0528 epoxide eq) of the cycloaliphatic epoxy resin
5 from the azeotropic epoxidation process and fractional vacuum distillation of Comparative Example 1 and DETA (1.0885 g, 0.0528 NH eq) were added to a glass bottle and vigorously stirred together. A portion (9.6 mg) of the homogeneous solution was removed for DSC analysis. An exotherm attributed to curing was observed with a 49.4 °C onset, 112.6 °C maximum, and a 191.0 °C endpoint accompanied by an enthalpy of 630.9 J/g.
10 The cured product recovered from the DSC analysis was a transparent, rigid solid with a light yellow color.

The remaining portion of the curable blend was added to an aluminum dish and cured in an oven using following schedule: 1 hr at 75 °C, 1 hr at 100 °C, 1 hr at 125 °C, and 1 hr at 150 °C. A portion (37.10 mg) of the transparent, light yellow colored casting
15 was removed for DSC analysis. A Tg of 63.0 °C was observed, with no indication of further curing or exothermic decomposition observed up to the 250 °C DSC analysis temperature. A second scan using the aforementioned conditions revealed a Tg of 60.2 °C. A third scan using the aforementioned conditions revealed a Tg of 58.8 °C.

Example 2 - Curing of Partially Hydrolyzed CHDM Epoxy Resin with DETA

A portion (8.2366 g, 0.0566 epoxide eq) of the partially hydrolyzed cycloaliphatic epoxy resin from the azeotropic epoxidation process and fractional vacuum distillation of Example 1 and DETA (1.1675 g, 0.0566 NH eq) were added to a glass bottle and vigorously stirred together. A portion (9.6 mg) of the homogeneous solution was removed for DSC analysis. An exotherm attributed to curing was observed with a 38.2 °C
25 onset, 110.4 °C maximum, and a 185.7 °C endpoint accompanied by an enthalpy of 643.0 J/g. The cured product recovered from the DSC analysis was a transparent, rigid solid with a light yellow color.

The remaining portion of the curable blend was added to an aluminum dish and cured in an oven using following schedule given in Comparative Example 2. A portion
30 (39.50 mg) of the transparent, light yellow colored casting was removed for DSC analysis. A Tg of 62.8 °C was observed, with no indication of further curing or exothermic decomposition observed up to the 250 °C DSC analysis temperature. A second scan using

the aforementioned conditions revealed a Tg of 59.2 °C. A third scan using the aforementioned conditions revealed a Tg of 62.0 °C.

A summary of the results obtained in Examples 1 and 2; and Comparative Examples A and B are described in Table V as follows:

5

Table V

Example	Onset to Cure (° C)	Cure Maximum (° C)	Cure Endpoint (° C)	Enthalpy (J/g)	Tg* (° C)	Viscosity (mPa-s @ 25 °C)
Example 1						73.5
Comparative Example A						133.4
Example 2	38.2	110.4	185.7	643.0	62.8, 59.2, 62.0	
Comparative Example B	49.4	112.6	191.0	630.9	63.0, 60.2, 58.8	

*Tg's determined on 1st, 2nd, and 3rd scans respectively

The results summarized in Table V above demonstrate significant reduction in onset to cure and higher reactivity on cure for the partially hydrolyzed CHDM epoxy resin of Example 2 containing 5.11 area % α -glycol glycidyl ethers versus the CHDM epoxy resin of Comparative Example B containing only 1.75 area % α -glycol glycidyl ethers. The results were achieved without deleterious effect on the Tg of the thermoset. The partially hydrolyzed CHDM epoxy resin of Example 1 provided significantly lower viscosity versus the CHDM epoxy resin of Comparative Example A.

15 Example 3 – Reactivity of Partially Hydrolyzed CHDM Epoxy Resin Containing 5.55 Area % α -Glycol Glycidyl Ethers

An epoxy resin of cis- and trans-1,4-CHDM was fractionally vacuum distilled to provide epoxy resin of cis- and trans-1,4-CHDM containing 5.55 area % α -glycol glycidyl ethers. The GC analysis obtained in this Example 3 is described in Table VI as follows:

20

Table VI

<u>COMPONENT</u>	<u>GC Area %</u>
minor peaks between CHDM retention time and CHDM MGE	0.07
monoglycidyl ether of cis- and trans-1,4-cyclohexanedimethanol (CHDM MGE)	0.40
minor peaks between CHDM MGE and CHDM DGE	0.79
diglycidyl ether of cis- and trans-1,4-cyclohexanedimethanol (CHDM DGE)	62.88
2-propanol, 1-(oxiranylmethoxy)-3-[[4- [(oxiranylmethoxy)methyl]cyclohexyl]methoxy]- and oxirane, 2-[[2-chloro-1- [[[4-[(oxiranylmethoxy)methyl]cyclohexyl]methoxy]methyl]ethoxy]methyl]-	4.26
α -glycol glycidyl ethers from partial hydrolysis	5.55
oxirane, 2-[[[4-[[2,3- bis(oxiranylmethoxy)propoxy]methyl]cyclohexyl]methoxy]methyl]- (plus minor amount of monochloro isomeric compounds)	2.16
cyclohexanemethanol, 4-[[2-hydroxy-3-[[4- [(oxiranylmethoxy)methyl]cyclohexyl]methoxy]propoxy]methyl]-	0.17
minor peaks	0.11
2-propanol, 1,3-bis[[4-[(oxiranylmethoxy)methyl]cyclohexyl]methoxy]-	7.21
unknown cluster of isomers	0.87
oxirane, 2-[[2-[[4-[(oxiranylmethoxy)methyl]cyclohexyl]methoxy]-1-[[[4- [(oxiranylmethoxy)methyl]cyclohexyl]methoxy]methyl]ethoxy]methyl]-	14.56
minor higher retention time oligomer peaks	0.97

Titration of a portion of the epoxy resin of cis- and trans-1,4-CHDM containing 5.55 area % α -glycol glycidyl ethers gave an EEW of 163. A portion (7.5583 g, 0.0465 epoxide eq) of the CHDM epoxy resin and DETA (0.9591 g, 0.0465 NH eq) were added to a glass bottle and vigorously stirred together. A portion (13.2 mg) of the homogeneous solution was removed for DSC analysis. An exotherm attributed to curing was observed with a 36.7 °C onset, 107.2 °C maximum, and a 186.6 °C endpoint accompanied by an enthalpy of 544.0 J/g. The cured product recovered from the DSC analysis was a transparent, rigid solid with a light yellow color.

The remaining portion of the curable blend was added to an aluminum dish and cured in an oven using following schedule: 1 hr at 75 °C, 1 hr at 100 °C, 1 hr at 125 °C, and 1 hr at 150 °C. A portion (34.10 mg) of the transparent, light yellow colored casting

was removed for DSC analysis. A Tg of 53.6 °C was observed, with no indication of further curing or exothermic decomposition observed up to the 200 °C DSC analysis temperature. A second scan using the aforementioned conditions revealed a Tg of 54.2 °C. A third scan using the aforementioned conditions revealed a Tg of 54.6 °C.

5 Comparative Example C – Reactivity of CHDM Epoxy Resin Containing 2.26 Area % α -Glycol Glycidyl Ethers

An epoxy resin of cis- and trans-1,4-CHDM was fractionally vacuum distilled to provide epoxy resin of cis- and trans-1,4-CHDM containing 2.26 area % α -glycol glycidyl ethers. The GC analysis obtained in this Comparative Example C is
10 described in Table VII as follows:

Table VII

<u>COMPONENT</u>	<u>GC Area %</u>
minor peaks between CHDM retention time and CHDM MGE	0.18
monoglycidyl ether of cis- and trans-1,4-cyclohexanedimethanol (CHDM MGE)	0.38
minor peaks between CHDM MGE and CHDM DGE	0.83
diglycidyl ether of cis- and trans-1,4-cyclohexanedimethanol (CHDM DGE)	61.03
2-propanol, 1-(oxiranylmethoxy)-3-[[4- [(oxiranylmethoxy)methyl]cyclohexyl]methoxy]- and oxirane, 2-[[2-chloro-1-[[[4- [(oxiranylmethoxy)methyl]cyclohexyl]methoxy]methyl]ethoxy]methyl]-	2.53
α -glycol glycidyl ethers from partial hydrolysis	2.26
oxirane, 2-[[[4-[[2,3- bis(oxiranylmethoxy)propoxy]methyl]cyclohexyl]methoxy]methyl]- (plus minor amount of monochloro isomeric compounds)	3.24
cyclohexanemethanol, 4-[[2-hydroxy-3-[[4- [(oxiranylmethoxy)methyl]cyclohexyl]methoxy]propoxy]methyl]-	0.27
minor peaks	0.17
2-propanol, 1,3-bis[[4-[(oxiranylmethoxy)methyl]cyclohexyl]methoxy]-	7.55
unknown cluster of isomers	0.50
oxirane, 2-[[2-[[4-[(oxiranylmethoxy)methyl]cyclohexyl]methoxy]-1-[[[4- [(oxiranylmethoxy)methyl]cyclohexyl]methoxy]methyl]ethoxy]methyl]-	18.77
minor higher retention time oligomer peaks	2.29

- Titration of a portion of a portion of the epoxy resin of cis- and trans-1,4-CHDM containing 2.26 area % α -glycol glycidyl ethers gave an EEW of 167. A portion (7.5259 g, 0.0451 epoxide eq) of the CHDM epoxy resin and DETA (0.9307 g, 0.0451 NH eq) were added to a glass bottle and vigorously stirred together. A portion (10.1 mg) of the homogeneous solution was removed for DSC analysis. An exotherm attributed to curing was observed with a 47.9 °C onset, 108.0 °C maximum, and a 183.4 °C endpoint accompanied by an enthalpy of 508.6 J/g. The cured product recovered from the DSC analysis was a transparent, rigid solid with a light yellow color.

The remaining portion of the curable blend was added to an aluminum dish and cured in an oven using following schedule: 1 hr at 75 °C, 1 hr at 100 °C, 1 hr at 125 °C, and 1 hr at 150 °C. A portion (39.3 mg) of the transparent, light yellow colored casting was removed for DSC analysis. A Tg of 56.6 °C was observed, with no indication of further curing or exothermic decomposition observed up to the 200 °C DSC analysis temperature. A second scan using the aforementioned conditions revealed a Tg of 57.5 °C. A third scan using the aforementioned conditions revealed a Tg of 55.7 °C.

A summary of the results obtained in Example 3 and Comparative Examples C are described in Table VIII as follows:

10

Table VIII

Example	Onset to Cure (°C)	Cure Maximum (°C)	Cure Endpoint (°C)	Enthalpy (J/g)	Tg (°C)
Example 3	36.7	107.2	186.6	544.0	53.6, 54.2, 54.6
Comparative Example C	47.9	108.0	183.4	508.6	56.6, 57.5, 55.7

The results summarized in Table VIII above demonstrate significant reduction in onset to cure and higher reactivity on cure for the partially hydrolyzed CHDM epoxy resin of Example 3 containing 5.55 area % α -glycol glycidyl ethers versus the CHDM epoxy resin of Comparative Example C containing only 2.26 area % α -glycol glycidyl ethers. The results were achieved without deleterious effect on the Tg of the thermoset.

15

CLAIMS:

1. A partially hydrolyzed aliphatic or cycloaliphatic epoxy resin composition comprising a partially hydrolyzed aliphatic or cycloaliphatic epoxy resin composition having an α -glycol moiety content of from about 2.3 area percent to about 25 area percent of the total components comprising the epoxy resin composition; wherein the area percent is measured by gas chromatographic analysis.

2. The epoxy resin composition of claim 1, wherein the aliphatic or cycloaliphatic epoxy resin is an epoxy resin of 1,4-cyclohexanedimethanol or a mixture of cis- and trans-1,3- and 1,4-cyclohexanedimethanol.

3. A process for preparing a partially hydrolyzed aliphatic or cycloaliphatic epoxy resin composition including the steps of:

(I) producing an aliphatic or cycloaliphatic epoxy resin composition by reacting a mixture of:

- (a) an aliphatic or cycloaliphatic hydroxyl containing material,
- (b) an epihalohydrin,
- (c) a basic acting substance,
- (d) a non-Lewis acid catalyst, and
- (e) optionally, a solvent, forming an epoxy resin composition;

(II) subjecting the aliphatic or cycloaliphatic epoxy resin composition produced in step (I) above to a separation process to recover the aliphatic or cycloaliphatic the epoxy resin composition; and

(III) hydrolyzing at least a portion of the aliphatic or cycloaliphatic epoxy resin composition to form a partially hydrolyzed aliphatic or cycloaliphatic epoxy resin composition having an α -glycol moiety content of from about 2.3 area percent to about 25 area percent of the total components comprising the epoxy resin composition; wherein the area percent is measured by gas chromatographic analysis.

4. The process of claim 2, wherein the hydrolyzing step includes adding a neutralizing agent to the aliphatic or cycloaliphatic epoxy resin composition.

5. The process of claim 4, wherein the neutralizing agent is sodium dihydrogen phosphate.

6. The process of claim 4, wherein the amount of the neutralizing agent used is in excess of that needed to neutralize the aliphatic or cycloaliphatic epoxy resin composition.

7. A curable epoxy resin composition comprising: (I) a partially hydrolyzed aliphatic or cycloaliphatic epoxy resin composition of claim 1; and (II) a curing agent.

8. The curable composition of claim 7, wherein the curing agent is an amine curing agent and the concentration of the amine curing agent is an equivalent ratio of amine NH:epoxy of from about 0.5:1 to about 1.5:1.

9. The curable composition of claim 7, including further a catalytic curing material.

10. The curable composition of claim 7, including further a second epoxy compound separate and different from the aliphatic and cycloaliphatic epoxy resin component (I), a curing catalyst; a filler, a reactive diluent, a flexibilizing agent, a processing aide, a toughening agent, or a mixture thereof.

11. A process for preparing a curable composition comprising admixing: (I) a partially hydrolyzed aliphatic or cycloaliphatic epoxy resin composition of claim 1; and (II) a curing agent.

12. A cured thermoset article prepared from the curable composition of claim 7.

13. A process for preparing a thermoset comprising:
(A) providing a mixture of: (I) a partially hydrolyzed aliphatic or cycloaliphatic epoxy resin composition of claim 1; and (II) a curing agent; and
(B) curing the curable composition of step (A).

14. A cured thermoset article prepared from the composition of claim 1.

15. A coating prepared from the curable composition of claim 7.

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G59/14
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

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)

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	WO 95/11266 A1 (DOW CHEMICAL CO [US]) 27 April 1995 (1995-04-27) cited in the application examples 1-4	1
X	----- US 4 404 335 A (CAVITT MICHAEL B [US]) 13 September 1983 (1983-09-13) cited in the application examples 1-5	1
A	----- US 3 632 836 A (WALKER EDDIE BOB) 4 January 1972 (1972-01-04) cited in the application example 1 -----	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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

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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

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"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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