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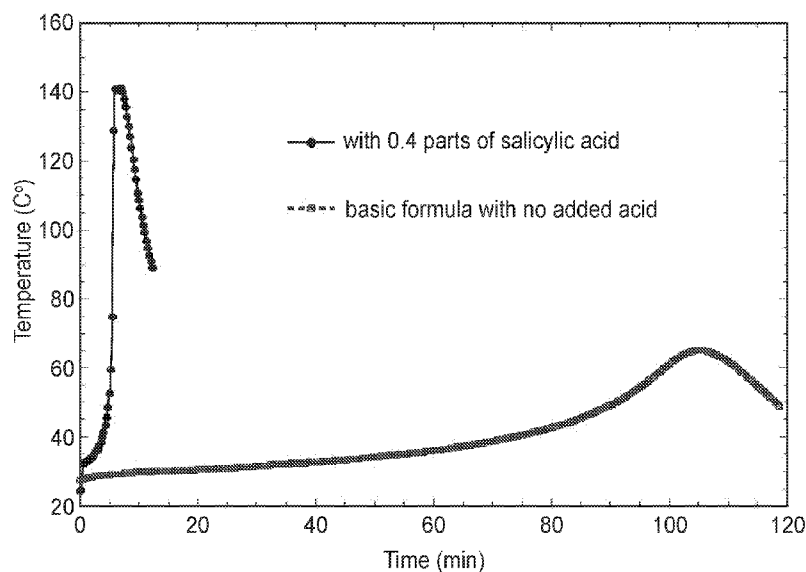
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[Continued on next page]

(54) **Title:** CURABLE EPOXY COMPOSITIONS AND METHODS FOR ACCELERATING THE CURING OF EPOXY COMPOSITIONS

**FIG. 1**

(57) **Abstract:** Methods for controlling the cure time of curable epoxy compositions include selecting an aromatic carboxylic acid accelerator that has a log P value in the range of from -0.5 to 4.0, where P is the partition coefficient. The curable epoxy compositions are essentially free of water and include an aromatic epoxy resin, an amine curing agent and the accelerator. When the amine curing agent is an aliphatic or cycloaliphatic amine, the curable composition cures in less than 1 hour at room temperature. When the amine curing agent is an aromatic amine, heat is applied to effect curing.



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CURABLE EPOXY COMPOSITIONS AND METHODS FOR ACCELERATING THE CURING OF EPOXY COMPOSITIONS

Field of the Disclosure

5 The present disclosure relates to curable thermoset compositions, especially epoxy-based compositions, and methods for accelerating the curing of the thermoset compositions.

Background

10 A wide variety of thermoset compositions have proven useful in a wide variety of applications. Thermoset compositions are those materials that irreversibly cures to form hard or rigid materials. This is in contrast to a thermoplastic material that becomes pliable or moldable above a specific temperature and solidifies upon cooling, and is able to repeat these processes, that is to say the material upon cooling is able to be reheated to become
15 pliable or moldable and solidify upon cooling. Thermoset compositions are used in a number of different applications including surface protection, bonding, and the like.

 There are typically two types of thermoset compositions, frequently referred to as “one-part” or “two-part” formulations.

 In two-part formulations, as the name implies, there are two different reaction
20 mixtures that are mixed together and cured to form the thermoset matrix. Typically each of the two parts contains a reactive material that when mixed with the other part reacts to form the thermoset matrix. One or both of the two parts may also contain additional additives such as fillers, property modifiers, and the like. The two parts are kept separate to prevent premature reaction and thus an advantage of two-part compositions is that as
25 long as the two parts are kept separate the composition is stable. There are a number of drawbacks of two-part compositions including the need to store, ship, and handle the two separate components separately, and the need to control the mixing process. Mixing must be controlled so as to provide the proper ratio of reactive components and also to ensure that a generally homogeneous mixture is formed, because once curing takes place an
30 irreversible matrix is formed. Depending upon the nature of the materials involved, control of mixing can be a complex undertaking.

One-part compositions on the other hand have all of the components already mixed together into a single composition. Thus the one-part composition need only be dispensed and cured without the need for carefully controlled mixing. However, since the components in the one-part composition are by nature reactive with each other, there are drawbacks to this type of composition as well. Depending upon the reactivity of the reactive components, the one-part formulation may either have a relatively short shelf life or the composition might need to be stored at a reduced temperature (in a refrigerator or freezer for example). Some one-part compositions are relatively stable at ambient temperatures, but may require high temperatures to fully cure, temperatures that may be too high for use in certain applications.

Epoxy resins are a commonly used class of thermoset materials. The epoxy resins are often cured with a curing agent such as an alcohol or amine which ring opens the epoxy ring forming a rigid matrix. Epoxy resins are supplied both in one-part and two-part compositions. Typically two-part compositions cure at a relatively low temperature, even room temperature and typically have the epoxy resin in one-part and an amine or other curing agent in the other part. One-part epoxy resin compositions are available in a wide variety of forms such as films, pastes, and powders. Examples of one-part epoxy compositions include epoxy adhesive films used for example in aerospace applications, epoxy paste adhesives, and epoxy powders used as protective coatings for rebar, pipes and the like.

Epoxy compositions also have some detrimental features. A common detriment of epoxy compositions, and thermoset compositions in general, is that because the cured matrices are rigid, they tend to be brittle. Brittle materials are ones that have hardness and rigidity but little tensile strength, breaking or shattering easily. Additionally, the curing of epoxy compositions can often require either relatively high temperatures, relatively long cure times, or both. A great deal of research has been invested into addressing these issues, including the development of new epoxy resins, new curing agents, and property modifying agents used to modify the brittleness.

A number of references teach epoxy resin curing systems that include accelerators. Among these references are US Patent No. 3,639,928 which discloses an accelerator combination of N-(3-aminopropyl)piperazine and salicylic acid that is synergistic for accelerating the cure of polyglycidyl ether of a polyhydric phenol cured with a

polyoxyalkylenepolyamine. The journal article "Accelerated Amine Curing of Epoxy Resins" by L.J. Gough and I.T. Smith in the *Journal of the Oil and Colour Chemists' Association*, Volume 43, 1960, pages 409-418, describes studies of the acceleration of the reaction between an amine curing agent and a low molecular weight epoxy resin.

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Summary

Disclosed herein are curable compositions, articles prepared from curable compositions, and methods for controlling the cure time of curable compositions.

10 Among the embodiments disclosed herein are curable compositions comprising an aromatic epoxy resin, an aliphatic or cycloaliphatic amine curing agent, and an accelerator comprising an aromatic carboxylic acid compound. The curable compositions are essentially free of water and the curing time of the curable is less than 1 hour at room temperature.

15 In other embodiments, the curable composition comprises an aromatic epoxy resin, an aromatic amine curing agent, and an accelerator comprising an aromatic carboxylic acid compound, where the curable composition is essentially free of water, and the curing temperature of the curable composition is 50-100°C less than for the same composition in the absence of the accelerator.

20 Also disclosed herein are two-part curable epoxy compositions comprising a first part comprising an aromatic epoxy resin, a second part comprising an aliphatic or cycloaliphatic amine curing agent, and an accelerator comprising an aromatic carboxylic acid compound, that is located either in the first part or the second part. The first part and the second part are essentially free from water, and the two parts, when mixed, form a curable composition with a curing time that is less than 1 hour at room temperature.

25 Also disclosed herein are methods for controlling the cure time of curable epoxy compositions. These methods comprise providing a curable mixture that is essentially free of water comprising an aromatic epoxy resin, and an aliphatic or cycloaliphatic amine curing agent, and selecting an accelerator comprising an aromatic carboxylic acid, wherein the accelerator has an log P value in the range of from -0.5 to 4.0, wherein P is the
30 partition coefficient, adding the accelerator to either the aromatic epoxy resin, aliphatic or cycloaliphatic amine curing agent, and mixing the aromatic epoxy resin, aliphatic amine curing agent and accelerator to form a curable composition. The mixed

curable composition is permitted to cure at room temperature, where the curing time of the curable composition is less than 1 hour.

Articles are also disclosed, the articles comprising a substrate with a first major surface and a second major surface, and a coating on the at least a portion of the second major surface of the substrate. The coating comprises a cured layer of a curable composition, where the curable composition comprises an aromatic epoxy resin, an aliphatic or cycloaliphatic amine curing agent, and an accelerator comprising an aromatic carboxylic acid compound, where the curable composition is essentially free of water, and the curing time of the curable composition is less than 1 hour at room temperature.

Brief Description of the Drawings

The present application may be more completely understood in consideration of the following detailed description of various embodiments of the disclosure in connection with the accompanying drawings.

Figure 1 is a graph showing exotherm traces of various examples and comparative examples of this disclosure.

Figure 2 is a graph showing exotherm traces of various examples of this disclosure.

Figure 3 is a graph plotting the Time to Maximum Exotherm Temperature vs the Log of the Partition Coefficient of the accelerator.

Figure 4 is a graph plotting the Time to Maximum Exotherm Temperature vs the pKa of the accelerator.

Figure 5 is a graph showing exotherm traces of various examples of this disclosure.

Figure 6 is a graph showing exotherm traces of various examples of this disclosure.

Figure 7 is a graph showing exotherm traces of various examples of this disclosure.

Figure 8 is a graph showing exotherm traces of various examples of this disclosure.

Figure 9 is a graph showing exotherm traces of various examples and comparative examples of this disclosure.

In the following description of the illustrated embodiments, reference is made to the accompanying drawings, in which is shown by way of illustration, various embodiments in which the disclosure may be practiced.

Detailed Description

Thermoset compositions, particularly thermoset coatings, have proven useful in a wide variety of applications including surface protection, bonding, and the like. Epoxy resin compositions are a particularly useful class of thermoset materials that have many desirable features including high internal strength and thus provide durable protective coatings and adhesives with high adhesion to a wide range of substrates. However, cured epoxy coatings tend to be brittle and also in order to form a coating with high temperature stability, often the resins need to be cured at very high temperatures and for long times, making them unsuitable for many substrates that cannot sustain the curing conditions.

Therefore, curable epoxy resin systems which can be cured at relatively lower temperatures and for shorter times and yet have high temperature stability are desirable and are still being sought.

Typically curable epoxy resin systems are used either as “one-part compositions”, meaning that the epoxy resin, curatives, and any property modifying additives are all present together, and “two-part compositions”, meaning that the epoxy resin/change extension agents and curatives are kept separate and mixed immediately prior to use. Each of the composition types has advantages and disadvantages. One part compositions have the advantages of convenience and ease of dispensing, but can have issues with premature curing upon storage. Also, because the curing of epoxy compositions is an exothermic process, if the mass of the one-part composition is relatively large, this premature curing can become self-accelerating and the heat produced can cause fires, or other damage. For this reason one-part compositions are often stored and shipped at reduced temperatures. The disadvantage of two-part compositions is that reactive components must be kept separate until use and then mixed in specific ratios, and upon mixing have a specified pot life (i.e. time after when the mixture is no longer usable) as the curing reaction can begin to occur. This often requires specific dispensing equipment or packaging to not only keep the two parts separate prior to use, but to measure out the precise quantities of each part and to mix them thoroughly. These disadvantages are offset by the convenience of shipping and handling and the ability to store the curable compositions for long periods of time as long as the two parts are kept separate.

In this disclosure two types of curable compositions are described. The first type of curable compositions, are room temperature curable compositions in which acceleration

of the cure means that the curable compositions cure more rapidly at room temperature than the same composition without the accelerant. The second type of curable compositions are ones that cure at elevated temperatures in which acceleration of the cure means that the temperature at which the compositions cure is reduced relative to the temperature of cure for the same composition without the accelerant.

In this disclosure, curable compositions are described that comprise room temperature curable compositions comprising: an aromatic epoxy resin; an aliphatic or cycloaliphatic amine curing agent; and an accelerator comprising an aromatic carboxylic acid compound. The curable composition is essentially free of water, and the curing time of the curable composition is less than 1 hour at room temperature.

The curable compositions can be formulated as two-part compositions. In some embodiments, the composition comprises: a first part comprising an aromatic epoxy resin; and an accelerator comprising an aromatic carboxylic acid compound; and a second part comprising an aliphatic or cycloaliphatic amine curing agent. In other embodiments, the composition comprises: a first part comprising an aromatic epoxy resin; and a second part comprising an aliphatic or cycloaliphatic amine curing agent, and an accelerator comprising an aromatic carboxylic acid compound.

In other embodiments, the curable composition comprises an aromatic epoxy resin, an aromatic amine curing agent, and an accelerator comprising an aromatic carboxylic acid compound. These curable compositions can be formulated as one part formulations as well as two part formulations and in order to cure heat is generally applied. As will be described in more detail below, DSC (Differential Scanning Calorimetry) can be used to study the effect of the accelerator upon the temperature of cure.

The effectiveness of the aromatic carboxylic acid compound as an accelerator for the aromatic epoxy resin/ aliphatic or cycloaliphatic amine curing agent curing system has been found to correlate to the value of "log P" for the aromatic carboxylic acid compound. This value is the logarithm of P, where P is the partition coefficient. Details of log P and the correlation of the log P value to cure acceleration will be explained below. It was also found that the effectiveness of the aromatic carboxylic acid compound as an accelerator for the aromatic epoxy resin/ aliphatic or cycloaliphatic amine curing agent curing system did not correlate to standard acid parameters such as pKa.

In a study reported in the journal article “Accelerated Amine Curing of Epoxy Resins” by L.J. Gough and I.T. Smith in the *Journal of the Oil and Colour Chemists’ Association*, Volume 43, 1960, pages 409-418, that the acceleration of the reaction between an amine curing agent a low molecular weight epoxy resin is accelerated by water (page 411 and Table I) and that for carboxylic acids, the acceleration effect correlates well with pKa (page 415 and Figure 1). In contrast, in this disclosure the acceleration of amine curing of epoxy resins is carried out in the absence of added water, and there is no correlation between acceleration and pKa, rather a correlation between acceleration and log P was discovered.

The curable compositions of this disclosure can be used in a wide array of applications, especially as coatings, encapsulants, and as structural adhesives. Examples of uses as coatings include, for example pipe coatings, and rebar coatings. Examples of uses as encapsulants, also sometimes referred to as potting compounds, include the encapsulation of wires and connections. Examples of uses as structural adhesives include the bonding of wide range of substrate materials including metals, ceramics, wood, or polymeric materials.

Unless otherwise indicated, all numbers expressing feature sizes, amounts, and physical properties used in the specification and claims are to be understood as being modified in all instances by the term “about.” Accordingly, unless indicated to the contrary, the numbers set forth are approximations that can vary depending upon the desired properties using the teachings disclosed herein.

The terms “a”, “an”, and “the” are used interchangeably with “at least one” to mean one or more of the elements being described.

The term “adhesive” as used herein refers to polymeric compositions useful to adhere together two adherends. Structural adhesives refer to adhesives that that can bond other high strength materials (e.g., wood, composites, or metal) so that the adhesive bond strength is in excess of 6.0 MPa (1000 psi).

The term “thermoset” refers to those materials that irreversibly cure to form a hard or rigid material.

The terms “Tg” and “glass transition temperature” are used interchangeably and refer to the glass transition temperature of a cured composition. Typically, unless

otherwise specified, the glass transition temperature is measured by DSC (Differential Scanning Calorimetry) using well understood techniques.

The terms “room temperature” and “ambient temperature” are used interchangeably to mean temperatures in the range of 20°C to 25°C.

5 The term “essentially free of water” as used herein refers to compositions to which no water is intentionally added and care is taken to ensure that all reactants and/or additives are free of water.

The terms “aliphatic” and “cycloaliphatic” as used herein refer to compounds with hydrocarbon groups that are alkyl or alkylene groups.

10 The term “alkyl” refers to a monovalent group that is a radical of an alkane, which is a saturated hydrocarbon. The alkyl can be linear, branched, cyclic, or combinations thereof and typically has 1 to 20 carbon atoms. In some embodiments, the alkyl group contains 1 to 18, 1 to 12, 1 to 10, 1 to 8, 1 to 6, or 1 to 4 carbon atoms. Examples of alkyl groups include, but are not limited to, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, 15 tert-butyl, n-pentyl, n-hexyl, cyclohexyl, n-heptyl, n-octyl, and ethylhexyl.

The term “alkylene” refers to a divalent group that is a radical of an alkane. The alkylene can be straight-chained, branched, cyclic, or combinations thereof. The alkylene often has 1 to 20 carbon atoms. In some embodiments, the alkylene contains 1 to 18, 1 to 12, 1 to 10, 1 to 8, 1 to 6, or 1 to 4 carbon atoms. The radical centers of the alkylene can 20 be on the same carbon atom (i.e., an alkylidene) or on different carbon atoms.

The term “aromatic” as used herein refers to compounds with hydrocarbon groups that are aryl or arylene groups.

The term “aryl” refers to a monovalent group that is aromatic and carbocyclic. The aryl can have one to five rings that are connected to or fused to the aromatic ring. 25 The other ring structures can be aromatic, non-aromatic, or combinations thereof. Examples of aryl groups include, but are not limited to, phenyl, biphenyl, terphenyl, anthryl, naphthyl, acenaphthyl, anthraquinonyl, phenanthryl, anthracenyl, pyrenyl, perylenyl, and fluorenyl.

The term “arylene” refers to a divalent group that is carbocyclic and aromatic. The 30 group has one to five rings that are connected, fused, or combinations thereof. The other rings can be aromatic, non-aromatic, or combinations thereof. In some embodiments, the

arylene group has up to 5 rings, up to 4 rings, up to 3 rings, up to 2 rings, or one aromatic ring. For example, the arylene group can be phenylene.

The term “log P” as used herein refers to the logarithm of “P” the partition coefficient. The terms “partition coefficient”, “partition constant”, “partition ratio”, or “distribution ratio” are used interchangeably. The partition coefficient is a well understood physical parameter. In the physical sciences, a partition coefficient (P) is the ratio of concentrations of a compound in a mixture of two immiscible phases at equilibrium. These coefficients are a measure of the difference in solubility of the compound in these two phases. In the chemical and pharmaceutical sciences, the two phases are often restricted to mean two immiscible solvents. In this context, a partition coefficient is the ratio of concentrations of a compound in the two phases of a mixture of two immiscible liquids at equilibrium. Normally one of the solvents chosen is aqueous while the second is hydrophobic such as 1-octanol. Hence, the partition-coefficient is a measure of the hydrophilic (“water-loving”) or hydrophobic (“water-fearing”) nature of a chemical substance.

The partition coefficient is a ratio of concentrations of un-ionized compound between the two liquid phases. The logarithm of the ratio of the concentrations of the un-ionized solute in the solvents is called log P. For example, in an octanol-water system:

$$\log P_{\text{oct/wat}} = \log \left(\frac{[\text{solute}]_{\text{octanol}}^{\text{un-ionized}}}{[\text{solute}]_{\text{water}}^{\text{un-ionized}}} \right)$$

When one of the solvents is water and the other is a non-polar solvent, then the log P value is also known as a measure of lipophilicity.

The terms “curing time” and “time to cure” are used interchangeably and refer to the time required for a curable composition to cure. The term “cure” refers to the polymerization of reactive compounds. When referring to epoxy compositions, curing typically involves crosslinking, but the term curing does not necessarily refer to crosslinking. The curing time can be measured in a variety of ways. In some embodiments, curing time is measured using DSC (Differential Scanning Calorimetry), where curing time is determined as the time necessary to reach the maximum exotherm temperature. Other methods can also be used to determine curing time for two-part

compositions, such as by continuous stirring with a stick, spoon, or blade until the mixture can longer be stirred.

Disclosed herein are curable compositions comprising an aromatic epoxy resin, an aliphatic or cycloaliphatic amine curing agent, and an accelerator comprising an aromatic carboxylic acid compound. The curable composition may also comprise an array of optional additives. The curable composition is essentially free of water, meaning that no water or water-containing compositions are added to the curable composition. The curing time of the curable composition is less than 1 hour at room temperature. This curing time is accelerated, meaning the curing time is reduced, relative to a composition comprising the same aromatic epoxy resin, and the same aliphatic or cycloaliphatic amine curing agent without the accelerator. The acceleration can be very dramatic. For example, in one embodiment, as is shown in the Examples section below, curing time can be reduced from 105 minutes to 7 minutes (as measured as the time to maximum exotherm by DSC as described above).

In some embodiments, the curing time of the curable composition is less than 0.5 hour at room temperature. In yet other embodiments, the curing time of the curable composition is less than 20 minutes at room temperature, or even less than 10 minutes at room temperature.

The curable composition comprises at least one aromatic epoxy resin. Typically the aromatic epoxy resin is a liquid epoxy resin. Suitable liquid epoxy resins include the DGEBA-type (diglycidyl ether of bisphenol A) and DGEBF-type (diglycidyl ether of bisphenol F) epoxy resins such as those commercially available from HEXION under the trade name EPON and Dow Chemical under the trade name D.E.R.. Other suitable aromatic epoxy resins are the multifunctional epoxy novolacs such as epoxy phenol novolac resins (EPN) and epoxy cresol novolac resins (ECN). Epoxy phenol novolac resins are made by epoxidation of the phenol-formaldehyde condensates (novolacs) obtained from acid catalyzed condensation of phenol and formaldehyde, which produces random ortho- and para-methylene bridges. Combinations of aromatic epoxy resins can also be used.

In addition to the base aromatic epoxy resin a variety of optional reactive diluents or modifiers can be used. Reactive diluents and modifiers include mono- and di-functional glycidyl ethers which can be used to reduce the viscosity of typical epoxy

resins without causing significant changes in final physical properties. Examples of suitable reactive diluents include butyl glycidyl ether, C12-C14 aliphatic glycidyl ether, phenyl glycidyl ether, cresyl glycidyl ether, and 2-ethylhexyl glycidyl ether. Commercially available diluents and modifier include the EPODIL resins commercially available from Air Products and Chemicals.

Typically the aromatic epoxy resin is the majority reactive component of the curable composition. Generally the curable composition comprises 60-90 parts by weight of aromatic epoxy resin per 100 parts total weight of reactive components.

The curable composition also comprises at least one aliphatic or cycloaliphatic amine curing agent. A wide variety of suitable curing agents can be used. Often, particularly suitable curing agents also include aromatic groups. A curing agent is considered to be an aliphatic amine curing agent as long as all of the bonds to the nitrogen atom of the amine group or groups are hydrogen atoms or aliphatic groups.

A wide range of aliphatic or cycloaliphatic amine curing agents are suitable. Typically the curing agent is a liquid curing agent. Solid curing agents are typically insoluble or have limited solubility in the epoxy resins and therefore do not have sufficient reactivity at room temperature to be suitable for use in the curable compositions of this disclosure. Examples of suitable aliphatic or cycloaliphatic amine curing agents include: liquid polyetheramines such as the commercially available JEFFAMINE T-403 and JEFFAMINE D-230 from Huntsman Corp.; polyamidoamines such as VESAMID 125 and GENAMID 490 commercially available from BASF; ethyleneamines such as DETA (diethylene triamine), TETA (trethylenetetramine), TEPA (tetraethylenepentamine), and AEP (N-aminoethylpiperazine); cycloaliphatics such as PACM (bis-(p-aminocyclohexyl)methane), DACH (diaminocyclohexane), TCD-diamine (the diaminomethyl tricyclodecane 3(4), 8(9)-bis(aminomethyl)-tricyclo[5.2.1.0(2.6)]decane (commercially available from OXEA Corporation, Dallas, TX)), and DMCH (bis-(dimethyldi-aminocyclohexyl)methane); and aromatic-aliphatic amines including xylene diamines and chain-extended compounds and derivatives of xylene diamines, such as meta-xylene diamine (m-XDA) and chain-extended compounds and derivatives of m-XDA such as the GASKAMINE products commercially available from Mitsubishi Gas Chemical Corporation, Tokyo, Japan (for example GASKAMINE 240 a styrene derivative of m-XDA and GASKAMINE 328 an epichlorohydrin derivative of m-XDA), chain-

extended compounds and derivatives of xylene diamines such as xylene diamine trimers (for example, "AMINE BLACK" or "SHO-AMINE BLACK" commercially available from Showa Denko), xylene diamine derivatives (for example, "SHO-AMINE N", "SHO-AMINE 1001", and "SHO-AMINE 1010" commercially available from Showa Denko),
5 and norbornene dimethylamine and chain-extended compounds and derivatives thereof. Particularly suitable aliphatic or cycloaliphatic amine curing agents are meta-xylene diamine (m-XDA), norbornene dimethylamine, and chain-extended compounds and derivatives thereof. Optionally, the amines may be adducted to a multifunctional epoxy resin by pre-reacting excess amine with some of the epoxy resin, as described by Clive H.
10 Hare in Protective Coatings: Fundamentals of Chemistry and Composition Technology Publishing Company, Pittsburgh, PA (ISBN 0-938477-90-0) Chapter 15-Epoxy Systems, pp 187-237. The resulting adducts are essentially high molecular weight amines with epoxy backbones.

Typically the aliphatic or cycloaliphatic amine curing agent comprises 10-35 parts
15 by weight of aliphatic or cycloaliphatic amine curing agent per 100 parts total weight of reactive components. In some embodiments the aliphatic or cycloaliphatic amine curing agent comprises 10-20 parts by weight or 12-18 parts by weight of aliphatic or cycloaliphatic amine curing agent per 100 parts total weight of reactive components.

The curable composition also comprises at least one accelerator comprising an
20 aromatic carboxylic acid compound. A wide variety of aromatic carboxylic acid compounds are suitable. As mentioned above, the effectiveness of the aromatic carboxylic acid compound as an accelerator for the aromatic epoxy resin/ aliphatic or cycloaliphatic amine curing agent curing system has been found to correlate to the value of "log P" for the aromatic carboxylic acid compound. This value is the logarithm of P, where P is the
25 partition coefficient. Details of log P are explained above. It has also found that the effectiveness of the aromatic carboxylic acid compound as an accelerator for the aromatic epoxy resin/ aliphatic or cycloaliphatic amine curing agent curing system did not correlate to standard acid parameters such as pKa. Typically, the accelerator has a log P value in the range of from -0.5 to 4.0. In some embodiments, the log P value is in the range of
30 from 0.5 to 4.0, in the range of from 1.0 to 4.0, or even in the range of from 3.0 to 4.0.

As mentioned above, the accelerator speeds up the reaction time at room temperature for the curing of the curable composition. Typically, the curing time of the

curable compositions of this disclosure are less than 1 hour at room temperature. As discussed above, the curing time can be measured in a variety of different ways. In the present Examples, curing time is determined by using DSC (Differential Scanning Calorimetry), where curing time is the time necessary to reach the maximum exotherm temperature. In general, the correlation of curing time to log P of the aromatic carboxylic acid accelerator has been observed to be: when the accelerator has a log P value in the range of from -0.5 to 4.0 the curing time of the curable composition is less than 1.0 hour; when the accelerator has a log P value in the range of from 0.5 to 4.0 the curing time of the curable composition is less than 0.5 hour; when the accelerator has a log P value in the range of from 1.0 to 4.0 the curing time of the curable composition is less than 20 minutes; and when the accelerator has a log P value in the range of from 3.0 to 4.0 the curing time of the curable composition is less than 10 minutes.

Examples of particularly suitable aromatic carboxylic acid accelerators include 3-methyl salicylic acid, salicylic acid, anthranilic acid, 2-hydroxynicotinic acid, and combinations thereof.

Typically the aromatic carboxylic acid accelerators are present in small quantities in the curable compositions. Generally, the aromatic carboxylic acid accelerators are present in amounts of from 0.01-5.0 parts by weight per 100 parts total weight of reactive components in the curable composition. In some embodiments, the aromatic carboxylic acid accelerators are present in amounts of from 0.02-2.0 parts by weight per 100 parts total weight of reactive components in the curable composition, amounts of from 0.02-1.0 parts by weight per 100 parts total weight of reactive components in the curable composition, or 0.02-0.5 parts by weight per 100 parts total weight of reactive components in the curable composition, or even 0.02-0.15 parts by weight per 100 parts total weight of reactive components in the curable composition.

The curable composition may contain additional optional additives. These optional additives can be either solids or liquids, and reactive or unreactive. Among the suitable additives are fillers, including thermally conductive fillers, flame retardants (such as ATH (aluminum trihydrate) or phosphate flame retardants), colorants such as pigments or dyes, nanoparticles or functionalized nanoparticles, chain extenders, toughening agents, or combinations thereof. These components are typically solids, but some of the additive components can be liquids, and these liquid components may be suitable.

Examples of non-reactive additives include fillers, flame retardants, nanoparticles, and toughening agents. Particularly suitable non-reactive additives are fillers such as metal oxides (silica, titania, magnesium oxide, and the like) and thermal conductivity enhancers such as boron nitride.

5 Examples of reactive additives include chain extension agents. Suitable chain extension agents include aromatic hydroxyl-functional materials such as di-hydroxyl phenolic compounds such as catechol and other di-hydroxyphenols, as well as compounds such as bisphenol A and bisphenol F. Examples of additional suitable chain extension agents are included in US Patent Publication Nos. 2014/0069583 and 2014/0296447
10 (Kincaid et al.).

In some specific embodiments of the curable composition the aromatic epoxy resin comprises: a diglycidyl ether of bis-phenol A, a diglycidyl ether of bis-phenol F, or a combination thereof; the aliphatic or cycloaliphatic amine curing agent comprises meta-xylene diamine, norbornene dimethylamine or a chain-extended compound or derivative
15 thereof; and the accelerator comprises salicylic acid, 3-methyl salicylic acid, anthranilic acid, 2-hydroxynicotinic acid, or combinations thereof.

The above described curable composition can be supplied as a two-part curable epoxy composition comprising a first part comprising an aromatic epoxy resin, and a second part comprising an aliphatic or cycloaliphatic amine curing agent. Additionally,
20 one of the two parts additionally comprises an accelerator comprising an aromatic carboxylic acid compound. In other words, the accelerator can be placed in either of the two parts.

Thus one embodiment of a two-part curable epoxy composition of this disclosure comprises a first part comprising an aromatic epoxy resin, and an accelerator comprising
25 an aromatic carboxylic acid compound, and a second part comprising an aliphatic or cycloaliphatic amine curing agent. The first part and the second part are essentially free from water, and the two parts when mixed form a curable composition with a curing time that is less than 1 hour at room temperature. The components of the two-part curable composition have all been described above.

30 Additionally, the two-part curable epoxy composition can also include a variety of additional additives, as described above. These additives can be added either to the first part or to the second part or to both as desired, as long addition of the additive to a

particular part does not interfere with the curing reaction upon mixing. Examples of suitable additives include fillers, thermally conductive fillers, flame retardants, nanoparticles or functionalized nanoparticles, chain extenders, toughening agents, and combinations thereof.

5 Another embodiment of a two-part curable epoxy composition of this disclosure comprises a first part comprising an aromatic epoxy resin, and a second part comprising an aliphatic or cycloaliphatic amine curing agent, and an accelerator comprising an aromatic carboxylic acid compound. The first part and the second part are essentially free from water, and the two parts when mixed form a curable composition with a curing time
10 that is less than 1 hour at room temperature. The components of the two-part curable composition have all been described above.

 Additionally, the two-part curable epoxy composition can also include a variety of additional additives, as described above. These additives can be added either to the first part or to the second part or to both as desired, as long addition of the additive to a
15 particular part does not interfere with the curing reaction upon mixing. Examples of suitable additives include fillers, thermally conductive fillers, flame retardants, nanoparticles or functionalized nanoparticles, chain extenders, toughening agents, and combinations thereof.

 As mentioned above, the two parts of the curable epoxy composition are kept
20 separate until mixed to form the curable composition of this disclosure. The two parts can be kept separate in a wide variety of ways, depending upon the desired use. For example, the two parts can be stored and shipped in separate sealed containers, or the two parts can be incorporated into a single container with two separate compartments. A wide variety of such containers are known in the art.

25 As mentioned above, other embodiments of this disclosure include curable compositions comprising an aromatic epoxy resin, an aromatic amine curing agent, and an accelerator comprising an aromatic carboxylic acid compound. The aromatic epoxy resins and the accelerators have been described in detail above.

 A wide variety of aromatic amine curing agents are suitable. Among the most
30 suitable are *m*-PDA (*m*-phenylene diamine), MDA (methylenedianiline), and DDS (diaminodiphenyl sulfone).

As mentioned above, curable compositions that use of aromatic amine curing agents typically are not room temperature curable and thus the application of heat is used to cure these compositions. In these formulations, rather than acceleration being a decrease in the time of cure, rather acceleration relates to a decrease in the cure temperature. For example, in an unaccelerated composition typically cures at a temperature of 150°C, an example of acceleration would be for the composition to cure at a temperature of 100°C.

The acceleration of curing can be modeled by the use of a DSC instrument. The sample is heated at a specific rate, typically 10°C per minute, and the thermal profile is studied to determine where the onset of an exothermic reaction occurs. In the present disclosure, the acceleration of compositions of aromatic epoxy resins and aromatic amine curing agents results in the onset of curing at a temperature that is 50-100°C less for the accelerated compositions than for the unaccelerated compositions. Examples of cure profiles are presented in the Examples section and the Figures.

Typically the aromatic amine curing agent comprises 10-35 parts by weight of aromatic amine curing agent per 100 parts total weight of reactive components. In some embodiments the aromatic amine curing agent comprises 10-20 parts by weight or 12-18 parts by weight of aromatic amine curing agent per 100 parts total weight of reactive components.

Also disclosed herein are methods of controlling the cure time of curable epoxy composition. As mentioned above, these methods involve the acceleration of the cure of the curable epoxy composition through the use of an accelerator. The accelerated curable epoxy compositions cure more rapidly than would the same curable epoxy compositions in the absence of the accelerator.

The method of controlling the cure time of curable epoxy composition comprises providing a curable mixture that is essentially free of water, where the curable mixture comprises an aromatic epoxy resin, and an aliphatic or cycloaliphatic amine curing agent, and selecting an accelerator comprising an aromatic carboxylic acid, adding the accelerator to either the aromatic epoxy resin or the aliphatic or cycloaliphatic amine curing agent, mixing the aromatic epoxy resin, aliphatic amine curing agent and accelerator to form a curable composition, and permitting the curable composition to cure at room temperature. The aromatic carboxylic acid accelerator has a log P value in the

range of from -0.5 to 4.0, where P is the partition coefficient, as described above. The curing time of the curable composition is less than 1 hour, at room temperature.

As mentioned above, the control of the cure time can be correlated to the log P value of the accelerator. Thus in some embodiments, the accelerator has a log P value in the range of from 0.5 to 4.0; and the curing time of the curable composition is less than 0.5 hours. In other embodiments, the accelerator has a log P value in the range of from 1.0 to 4.0; and the curing time of the curable composition is less than 20 minutes. In still other embodiments, the accelerator has a log P value in the range of from 3.0 to 4.0; and the curing time of the curable composition is less than 10 minutes.

Also disclosed herein are articles prepared from the curable compositions described above. The curable compositions are coated onto a substrate and permitted to cure. The articles comprise a substrate comprising a first major surface and a second major surface, and a coating on the at least a portion of the second major surface of the substrate, where the coating comprises a cured layer of a curable composition. The curable composition has been described in detail above and comprises an aromatic epoxy resin, an aliphatic or cycloaliphatic amine curing agent, and an accelerator comprising an aromatic carboxylic acid compound, where the curable composition is essentially free of water, and where the curing time of the curable composition is less than 1 hour at room temperature. As described above, the curable composition can be provided as a two-part composition and mixed to form the curable composition, and the curable composition can also include a variety of additional additives.

The coatings can be coated on a wide range of substrates. Examples of suitable substrates include metal substrates, ceramic substrates, glass substrates, or polymeric substrates. The substrates can be in a variety of shapes such as plates or tubes, and may have smooth or irregular surfaces and may be hollow or solid.

The curable composition can be applied to a substrate to form a curable layer using a variety of techniques, including dip coating, forward and reverse roll coating, wire wound rod coating, and die coating. Die coaters include knife coaters, slot coaters, slide coaters, fluid bearing coaters, slide curtain coaters, and drop die curtain coaters. Upon coating the curable composition is permitted to cure at ambient temperature to form a cured coating.

The thickness of the coating varies depending upon the desired use for the coating. Typically the coatings range from 25 micrometers (1 mil) to 1 millimeter in thickness. In some embodiments, particularly for the pipe coatings described below, the thickness can be considerably greater. In embodiments where the coating is primarily for corrosion inhibition and pipe protection, coatings of from 25 micrometers (1 mil) to 1 millimeter in thickness are typically sufficient. In other instances, when the coating is relied upon to assist in providing structural integrity to the pipe, coatings with a thickness of 5 millimeters or greater are typical. In yet other embodiments in which the curable composition is utilized to impregnate a woven or nonwoven web of material such as a sock or other reinforcement (sometimes referred to as a CIPP, or cure in place pipe), the coating thickness can be up to 50 millimeters in thickness.

As mentioned above, in some embodiments, the curable composition is a pipe coating. In these embodiments, the substrate comprises a metal substrate which is a pipe, and the second major surface of the substrate comprises an external surface of the pipe. One advantage of the curable compositions of the present disclosure for use as pipe coatings, is that they cure rapidly at ambient temperature, and thus can be readily used in the field to coat or repair coatings without the need for specialized curing equipment. In other embodiments, the pipe coating can be applied to the inside surface of the pipe, i.e. the second major surface of the substrate comprises an internal surface of the pipe. Such coatings can be much more difficult to apply and may require specialized equipment. Additionally, the curable compositions can be used as coatings for pipeline joints. The pipeline joint coatings can be applied either internally or externally.

Another type of article which may be formed using the curable compositions of this disclosure are adhesive laminates. Adhesive laminates or articles of the type: first substrate/adhesive layer/second substrate. The curable compositions of this disclosure can be structural adhesives, meaning that upon curing they form structural bonds between the first substrate and the second substrate. The use of curable epoxy compositions, both one-part and two-part epoxy compositions, is well understood in the art.

This disclosure includes the following embodiments:

Among the embodiments are curable compositions. Embodiment 1 includes a curable composition comprising: an aromatic epoxy resin; an aliphatic or cycloaliphatic amine curing agent; and an accelerator comprising an aromatic carboxylic acid compound,

wherein the curable composition is essentially free of water, and wherein the curing time of the curable composition is less than 1 hour at room temperature.

Embodiment 2 is the curable composition of embodiment 1, wherein the curing time of the curable composition is less than 0.5 hour at room temperature.

5 Embodiment 3 is the curable composition of embodiment 1, wherein the curing time of the curable composition is less than 20 minutes at room temperature.

Embodiment 4 is the curable composition of embodiment 1, wherein the curing time of the curable composition is less than 10 minutes at room temperature.

10 Embodiment 5 is the curable composition of any of embodiments 1-4, wherein the accelerator has a log P value of from -0.5 to 4.0 where P is the partition coefficient.

Embodiment 6 is the curable composition of any of embodiments 1-4, wherein the accelerator has a log P value of from 0.5 to 4.0 where P is the partition coefficient.

Embodiment 7 is the curable composition of any of embodiments 1-4, wherein the accelerator has a log P value of from 1.0 to 4.0 where P is the partition coefficient.

15 Embodiment 8 is the curable composition of any of embodiments 1-4, wherein the accelerator has a log P value of from 3.0 to 4.0 where P is the partition coefficient.

Embodiment 9 is the curable composition of any of embodiments 1-8, wherein the accelerator comprises 3-methyl salicylic acid, salicylic acid, anthranilic acid, 2-hydroxynicotinic acid, or combinations thereof.

20 Embodiment 10 is the curable composition of any of embodiments 1-9, wherein the aliphatic or cycloaliphatic amine curing agent comprises a xylene diamine, a norbornene dimethylamine, or a chain-extended compound thereof.

Embodiment 11 is the curable composition of embodiment 10, wherein the aliphatic or cycloaliphatic amine curing agent comprises meta xylene diamine, norbornene dimethylamine, or a chain-extended compound thereof.

25 Embodiment 12 is the curable composition of any of embodiments 1-11, wherein the aromatic epoxy resin comprises a diglycidyl ether of bis-phenol A, a diglycidyl ether of bis-phenol F, or a combination thereof.

30 Embodiment 13 is the curable composition of any of embodiments 1-12, wherein the aromatic epoxy resin comprises a diglycidyl ether of bis-phenol A, a diglycidyl ether of bis-phenol F, or a combination thereof; the aliphatic or cycloaliphatic amine curing agent comprises meta xylene diamine, norbornene dimethylamine or a chain-extended

compound thereof; and the accelerator comprises salicylic acid, 3-methyl salicylic acid, anthranilic acid, 2-hydroxynicotinic acid, or combinations thereof.

Embodiment 14 is the curable composition of any of embodiments 1-13, wherein the curable composition comprises 60-90 parts by weight of aromatic epoxy resin per 100 parts total weight of reactive components.

Embodiment 15 is the curable composition of embodiment 14, wherein the curable composition comprises 10-35 parts by weight of aliphatic or cycloaliphatic amine curing agent per 100 parts total weight of reactive components.

Embodiment 16 is the curable composition of embodiment 14 or 15, wherein the curable composition comprises 0.01-5.0 parts by weight of aromatic carboxylic acid accelerator per 100 parts total weight of reactive components in the curable composition.

Also disclosed are two-part curable epoxy compositions. Embodiment 17 includes a two-part curable epoxy composition comprising: a first part comprising: an aromatic epoxy resin; a second part comprising: an aliphatic or cycloaliphatic amine curing agent; and an accelerator comprising an aromatic carboxylic acid compound, wherein the accelerator is located either in the first part or the second part; and wherein the first part and the second part are essentially free from water, and wherein the two parts when mixed form a curable composition with a curing time that is less than 1 hour at room temperature.

Embodiment 18 is the two-part curable epoxy composition of embodiment 17, wherein the first part comprises: an aromatic epoxy resin; and an accelerator comprising an aromatic carboxylic acid compound; and the second part comprises: an aliphatic or cycloaliphatic amine curing agent.

Embodiment 19 is the two-part curable epoxy composition of embodiment 17, wherein the first part comprises: an aromatic epoxy resin; and the second part comprises: an aliphatic or cycloaliphatic amine curing agent; and an accelerator comprising an aromatic carboxylic acid compound.

Embodiment 20 is the two-part curable epoxy composition of any of embodiments 17-19, wherein the first part or the second part comprises an additional additive selected from fillers, thermally conductive fillers, flame retardants, nanoparticles or functionalized nanoparticles, chain extenders, toughening agents, or combinations thereof.

Embodiment 21 is the two-part curable epoxy composition of any of embodiments 17-20, wherein the curing time of the formed curable composition is less than 0.5 hour at room temperature.

5 Embodiment 22 is the two-part curable epoxy composition of any of embodiments 17-20, wherein the curing time of the formed curable composition is less than 20 minutes at room temperature.

Embodiment 23 is the two-part curable epoxy composition of any of embodiments 17-20, wherein the curing time of the formed curable composition is less than 10 minutes at room temperature.

10 Embodiment 24 is the two-part curable epoxy composition of any of embodiments 17-20, wherein the accelerator has a log P value of from -0.5 to 4.0 where P is the partition coefficient.

15 Embodiment 25 is the two-part curable epoxy composition of any of embodiments 17-20, wherein the accelerator has a log P value of from 0.5 to 4.0 where P is the partition coefficient.

Embodiment 26 is the two-part curable epoxy composition of any of embodiments 17-20, wherein the accelerator has a log P value of from 1.0 to 4.0 where P is the partition coefficient.

20 Embodiment 27 is the two-part curable epoxy composition of any of embodiments 17-20, wherein the accelerator has a log P value of from 3.0 to 4.0 where P is the partition coefficient.

Embodiment 28 is the two-part curable epoxy composition of any of embodiments 17-27, wherein the accelerator comprises 3-methyl salicylic acid, salicylic acid, anthranilic acid, 2-hydroxynicotinic acid, or combinations thereof.

25 Embodiment 29 is the two-part curable epoxy composition of any of embodiments 17-28, wherein the aliphatic or cycloaliphatic amine curing agent comprises a xylene diamine, a norbornene dimethylamine, or a chain-extended compound thereof.

30 Embodiment 30 is the two-part curable epoxy composition of embodiment 29, wherein the aliphatic or cycloaliphatic amine curing agent comprises meta xylene diamine, norbornene dimethylamine, or a chain-extended compound thereof.

Embodiment 31 is the two-part curable epoxy composition of any of embodiments 17-30, wherein the aromatic epoxy resin comprises a diglycidyl ether of bis-phenol A, a diglycidyl ether of bis-phenol F, or a combination thereof.

Embodiment 32 is the two-part curable epoxy composition of any of embodiments 17-31, wherein the aromatic epoxy resin comprises a diglycidyl ether of bis-phenol A, a diglycidyl ether of bis-phenol F, or a combination thereof; the aliphatic or cycloaliphatic amine curing agent comprises meta xylene diamine, norbornene dimethylamine or a chain-extended compound thereof; and the accelerator comprises salicylic acid, 3-methyl salicylic acid, anthranilic acid, 2-hydroxynicotinic acid, or combinations thereof.

Embodiment 33 is the two-part curable epoxy composition of any of embodiments 17-32, wherein the formed curable composition comprises 60-90 parts by weight of aromatic epoxy resin per 100 parts total weight of reactive components.

Embodiment 34 is the two-part curable epoxy composition of any of embodiments 17-33, wherein the formed curable composition comprises 10-35 parts by weight of aliphatic or cycloaliphatic amine curing agent per 100 parts total weight of reactive components.

Embodiment 35 is the two-part curable epoxy composition of any of embodiments 17-34, wherein the formed curable composition comprises 0.01-5.0 parts by weight of aromatic carboxylic acid accelerator per 100 parts total weight of reactive components in the curable composition.

Also disclosed are methods of controlling the cure time of curable epoxy compositions. Embodiment 36 includes a method of controlling the cure time of a curable epoxy composition comprising: providing a curable mixture that is essentially free of water comprising: an aromatic epoxy resin; and an aliphatic or cycloaliphatic amine curing agent; and selecting an accelerator comprising an aromatic carboxylic acid, wherein the accelerator has an log P value in the range of from -0.5 to 4.0, wherein P is the partition coefficient; adding the accelerator to either the aromatic epoxy resin or the aliphatic or cycloaliphatic amine curing agent; mixing the aromatic epoxy resin, aliphatic amine curing agent and accelerator to form a curable composition; permitting the curable composition to cure at room temperature, wherein the curing time of the curable composition is less than 1 hour.

Embodiment 37 is the method of embodiment 36, wherein the curing time of the curable composition is determined using DSC (Differential Scanning Calorimetry).

Embodiment 38 is the method of embodiment 35 or 36, wherein the curing time of the curable composition is less than 0.5 hour at room temperature.

5 Embodiment 39 is the method of embodiment 35 or 36, wherein the curing time of the curable composition is less than 20 minutes at room temperature.

Embodiment 40 is the method of embodiment 35 or 36, wherein the curing time of the curable composition is less than 10 minutes at room temperature.

10 Embodiment 41 is the method of embodiment 35 or 36, wherein the accelerator has a log P value of from -0.5 to 4.0 where P is the partition coefficient.

Embodiment 42 is the method of embodiment 35 or 36, wherein the accelerator has a log P value of from 0.5 to 4.0 where P is the partition coefficient.

Embodiment 43 is the method of embodiment 35 or 36, wherein the accelerator has a log P value of from 1.0 to 4.0 where P is the partition coefficient.

15 Embodiment 44 is the method of embodiment 35 or 36, wherein the accelerator has a log P value of from 3.0 to 4.0 where P is the partition coefficient.

Embodiment 45 is the method of any of embodiments 35-44, wherein the accelerator comprises 3-methyl salicylic acid, salicylic acid, anthranilic acid, 2-hydroxynicotinic acid, or combinations thereof.

20 Embodiment 46 is the method of any of embodiments 35-45, wherein the aliphatic or cycloaliphatic amine curing agent comprises a xylene diamine, a TCD-diamine, a norbornene dimethylamine, or a chain-extended compound thereof.

Embodiment 47 is the method of embodiment 46, wherein the aliphatic or cycloaliphatic amine curing agent comprises meta xylene diamine, norbornene dimethylamine, or a chain-extended compound thereof.

25 Embodiment 48 is the method of any of embodiments 35-47, wherein the aromatic epoxy resin comprises a diglycidyl ether of bis-phenol A, a diglycidyl ether of bis-phenol F, or a combination thereof.

30 Embodiment 49 is the method of any of embodiments 35-48, wherein the aromatic epoxy resin comprises a diglycidyl ether of bis-phenol A, a diglycidyl ether of bis-phenol F, or a combination thereof; the aliphatic or cycloaliphatic amine curing agent comprises meta xylene diamine, norbornene dimethylamine or a chain-extended compound thereof;

and the accelerator comprises salicylic acid, 3-methyl salicylic acid, anthranilic acid, 2-hydroxynicotinic acid, or combinations thereof.

Embodiment 50 is the method of any of embodiments 35-49, wherein the curable composition comprises 60-90 parts by weight of aromatic epoxy resin per 100 parts total weight of reactive components.

Embodiment 51 is the method of embodiment 50, wherein the curable composition comprises 10-35 parts by weight of aliphatic or cycloaliphatic amine curing agent per 100 parts total weight of reactive components.

Embodiment 52 is the method of embodiment 49 or 50, wherein the curable composition comprises 0.01-5.0 parts by weight of aromatic carboxylic acid accelerator per 100 parts total weight of reactive components in the curable composition.

Embodiment 53 is the method of any of embodiments 35-52, wherein the accelerator has a log P value in the range of from 0.5 to 4.0; and the curing time of the curable composition is less than 0.5 hours.

Embodiment 54 is the method of any of embodiments 35-52, wherein the accelerator has a log P value in the range of from 1.0 to 4.0; and the curing time of the curable composition is less than 20 minutes.

Embodiment 55 is the method of any of embodiments 35-52, wherein the accelerator has a log P value in the range of from 3.0 to 4.0; and the curing time of the curable composition is less than 10 minutes.

Among the embodiments are articles. Embodiment 56 includes an article comprising: a substrate comprising a first major surface and a second major surface; and a coating on at least a portion of the second major surface of the substrate, wherein the coating comprises a cured layer of a curable composition, wherein the curable composition comprises: an aromatic epoxy resin; an aliphatic or cycloaliphatic amine curing agent; and an accelerator comprising an aromatic carboxylic acid compound, wherein the curable composition is essentially free of water, and wherein the curing time of the curable composition is less than 1 hour at room temperature.

Embodiment 57 is the article of embodiment 56, wherein the curing time of the curable composition is less than 0.5 hour at room temperature.

Embodiment 58 is the article of embodiment 56, wherein the curing time of the curable composition is less than 20 minutes at room temperature.

Embodiment 59 is the article of embodiment 56, wherein the curing time of the curable composition is less than 10 minutes at room temperature.

Embodiment 60 is the article of any of embodiments 56-59, wherein the accelerator has a log P value of from -0.5 to 4.0 where P is the partition coefficient.

5 Embodiment 61 is the article of any of embodiments 56-59, wherein the accelerator has a log P value of from 0.5 to 4.0 where P is the partition coefficient.

Embodiment 62 is the article of any of embodiments 56-59, wherein the accelerator has a log P value of from 1.0 to 4.0 where P is the partition coefficient.

10 Embodiment 63 is the article of any of embodiments 56-59, wherein the accelerator has a log P value of from 3.0 to 4.0 where P is the partition coefficient.

Embodiment 64 is the article of any of embodiments 56-63, wherein the accelerator comprises 3-methyl salicylic acid, salicylic acid, anthranilic acid, 2-hydroxynicotinic acid, or combinations thereof.

15 Embodiment 65 is the article of any of embodiments 56-64, wherein the aliphatic or cycloaliphatic amine curing agent comprises a xylene diamine, a norbornene dimethylamine, or a chain-extended compound thereof.

Embodiment 66 is the article of embodiment 65, wherein the aliphatic or cycloaliphatic amine curing agent comprises meta xylene diamine, norbornene dimethylamine, or a chain-extended compound thereof.

20 Embodiment 67 is the article of any of embodiments 56-66, wherein the aromatic epoxy resin comprises a diglycidyl ether of bis-phenol A, a diglycidyl ether of bis-phenol F, or a combination thereof.

25 Embodiment 68 is the article of any of embodiments 56-67, wherein the aromatic epoxy resin comprises a diglycidyl ether of bis-phenol A, a diglycidyl ether of bis-phenol F, or a combination thereof; the aliphatic or cycloaliphatic amine curing agent comprises meta xylene diamine, norbornene dimethylamine or a chain-extended compound thereof; and the accelerator comprises salicylic acid, 3-methyl salicylic acid, anthranilic acid, 2-hydroxynicotinic acid, or combinations thereof.

30 Embodiment 69 is the article of any of embodiments 56-68, wherein the curable composition comprises 60-90 parts by weight of aromatic epoxy resin per 100 parts total weight of reactive components.

Embodiment 70 is the article of embodiment 69, wherein the curable composition comprises 10-35 parts by weight of aliphatic or cycloaliphatic amine curing agent per 100 parts total weight of reactive components.

Embodiment 71 is the article of embodiment 69 or 70, wherein the curable composition comprises 0.01-5.0 parts by weight of aromatic carboxylic acid accelerator per 100 parts total weight of reactive components in the curable composition.

Embodiment 72 is the article of any of embodiments 56-71, wherein the substrate comprises a metal substrate, a ceramic substrate, a glass substrate, a polymeric substrate, or a wooden substrate.

Embodiment 73 is the article of embodiments 72, wherein the substrate comprises a metal substrate comprising a pipe, and wherein the second major surface of the substrate comprises an external surface of the pipe.

Embodiment 74 is the article of embodiment 72, wherein the substrate comprises a metal substrate comprising a pipe, and wherein the second major surface of the substrate comprises an internal surface of the pipe.

Embodiment 75 is the article of any of embodiments 56-74, wherein the coating has a thickness of from 25 micrometers to 5 millimeters.

Embodiment 76 is the article of any of embodiments 56-74, wherein the coating has a thickness of from 25 micrometers to 1 millimeter.

Embodiment 77 is the article of any of embodiments 56-74, wherein the coating has a thickness of up to 50 millimeters.

Among the embodiments are curable compositions. Embodiment 78 includes a curable composition comprising: an aromatic epoxy resin; an aromatic amine curing agent; and an accelerator comprising an aromatic carboxylic acid compound, wherein the curable composition is essentially free of water, and wherein the curing temperature of the curable composition is 50-100°C less than for the same composition in the absence of the accelerator.

Embodiment 79 is the curable composition of embodiment 78, wherein the accelerator comprises 3-methyl salicylic acid, salicylic acid, anthranilic acid, 2-hydroxynicotinic acid, or combinations thereof.

Embodiment 80 is the curable composition of embodiments 78 or 79, wherein the aromatic amine curing agent comprises m-PDA (*m*-phenylene diamine), MDA (methylenedianiline), DDS (diaminodiphenyl sulfone), or combinations thereof.

5 Embodiment 81 is the curable composition of any of embodiments 78-80, wherein the aromatic epoxy resin comprises a diglycidyl ether of bis-phenol A, a diglycidyl ether of bis-phenol F, or a combination thereof.

Embodiment 82 is the curable composition of any of embodiments 78-81, wherein the aromatic epoxy resin comprises a diglycidyl ether of bis-phenol A, a diglycidyl ether of bis-phenol F, or a combination thereof; the aromatic amine curing agent comprises m-PDA (*m*-phenylene diamine), MDA (methylenedianiline), DDS (diaminodiphenyl sulfone), or combinations thereof; and the accelerator comprises salicylic acid, 3-methyl salicylic acid, anthranilic acid, 2-hydroxynicotinic acid, or combinations thereof.

Embodiment 83 is the curable composition of any of embodiments 78-82, wherein the curable composition comprises 60-90 parts by weight of aromatic epoxy resin per 100 parts total weight of reactive components.

Embodiment 84 is the curable composition of embodiment 83, wherein the curable composition comprises 10-35 parts by weight of aromatic amine curing agent per 100 parts total weight of reactive components.

Embodiment 85 is the curable composition of embodiment 83 or 84, wherein the curable composition comprises 0.01-5.0 parts by weight of aromatic carboxylic acid accelerator per 100 parts total weight of reactive components in the curable composition.

Among the embodiments are structural adhesives. Embodiment 86 is a structural adhesive comprising the curable composition of any of embodiments 1-16.

Embodiment 87 is the structural adhesive of embodiment 86, wherein the structural adhesive comprises a two-part curable epoxy composition of any of embodiments 17-35.

Embodiment 88 is the structural adhesive of embodiment 86 or 87, wherein the cure time of the structural adhesive is controlled by any of the methods of embodiments 36-55.

Embodiment 89 is an article comprising a first substrate comprising a first major surface and a second major surface; and a coating on at least a portion of the second major surface of the first substrate, wherein the coating comprises a cured layer of a curable composition, wherein the curable composition comprises: an aromatic epoxy resin; an

aliphatic or cycloaliphatic amine curing agent; and an accelerator comprising an aromatic carboxylic acid compound, wherein the curable composition is essentially free of water, and wherein the curing time of the curable composition is less than 1 hour at room temperature, and a second substrate comprising a first major surface and a second major surface, wherein the first major surface of the second substrate is in contact with the cured layer of the curable composition, such that the cured layer of the curable composition forms a structural adhesive bond between the first substrate and the second substrate.

Embodiment 90 is the article of embodiment 89, wherein the curing time of the curable composition is less than 0.5 hour at room temperature.

Embodiment 91 is the article of embodiment 89, wherein the curing time of the curable composition is less than 20 minutes at room temperature.

Embodiment 92 is the article of embodiment 89, wherein the curing time of the curable composition is less than 10 minutes at room temperature.

Embodiment 93 is the article of any of embodiments 89-92, wherein the accelerator has a log P value of from -0.5 to 4.0 where P is the partition coefficient.

Embodiment 94 is the article of any of embodiments 89-92, wherein the accelerator has a log P value of from 0.5 to 4.0 where P is the partition coefficient.

Embodiment 95 is the article of any of embodiments 89-92, wherein the accelerator has a log P value of from 1.0 to 4.0 where P is the partition coefficient.

Embodiment 96 is the article of any of embodiments 89-92, wherein the accelerator has a log P value of from 3.0 to 4.0 where P is the partition coefficient.

Embodiment 97 is the article of any of embodiments 89-96, wherein the accelerator comprises 3-methyl salicylic acid, salicylic acid, anthranilic acid, 2-hydroxynicotinic acid, or combinations thereof.

Embodiment 98 is the article of any of embodiments 89-97, wherein the aliphatic or cycloaliphatic amine curing agent comprises a xylene diamine, a norbornene dimethylamine, or a chain-extended compound thereof.

Embodiment 99 is the article of embodiment 98, wherein the aliphatic or cycloaliphatic amine curing agent comprises meta xylene diamine, norbornene dimethylamine, or a chain-extended compound thereof.

Embodiment 100 is the article of any of embodiments 89-98, wherein the aromatic epoxy resin comprises a diglycidyl ether of bis-phenol A, a diglycidyl ether of bis-phenol F, or a combination thereof.

Embodiment 101 is the article of any of embodiments 89-100, wherein the aromatic epoxy resin comprises a diglycidyl ether of bis-phenol A, a diglycidyl ether of bis-phenol F, or a combination thereof; the aliphatic or cycloaliphatic amine curing agent comprises meta xylene diamine, norbornene dimethylamine or a chain-extended compound thereof; and the accelerator comprises salicylic acid, 3-methyl salicylic acid, anthranilic acid, 2-hydroxynicotinic acid, or combinations thereof.

Embodiment 102 is the article of any of embodiments 89-101, wherein the curable composition comprises 60-90 parts by weight of aromatic epoxy resin per 100 parts total weight of reactive components.

Embodiment 103 is the article of embodiment 102, wherein the curable composition comprises 10-35 parts by weight of aliphatic or cycloaliphatic amine curing agent per 100 parts total weight of reactive components.

Embodiment 104 is the article of embodiment 102 or 103, wherein the curable composition comprises 0.01-5.0 parts by weight of aromatic carboxylic acid accelerator per 100 parts total weight of reactive components in the curable composition.

Embodiment 105 is the article of any of embodiments 89-104, wherein the first substrate comprises a metal substrate, a ceramic substrate, a glass substrate, a polymeric substrate, or a wooden substrate.

Embodiment 106 is the article of any of embodiments 89-105, wherein the second substrate comprises a metal substrate, a ceramic substrate, a glass substrate, a polymeric substrate, or a wooden substrate.

Embodiment 107 is the article of any of embodiments 89-106, wherein the coating has a thickness of from 25 micrometers to 1 millimeter.

Embodiment 108 is a structural adhesive comprising the curable composition of any of embodiments 78-81.

Examples

Acid accelerated epoxy formulations were prepared and cured.

These examples are merely for illustrative purposes only and are not meant to be

limiting on the scope of the appended claims. All parts, percentages, ratios, etc. in the examples and the rest of the specification are by weight, unless noted otherwise. Solvents and other reagents used were obtained from Sigma-Aldrich Chemical Company, St. Louis, Missouri unless otherwise noted.

5

Table of Abbreviations

Abbreviation	Description
EP1	Epoxy, Bisphenol F available from Dow Chemical Company, Midland, MI as D.E.R. 354.
EP2	Epoxy, Bisphenol A, available from Hexion Inc., Columbus, OH as EPON 828.
CA1	Curing agent, Meta-xylenediamine available from Mitsubishi Gas Chemical Company, INC., Chiyoda-ku, Tokyo, Japan as MXDA
CA2	Curing agent, 2-Methylpentamethylenediamine available from INVISTA, Wilmington, DE as DYTEK A.
CA3	Curing agent, Ethylene Diamine available from Alfa Aesar, Shore Rd. Heysham LA3 2XY. England.
CA4	Curing agent, aromatic amine, Diethyltoluenediamine available from Albemarle Corp., Baton Rouge, LA as ETHACURE 100.
A1	Acid, 99% purity Salicylic available from Alpha Aesar, Shore Rd. Heysham LA3 2XY. England.
A2	Acid, Ortho-Anisic available from Sigma-Aldrich Chemical Company
A3	Acid, Benzoic available from Sigma-Aldrich Chemical Company
A4	Acid, 3-Methyl Salicylic available from Sigma-Aldrich Chemical Company
A5	Acid, Anthranilic available from Sigma-Aldrich Chemical Company
A6	Acid, 2-Hydroxynicotinic available from Sigma-Aldrich Chemical Company

Methods for Examples

Method for mixing acid and amine:

The specified amount of acid was finely ground, with a mortar and pestle, and put into a vial. A type K thermocouple was placed in the vial and hooked up to the data recording device, Omega Multilogger Thermometer HH506RA. The chosen amount of curing agent (amine) was poured into the vial and at the same time the data logger was started. The temperature was recorded every 2 seconds and monitored for several minutes.

Method for mixing epoxy/acid/amine:

The chosen amount of acid was crushed with a mortar and pestle and weighed out into a vial. A small amount of epoxy was weighed out and poured into the vial containing the acid. The epoxy was mixed with the acid to a paste like consistency until no large aggregates of acid could be seen. The remaining epoxy was then mixed in with the paste solution. It is important to have finely crushed acid and no apparent aggregates. Large aggregates will slow the time until the peak exotherm. A weighed out sample of the amine was then poured into the epoxy side. The solution was vigorously stirred until an even mixture resulted. A type K thermocouple was placed immediately in the vial and hooked up to the data recording device, Omega Multilogger Thermometer HH506RA, and the temperature was recorded every 15 seconds.

Example 1:

Example 1 was a mixture of 7 grams of EP1 epoxy cured with 3 grams of amine CA1 with an acid accelerant, 0.4 grams A1 ($pK_a=3$). The accelerant was premixed into the epoxy prior to contacting with the amine curing agent. The exotherm was monitored by immersion of a K-type thermocouple into 10 grams of the mixture. A hand held Omega HH506RA temperature logger was utilized to acquire and store the data. A data point was collected every 15 seconds. The data are presented in Figure 1.

Comparative Example 1

Comparative Example 1 was a mixture of 7 grams of EP1 epoxy cured with 3 grams of amine CA1. The exotherm was monitored by immersion of a K-type thermocouple into 10 grams of the mixture. A hand held Omega HH506RA temperature

logger was utilized to acquire and store the data. A data point was collected every 15 seconds. The data are presented in Figure 1.

Example 2- Carboxylic acids with various partition coefficients in epoxy/amine mixtures

Examples 2A-2D were mixtures of 10 grams of EP2 epoxy cured with 2 grams of amine CA1 with 0.5 grams of various acid accelerants as shown in Table 1. The method described above was used to mix and record temperature data. The results are shown in Figure 2. Figure 3 shows the fit of time to maximum exotherm temperature vs. log of the partition coefficient. Figure 4 shows the data for the time to maximum exotherm temperature vs pKa, demonstrating that there is not a straight line fit correlation.

Table 1. Various Carboxylic Acids, Reaction Exotherm Data and Constants.

Example	Acid	Max Exotherm Temp	Time to Max Exotherm Temp	Reaction onset Temp	Time to Reaction Onset Temp	pKa	log P	P
		C	min	C	min			
E2A	A4	221	8	49	7	2.72	3.04	1096.5
E2B	A1	171	12	49	10	2.75	2.44	275.42
E2C	A5	169	19	41	17	2.15	1.2	15.85
E2D	A6	134	40	49	37	4.97	-0.13	0.74

Example 3- Effect of acid on cure exotherm of various amines and epoxy.

Examples 3A-3C were mixtures of 10 grams of EP2 epoxy cured with stoichiometric proportions of various amines (E3A 1.6 grams CA2, E3B 2.0 grams CA1, E3C 1.5 grams CA3) with 0.5 grams of A4 acid. The method described above was used to mix and record temperature data. The results are shown in Figure 5.

Example 4- Effect of acid amount on working time of amines and epoxy.

Examples 4A-4C were mixtures of 10 grams of EP2 epoxy cured with 2 grams of amine CA1 with various amounts of acid A1 (E4A 0.3 grams, E4B 1.0 grams, E4C 2.0

grams). The method described above was used to mix and record temperature data. The results are shown in Figure 6.

Example 5- Effect of mixtures of acid on working time of amines and epoxy.

5 Examples 5A-5D were mixtures of 10 grams of EP2 epoxy cured with 2 grams of amine CA1 with various mixtures of acid A1 and A2 as shown in Table 2. The method described above was used to mix and record temperature data. The results are shown in Figure 7.

10 Table 2 Acid Mixtures for Example 5

Example	Acid A1 (grams)	Acid A2 (grams)
E5A	0.250	0.00
E5B	0.00	0.250
E5C	0.250	0.250
E5D	0.125	0.125

Example 6- Effect of acid addition to epoxy or amine side.

Examples 6A-6D were mixtures of 10 grams of EP2 epoxy cured with 2 grams of amine CA3 or CA1 with 0.5 grams of acid A1 as shown in Table 3. The method described above was used to mix and record temperature data. In one instance, salicylic acid (A1) was added to the epoxy side (EP2), dispersed well and then amine was added to this mixture. Alternatively, salicylic acid (A1) was added to the amine side and then mixed with epoxy (EP2). In either case a reaction exotherm took place followed by hardening of the mixture. The results are shown in Figure 8.

Table 3 Mixtures for Example 6

Example	First Mixture	Second Mixture
E6A	A1 and EP2	CA3 to first mixture
E6B	A1 and CA3	EP2 to first mixture
E6C	A1 and EP2	CA1 to first mixture

E6D	A1 and CA1	EP2 to first mixture
-----	------------	----------------------

Example 7- Effect of carboxylic acid the cure of an aromatic amine and epoxy.

Examples 7A-7B were mixtures of 3 parts EP2 epoxy cured with 0.72 parts aromatic amine CA4 with 0.12 parts of acid A1 for E7A and 0.12 parts of acid A2 for E7B. The method described above was used to mix. The effectiveness of the acceleration for the acids was observed by DSC (Differential Scanning Calorimetry) scan as shown in Figure 9.

Comparative Example 2

Comparative Example 2 was mixture of 3 parts EP2 epoxy cured with 0.72 parts aromatic amine CA4. The method described above was used to mix. The exotherm was observed by DSC (Differential Scanning Calorimetry) scan as shown in Figure 9.

What is claimed is:

1. A curable composition comprising:

an aromatic epoxy resin;

an aliphatic or cycloaliphatic amine curing agent; and

5 an accelerator comprising an aromatic carboxylic acid compound,

wherein the curable composition is essentially free of water, and wherein the curing time of the curable composition is less than 1 hour at room temperature.

10 2. The curable composition of claim 1, wherein the curing time of the curable composition is less than 0.5 hour at room temperature.

3. The curable composition of claim 1, wherein the curing time of the curable composition is less than 20 minutes at room temperature.

15 4. The curable composition of claim 1, wherein the curing time of the curable composition is less than 10 minutes at room temperature.

5. The curable composition of claim 1, wherein the accelerator has a log P value of from -0.5 to 4.0 where P is the partition coefficient.

20

6. The curable composition of claim 1, wherein the accelerator comprises 3-methyl salicylic acid, salicylic acid, anthranilic acid, 2-hydroxynicotinic acid, or combinations thereof.

25 7. The curable composition of claim 1, wherein the aromatic epoxy resin comprises a diglycidyl ether of bis-phenol A, a diglycidyl ether of bis-phenol F, or a combination thereof; the aliphatic or cycloaliphatic amine curing agent comprises meta xylene diamine, norbornene dimethylamine or a chain-extended compound thereof; and the accelerator comprises salicylic acid, 3-methyl salicylic acid, anthranilic acid, 2-hydroxynicotinic acid,
30 or combinations thereof.

8. A two-part curable epoxy composition comprising:

a first part comprising:

an aromatic epoxy resin;

a second part comprising:

an aliphatic or cycloaliphatic amine curing agent; and

5 an accelerator comprising an aromatic carboxylic acid compound, wherein the accelerator is located either in the first part or the second part; and

wherein the first part and the second part are essentially free from water, and wherein the 2 parts when mixed form a curable composition with a curing time that is less than 1 hour at room temperature.

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9. The two-part curable epoxy adhesive composition of claim 8, wherein the accelerator comprising an aromatic carboxylic acid compound is located in the first part.

15

10. The two-part curable epoxy adhesive composition of claim 8, wherein the accelerator comprising an aromatic carboxylic acid compound is located in the second part.

20

11. The two-part curable epoxy adhesive composition of claim 8, wherein the first part or the second part comprises an additional additive selected from fillers, thermally conductive fillers, flame retardants, nanoparticles or functionalized nanoparticles, chain extenders, toughening agents, or combinations thereof.

25

12. A method of controlling the cure time of curable epoxy composition comprising:

providing a curable mixture that is essentially free of water comprising:

an aromatic epoxy resin; and

an aliphatic or cycloaliphatic amine curing agent; and

selecting an accelerator comprising an aromatic carboxylic acid, wherein the accelerator has a log P value in the range of from -0.5 to 4.0, wherein P is the partition coefficient;

30

adding the accelerator to either the aromatic epoxy resin or the aliphatic or cycloaliphatic amine curing agent;

mixing the aromatic epoxy resin, aliphatic amine curing agent and accelerator to form

a curable composition;
permitting the curable composition to cure at room temperature, wherein the curing time of the curable composition is less than 1 hour.

5 13. The method of claim 12, wherein the accelerator has a log P value in the range of from 0.5 to 4.0; and the curing time of the curable composition is less than 0.5 hours.

14. The method of claim 12, wherein the accelerator has a log P value in the range of from 1.0 to 4.0; and the curing time of the curable composition is less than 20 minutes.

10

15. The method of claim 12, wherein the accelerator has a log P value in the range of from 3.0 to 4.0; and the curing time of the curable composition is less than 10 minutes.

16. An article comprising:

15

a first substrate comprising a first major surface and a second major surface; and
a coating on the at least a portion of the second major surface of the first substrate,
wherein the coating comprises a cured layer of a curable composition, where the
curable composition comprises:

an aromatic epoxy resin;

20

an aliphatic or cycloaliphatic amine curing agent; and

an accelerator comprising an aromatic carboxylic acid compound,

wherein the curable composition is essentially free of water, and wherein

the

curing time of the curable composition is less than 1 hour at room

25

temperature.

17. The article of claim 16, wherein the first substrate comprises a metal substrate, a ceramic substrate, a glass substrate, a polymeric substrate, or a wooden substrate.

30

18. The article of claim 17, wherein the first substrate comprises a metal substrate comprising a pipe, and wherein the second major surface of the first substrate comprises an external surface of the pipe.

19. The article of claim 16, wherein the coating has a thickness of from 25 micrometers to 5 millimeters.

5 20. The article of claim 16, further comprising a second substrate comprising a first major surface and a second major surface, wherein the first major surface of the second substrate is in contact with the cured layer of the curable composition such that the cured layer of the curable composition forms a structural adhesive bond between the first substrate and the second substrate.

10 21. A curable composition comprising:

an aromatic epoxy resin;

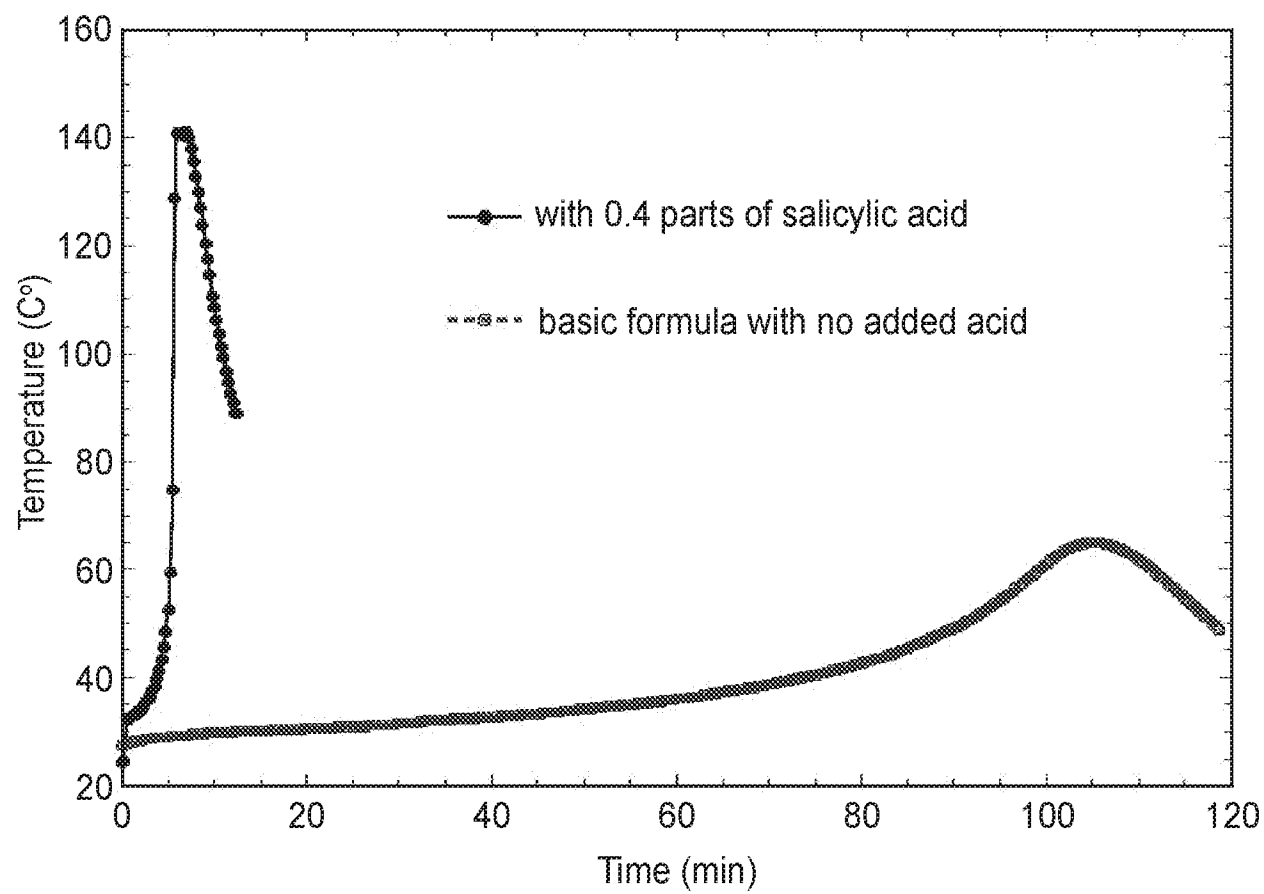
an aromatic amine curing agent; and

an accelerator comprising an aromatic carboxylic acid compound,

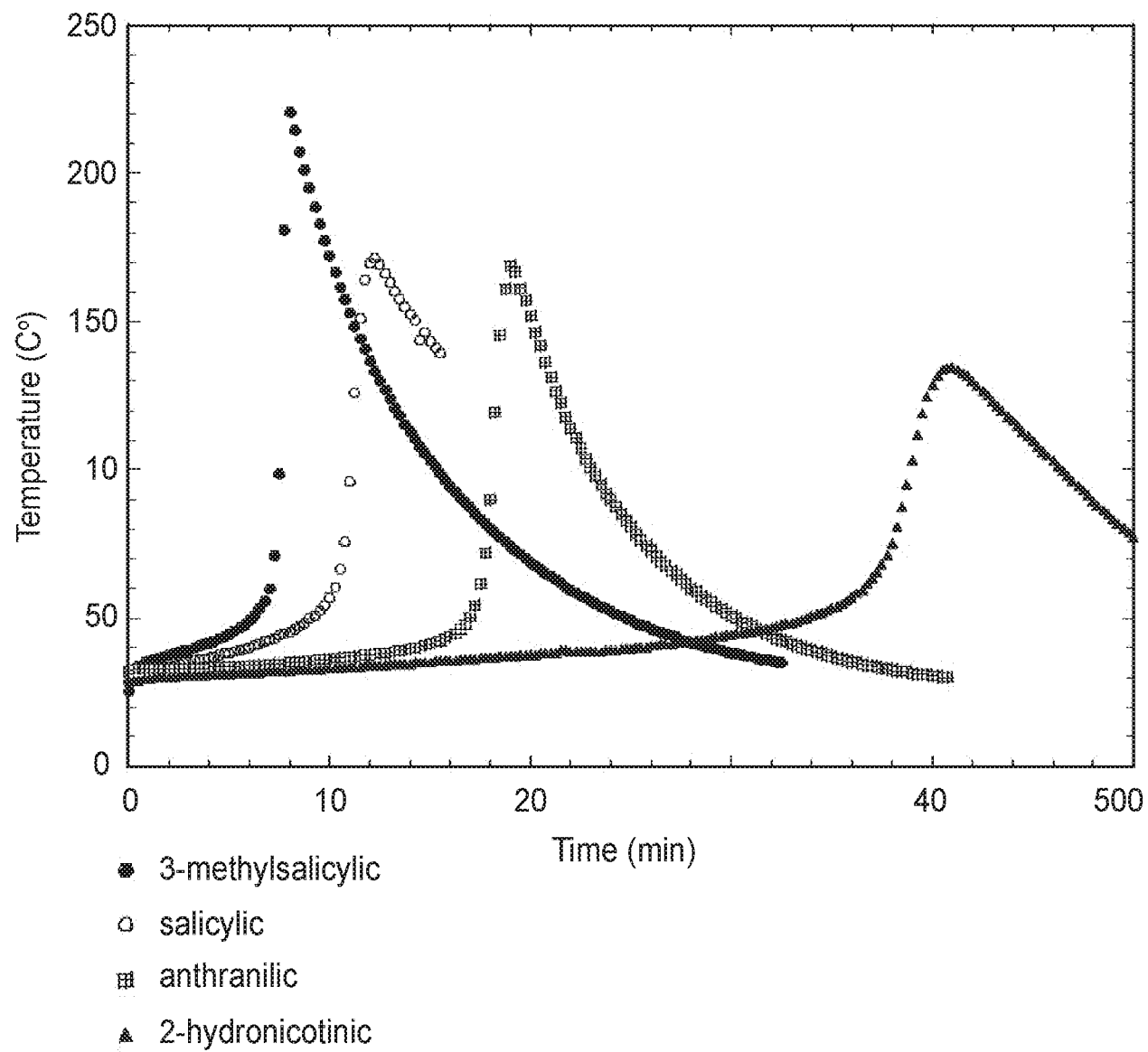
15 wherein the curable composition is essentially free of water, and wherein the curing temperature of the curable composition is 50-100°C less than for the same composition in the absence of the accelerator.

20 22. The curable composition of claim 21, wherein the accelerator comprises 3-methyl salicylic acid, salicylic acid, anthranilic acid, 2-hydroxynicotinic acid, or combinations thereof.

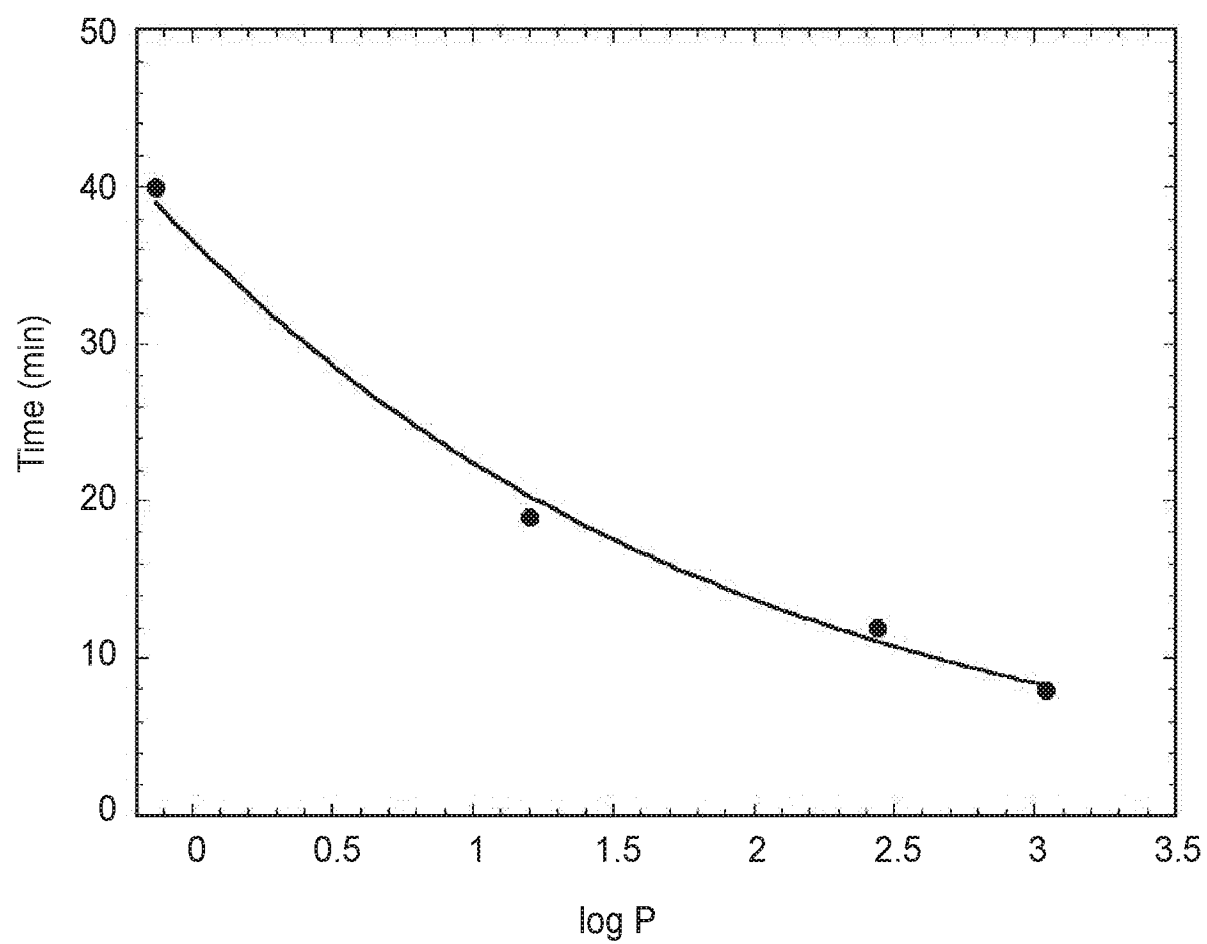
1/9

*FIG. 1*

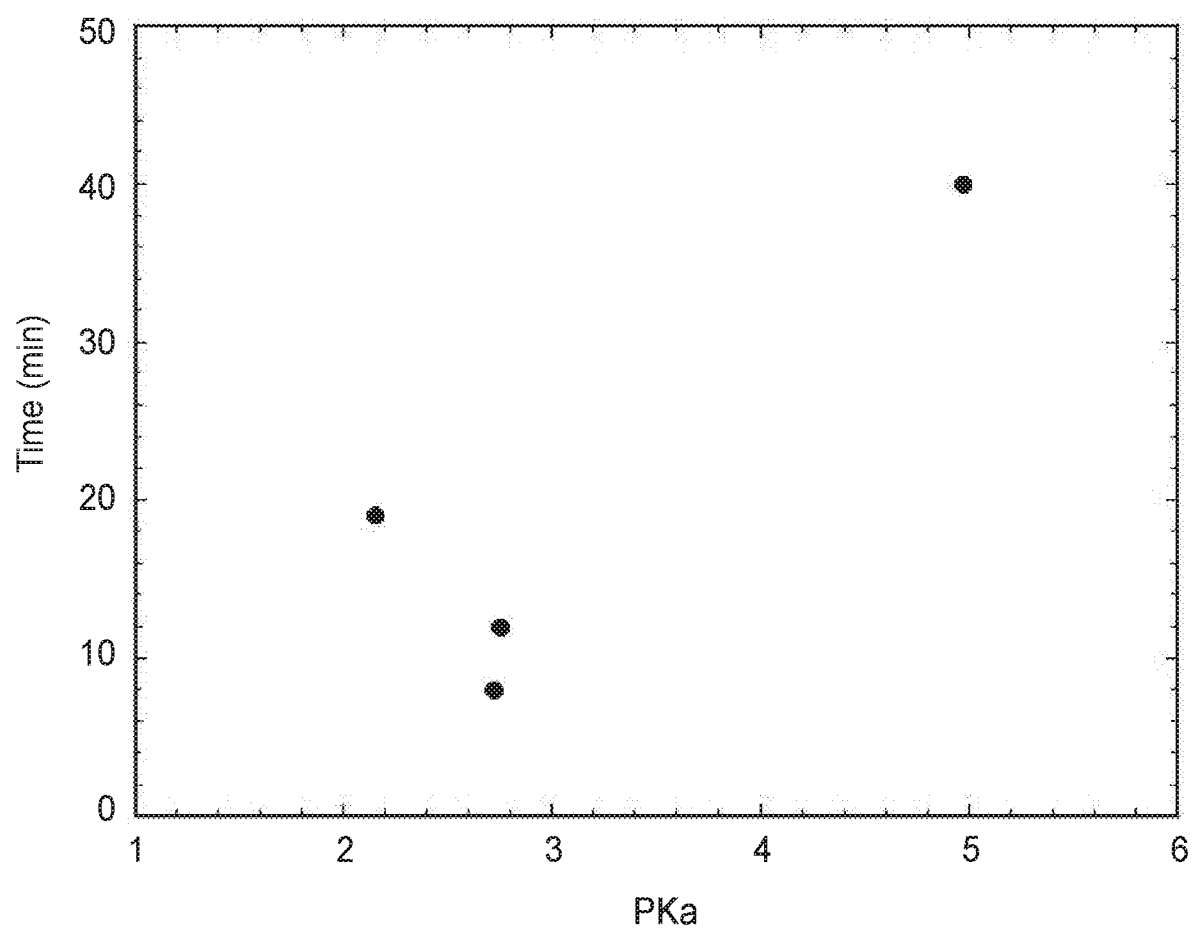
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*FIG. 2*

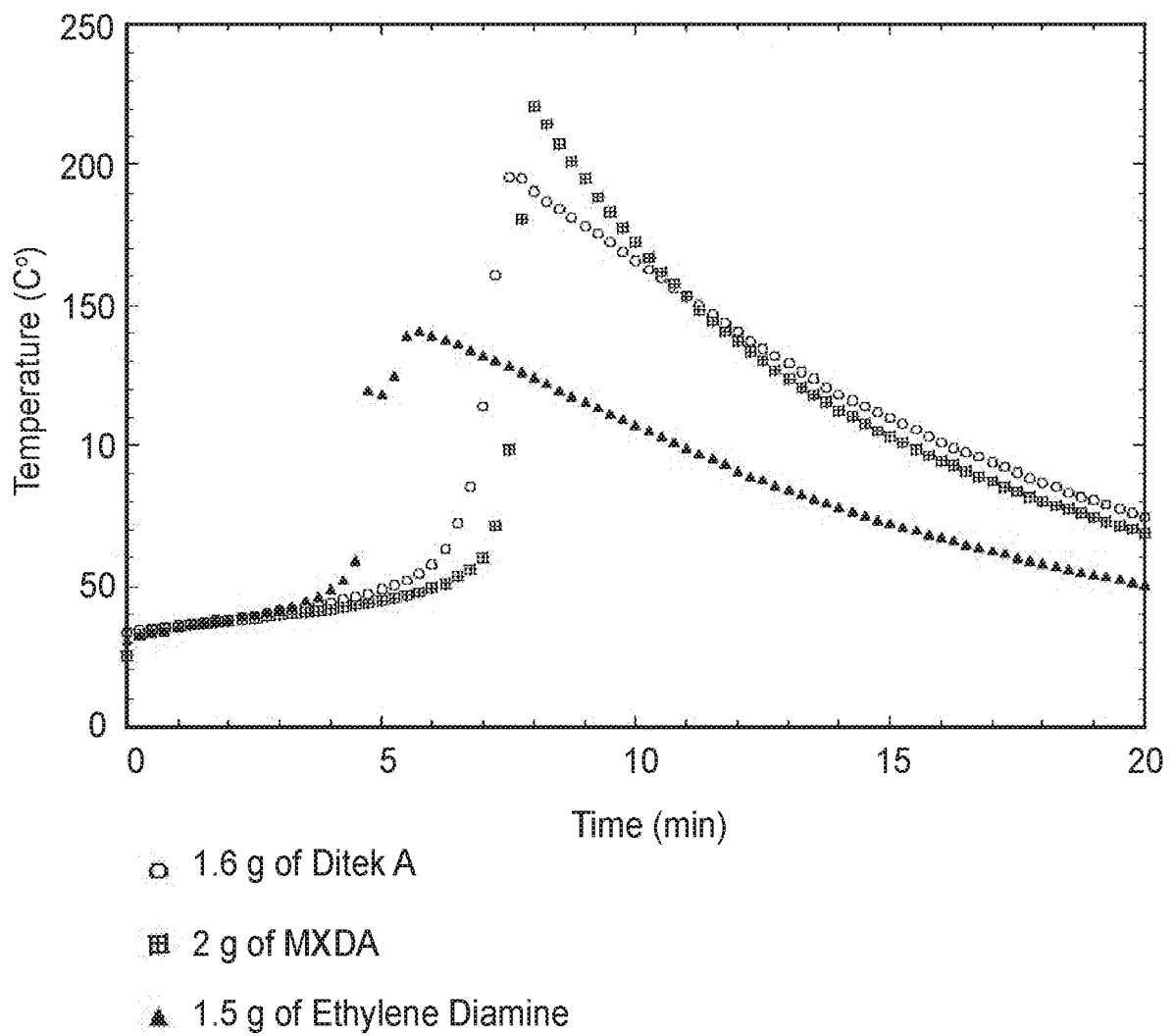
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*FIG. 3*

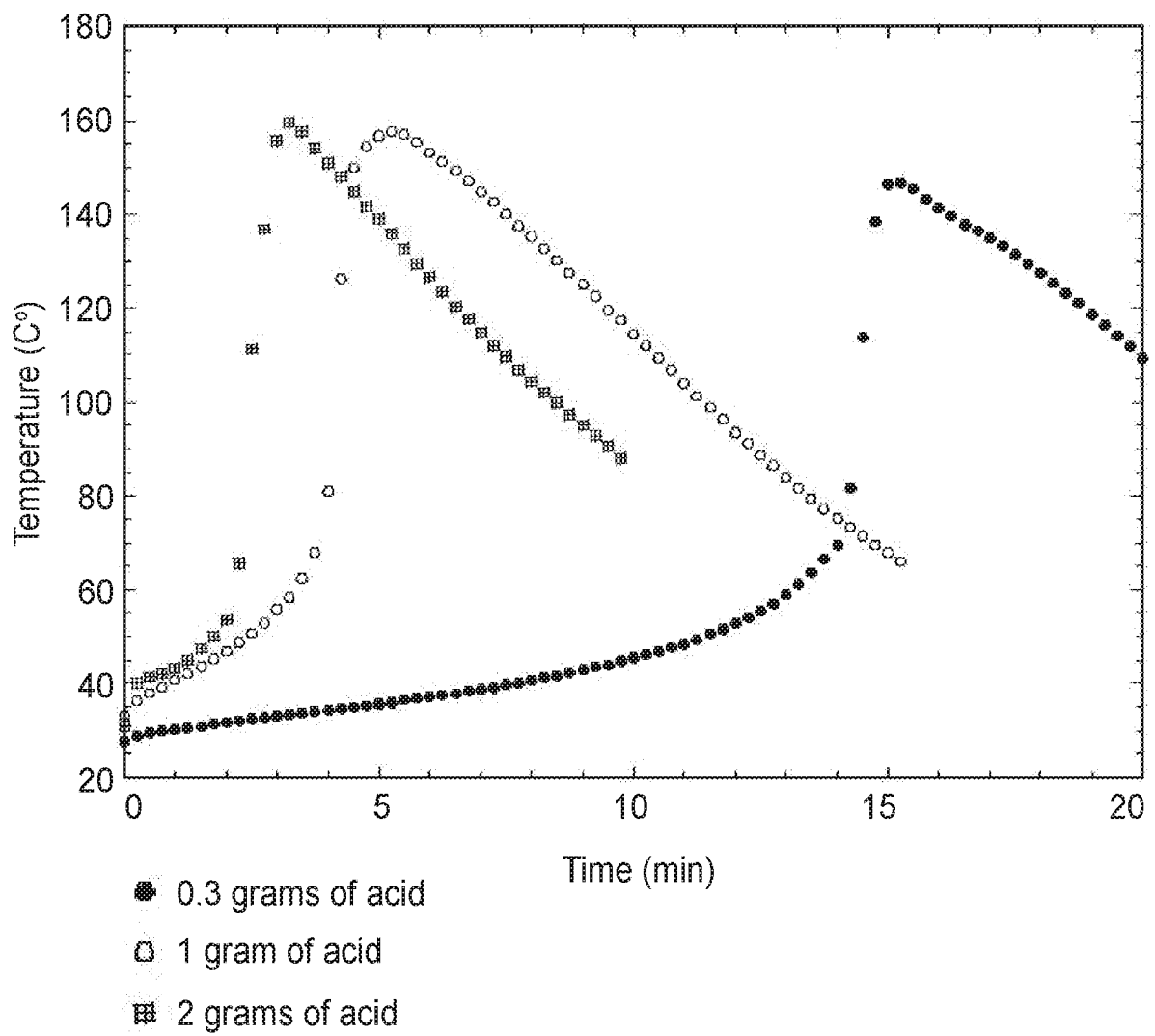
4/9

*FIG. 4*

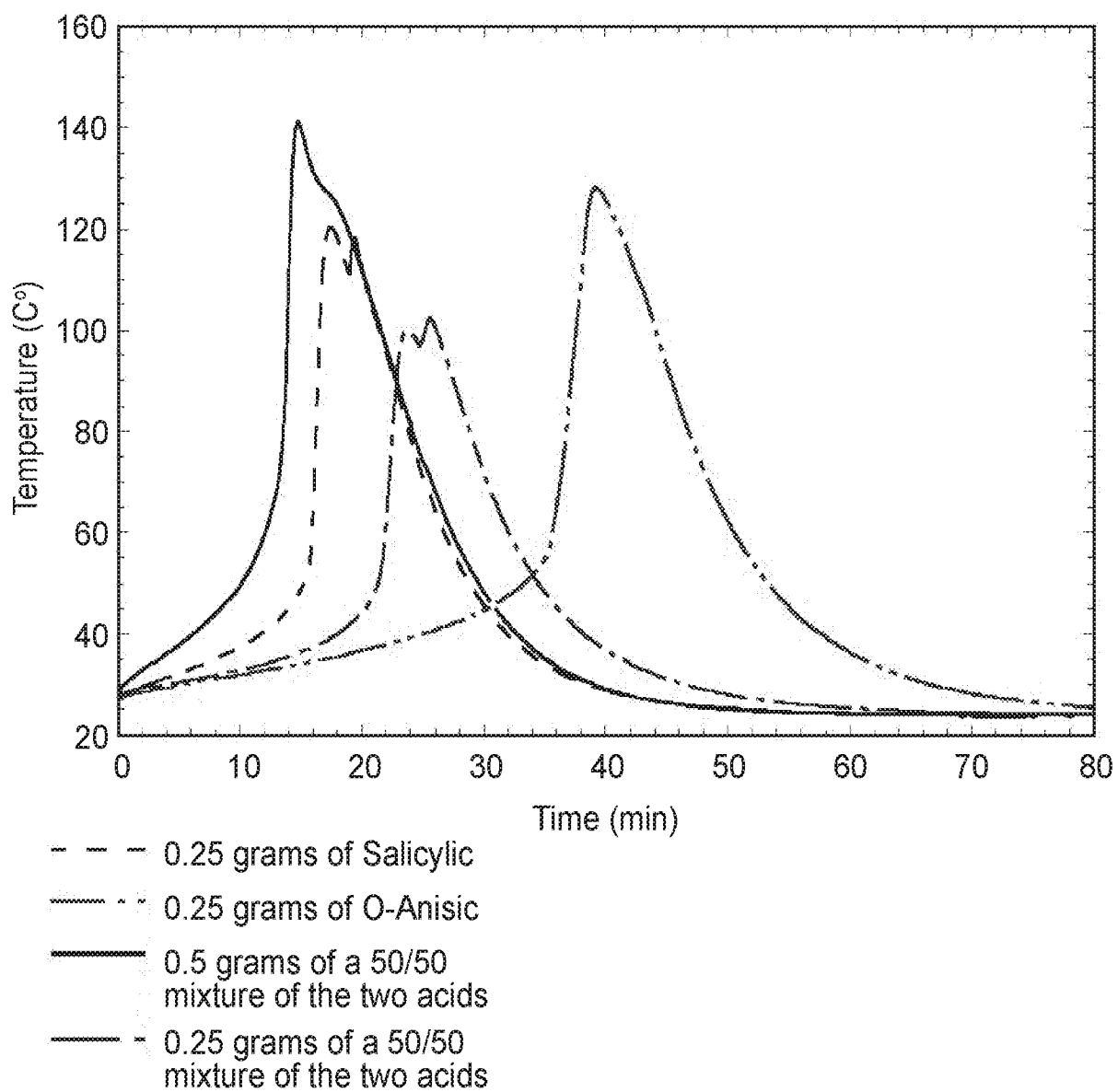
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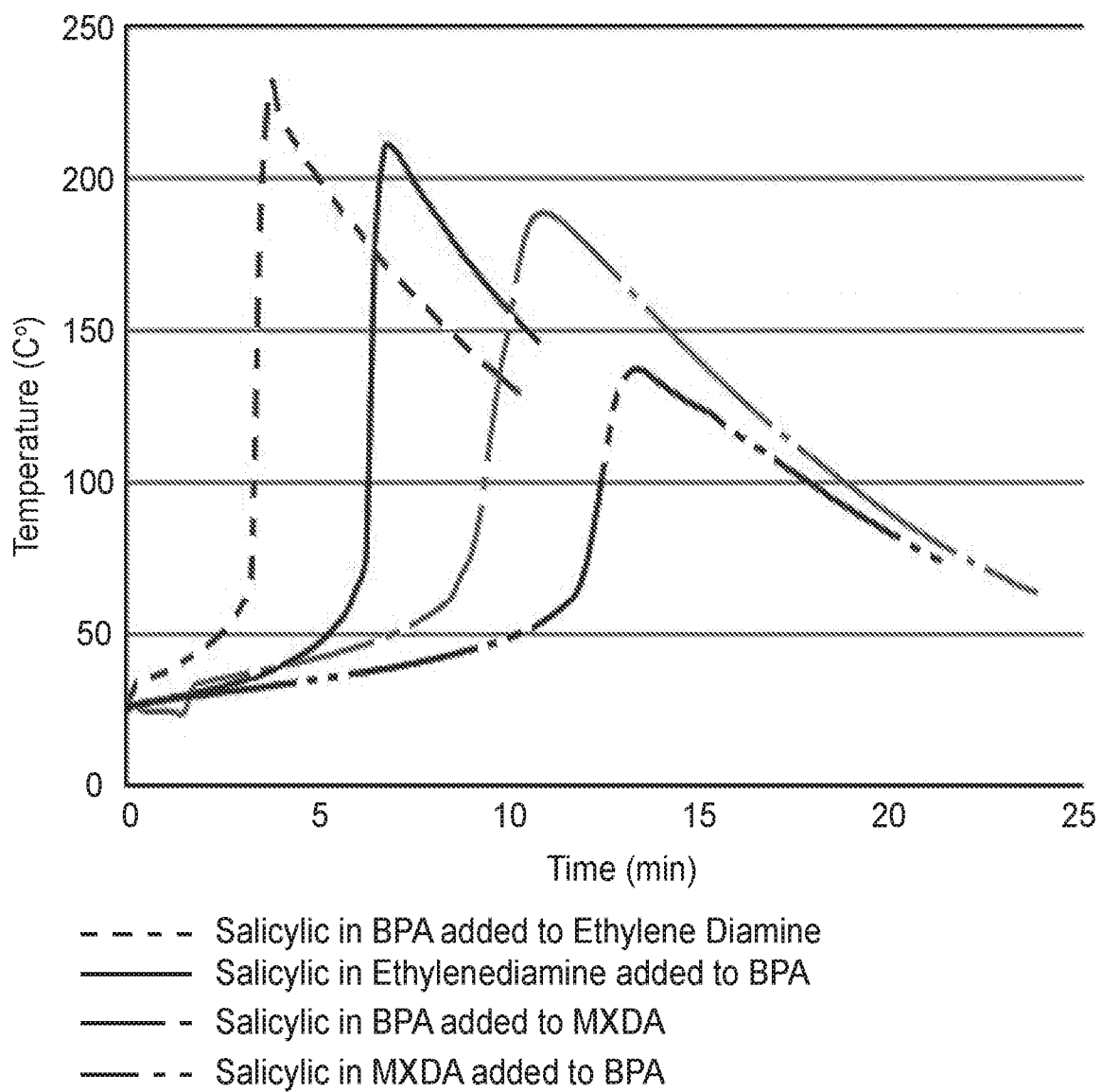
*FIG. 5*

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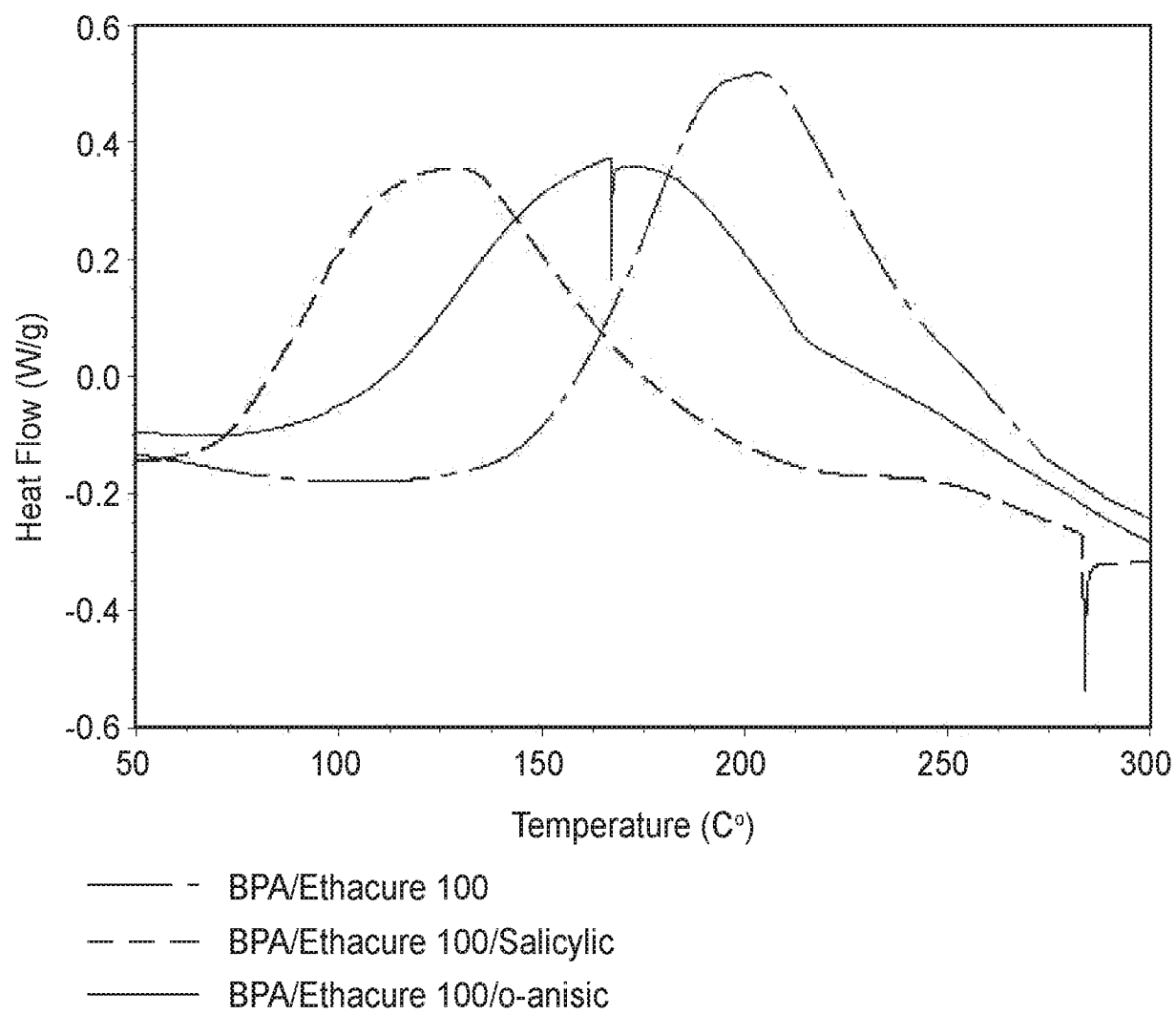
*FIG. 6*

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*FIG. 7*

*FIG. 8*

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*FIG. 9*

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/067092

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08G59/50 C08G59/68
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)

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 264 758 A (WADDILL HAROLD G) 28 April 1981 (1981-04-28) claim 1 table II column 2, line 12 - line 30 -----	1-22
X	US 3 740 373 A (BENTLEY F ET AL) 19 June 1973 (1973-06-19) claim 1 table II example V -----	1-6, 12-17
X	US 3 639 928 A (BENTLEY FLOYD EDWARD ET AL) 8 February 1972 (1972-02-08) examples 3,4-6 column 2, line 8 - line 10 ----- -/--	1-6,8, 10,12-17



Further documents are listed in the continuation of Box C.



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Date of the actual completion of the international search

13 April 2017

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INTERNATIONAL SEARCH REPORT

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 127 514 A (WADDILL HAROLD G) 28 November 1978 (1978-11-28) example 4 column 2, line 30 - line 40 -----	1-6,8, 10,12-17
X	US 2008/027169 A1 (ORTELT MARTINA [DE]) 31 January 2008 (2008-01-31) tables 1,2 paragraph [0018] paragraph [0024] paragraph [0028] -----	1-6,8, 10-17, 21,22
X	JP S59 93758 A (MITSUI PETROCHEMICAL IND) 30 May 1984 (1984-05-30) claim 1 abstract -----	1-6, 16-18, 21,22

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2016/067092

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4264758	A	28-04-1981	BR 8005841 A 19-05-1981
		CA 1181194 A 15-01-1985	
		DE 3039546 A1 14-05-1981	
		FR 2468623 A1 08-05-1981	
		GB 2061951 A 20-05-1981	
		IT 1133741 B 09-07-1986	
		JP S5667334 A 06-06-1981	
		JP S5713573 B2 18-03-1982	
		US 4264758 A 28-04-1981	
US 3740373	A	19-06-1973	NONE
US 3639928	A	08-02-1972	NONE
US 4127514	A	28-11-1978	NONE
US 2008027169	A1	31-01-2008	AT 393796 T 15-05-2008
		CN 1860164 A 08-11-2006	
		DE 102004024439 A1 08-12-2005	
		EP 1745096 A1 24-01-2007	
		JP 2007537319 A 20-12-2007	
		US 2008027169 A1 31-01-2008	
		WO 2005111135 A1 24-11-2005	
JP S5993758	A	30-05-1984	NONE