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(54) Title: STORAGE-STABLE HEAT-ACTIVATED TERTIARY AMINE CATALYSTS FOR EPOXY RESINS

(57) Abstract: Epoxy adhesive compositions contain a heat activatable catalyst. The heat activatable catalyst includes a tertiary amine catalyst and a novolac resin that has a weight average molecular weight of at least 3000. One-component epoxy adhesive formulations that contain the heat activatable catalyst have unexpectedly good storage stability.



WO 2012/000171 A1

STORAGE-STABLE HEAT-ACTIVATED TERTIARY AMINE CATALYSTS FOR EPOXY RESINS

5 This invention relates to tertiary amine catalysts for epoxy resins, and epoxy adhesives containing such catalysts.

Epoxy adhesive systems contain at least an epoxy resin, a hardener that reacts with oxirane groups on the epoxy resin to cure the polymer, and one or more catalysts. These can be generally characterized as being of two main types. The first type is a two-part system, in which the epoxy resin and the hardener are packaged separately, and are not
10 brought together until immediately before the adhesive is to be applied and cured. The two-part adhesives have the advantage of very long shelf life, but are more difficult to use because the two components must be metered and mixed at the time of application. Metering and mixing errors can lead to inadequate curing and/or poor development of adhesive properties.

15 One-part adhesives, on the other hand, are much easier to use because the metering and mixing steps are eliminated. These adhesives are formulated with the proper ratio of epoxy resin and hardener, and so they usually cure well and develop good properties. In order to provide these products with the necessary shelf-stability, so they do not cure prematurely, they are usually formulated with a solid hardener and a heat-activated catalyst. Upon application, the adhesive is brought to an elevated temperature, usually
20 80°C or higher, to melt the hardener and activate the catalyst. This allows the adhesive to cure.

Many adhesives used in automotive applications are one-component types. These are often based on a rubber-modified epoxy resin and a reactive "toughener". Adhesives of
25 these types are described in, for example, U. S. Patent No. 5,202,390, U. S. Patent No. 5,278,257, WO 2005/118734, U. S. Published Patent Application No. 2005/0070634, U. S. Published Patent Application No. 2005/0209401, U. S. Published Patent Application 2006/0276601 and EP-A-0 308 664.

The heat-activated catalyst in these systems is typically an aminophenol compound
30 which is incorporated into a solid matrix material. The matrix material contains multiple phenolic groups. One matrix material is a polymer of a vinyl phenolic compound, such as is

described in US 4,713,432. A second matrix material is an oligomeric novolac resin, such as is described in US 4,701,378. The poly(vinyl phenol) types have heretofore been the matrix materials of choice, as the novolac resins of US 4,701,378 have demonstrated somewhat poorer shelf stability when incorporated into a one-component epoxy adhesive formulation. However, long shelf stability is still desired.

This invention comprises in one aspect a mixture of a solid or liquid tertiary amine compound that has a boiling temperature of at least 130°C and a novolac resin that has a weight average molecular weight (M_w) of at least about 3000.

This invention is also a one-component epoxy adhesive, comprising:

- A) one or more epoxy resins;
- B) at least epoxy hardener having a melting temperature of at least 50°C; and
- C) a heat activatable catalyst comprising a mixture of a solid or liquid tertiary amine compound that has a boiling temperature of at least 130°C, and a novolac resin that has a weight average molecular weight of at least about 3000;

In certain aspects, the invention is a toughened one-component epoxy adhesive, comprising

- A) one or more epoxy resins;
- B) at least one epoxy hardener having a melting temperature of at least 50°C; and
- C) a heat activatable catalyst comprising a mixture of a solid or liquid tertiary amine compound that has a boiling temperature of at least 130°C and a novolac resin that has a molecular weight of at least about 3000;
- D) at least one rubber, amine-epoxy adduct or fatty acid-epoxy adduct; and
- E) at least one elastomeric toughener that has blocked or capped isocyanate groups.

In any of the foregoing aspects, the novolac resin preferably has a weight average molecular weight of at least 5000. The weight average molecular weight may be 30,000 or higher. All molecular weights herein are expressed in daltons.

It has been found that the selection of a high molecular weight novolac resin provides the heat-activatable catalyst, and one-component epoxy adhesives containing the catalyst, with exceptional storage stability. The one-component epoxy adhesives often exhibit storage stabilities that are up to several months longer (at 25°C) than are obtained with the conventionally preferred poly(vinyl phenol)-encapsulated catalyst. This result is

considered quite surprising in that the weight average molecular weight of the novolac has not heretofore been understood to have any significant relationship to the performance of the catalyst. In US 4,701,378, not only is the molecular weight somewhat limited, but within the described molecular weight range, there does not appear to be a correlation
5 between molecular weight and storage stability of the catalyst.

The invention has the further advantage of providing good curing characteristics to the epoxy adhesive formulation, once heated to a necessary activation temperature. The activation temperatures are in general not higher, or not significantly higher, than those required for conventional poly(vinyl phenol)-encapsulated catalysts, and thus no significant
10 difference in the curing conditions are needed with this invention.

The catalyst of the invention contains a certain tertiary amine compound and a novolac resin having a weight average molecular weight of at least 3000. The tertiary amine compound is characterized in having at least one tertiary amino group, in which the amine nitrogen atom is preferably bound to aliphatic carbons. The tertiary amine
15 compound is a solid or liquid at room temperature (about 23°C). It also has a boiling temperature of at least 130 °C, preferably at least 150°C and still more preferably at least 200°C.

Examples of suitable tertiary amine compounds include, for example, trialkylamines such as triethylamine, trimethylamine, tertiary diamines such as N,N,N'-tetramethylbutane
20 diamine, 1,7-bis(dimethylamino)heptane, bis(4-dimethylaminophenyl)methane and triethylene diamine, aromatic amines such as N,N-dimethylaniline, nitrogen-containing heterocyclic compounds such as 1-methylimidazole, benzimidazole, 2-phenylimidazole and quinoline, and well as aminophenols.

The preferred aminophenol catalyst contains at least one phenolic hydroxyl group, by which it is mean a hydroxyl group bonded directly to a ring carbon atom of an aromatic
25 ring structure. The aminophenol catalyst also contains at least one aliphatic tertiary amino group. The aminophenol catalyst may contain two or more of such aliphatic tertiary amino groups. Examples of suitable aminophenol catalysts include 2-(dimethylaminomethyl)phenol, 2,6-bis(dimethylaminomethyl)phenol, 2,4-bis(dimethylaminomethyl)phenol and, especially, 2,4,6-tris(dimethylaminomethyl)phenol.
30

The novolac is a condensation product of an aldehyde, especially formaldehyde, and a phenolic compound. The phenolic compound can be produced from monohydric phenols such as phenol, an alkyl phenol, an alkoxyphenol or a halogenated phenol, or from polyhydric phenols such as resorcinol, catechol, hydroquinone, bisphenol, bisphenol A, bisphenol AP (1,1-bis(4-hydroxylphenyl)-1-phenyl ethane), bisphenol F, bisphenol K, bisphenol M, and the like. The bisphenol compound is preferably unsubstituted at both meta-positions, or at a meta-position and a para- position, relative to the hydroxyl group, so reactive sites are available at which the condensation reaction can occur to provide bridging sites between molecules of the phenolic compound.

The ratios of starting materials and reaction conditions are selected such that the novolac formed in the condensation reaction has a weight molecular weight of at least 3000. The weight average molecular weight of the novolac resin can be at least 5000, and may be 30,000 or more. The molecular weight is limited only by the need for the novolac resin to soften or melt at a reasonable temperature, so it can be mixed with the aminophenol compound to produce the heat-activatable catalyst. Preferably, the novolac resin softens at a temperature of from about 90 to about 200°C, especially from about 130 to 200°C.

A preferred novolac resin is a phenol-formaldehyde resin having a weight average molecular weight of from 10,000 to 25,000.

A heat-activatable catalyst is conveniently prepared by heating the novolac resin and the aminophenol together until a clear liquid is obtained. The novolac resin and/or the aminophenol may be dissolved in a non-reactive solvent, such as a lower alcohol. Mixing ratios are preferably such that at least 0.1 phenolic hydroxyl groups are provided per tertiary amine group provided by the catalyst. It is more preferred that enough of the novolac resin is present to provide at least one phenolic hydroxyl group, and still more preferably at least two phenolic hydroxyl groups, per tertiary amine group provided by the catalyst. Up to 10, more preferably up to three, phenolic hydroxyl groups may be provided per tertiary amine group provided by the catalyst. A weight ratio of catalyst: novolac resin from 20:80 to 80:20, preferably from 70:30 to 30:70, and more preferably from 40:60 to 70:30 is useful. After a clear solution is obtained, any solvent that is present is removed, suitably by evaporation, and the resulting mixture is cooled to solidify the mixture. The product is a mixture of the tertiary amine catalyst and novolac resin; this mixture is

believed to take the form of a solid solution of the materials. The phenolic groups of the novolac resin are believed to complex with the tertiary amine groups of the catalyst material; it is further believed that the complex formation contributes to the latent effect of the catalyst and also to its storage stability in the presence of an epoxy resin and hardener.

5 An epoxy adhesive according to the invention contains at least one epoxy resin. All or part of the epoxy resin may be present in the form of a rubber-modified epoxy resin, as discussed more below. A wide range of epoxy resins can be used, including those described at column 2 line 66 to column 4 line 24 of U.S. Patent 4,734,332, incorporated herein by reference.

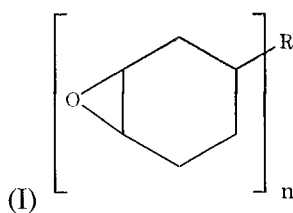
10 Suitable epoxy resins include the diglycidyl ethers of polyhydric phenol compounds such as resorcinol, catechol, hydroquinone, bisphenol, bisphenol A, bisphenol AP (1,1-bis(4-hydroxyphenyl)-1-phenyl ethane), bisphenol F, bisphenol K, bisphenol M, tetramethylbiphenol, diglycidyl ethers of aliphatic glycols and polyether glycols such as the diglycidyl ethers of C₂₋₂₄ alkylene glycols and poly(ethylene oxide) or poly(propylene oxide)
15 glycols; polyglycidyl ethers of phenol-formaldehyde novolac resins, alkyl substituted phenol-formaldehyde resins (epoxy novolac resins), phenol-hydroxybenzaldehyde resins, cresol-hydroxybenzaldehyde resins, dicyclopentadiene-phenol resins and dicyclopentadiene-substituted phenol resins, and any combination thereof.

Suitable diglycidyl ethers include diglycidyl ethers of bisphenol A resins such as are
20 sold by Dow Chemical under the designations D.E.R.® 330, D.E.R.® 331, D.E.R.® 332, D.E.R.® 383, D.E.R. 661 and D.E.R.® 662 resins.

Commercially available diglycidyl ethers of polyglycols include those sold as D.E.R.® 732 and D.E.R.® 736 by Dow Chemical.

Epoxy novolac resins can be used. Such resins are available commercially as
25 D.E.N.® 354, D.E.N.® 431, D.E.N.® 438 and D.E.N.® 439 from Dow Chemical.

Other suitable additional epoxy resins are cycloaliphatic epoxides. A cycloaliphatic epoxide includes a saturated carbon ring having an epoxy oxygen bonded to two vicinal atoms in the carbon ring, as illustrated by the following structure I:



wherein R is an aliphatic, cycloaliphatic and/or aromatic group and n is a number from 1 to 10, preferably from 2 to 4. When n is 1, the cycloaliphatic epoxide is a monoepoxide. Di- or epoxy resins are formed when n is 2 or more. Mixtures of mono-, di- and/or epoxy resins can be used. Cycloaliphatic epoxy resins as described in U.S. Patent No. 3,686,359, incorporated herein by reference, may be used in the present invention. Cycloaliphatic epoxy resins of particular interest are (3,4-epoxycyclohexyl-methyl)-3,4-epoxy-cyclohexane carboxylate, bis-(3,4-epoxycyclohexyl) adipate, vinylcyclohexene monoxide and mixtures thereof.

Other suitable epoxy resins include oxazolidone-containing compounds as described in U. S. Patent No. 5,112,932. In addition, an advanced epoxy-isocyanate copolymer such as those sold commercially as D.E.R. 592 and D.E.R. 6508 (Dow Chemical) can be used.

The epoxy resin preferably is a bisphenol-type epoxy resin or mixture thereof with up to 10 percent by weight of another type of epoxy resin. Preferably the bisphenol type epoxy resin is a liquid epoxy resin or a mixture of a solid epoxy resin dispersed in a liquid epoxy resin. The most preferred epoxy resins are bisphenol-A based epoxy resins and bisphenol-F based epoxy resins.

An especially preferred epoxy resin is a mixture of a diglycidyl ether of at least one polyhydric phenol, preferably bisphenol-A or bisphenol-F, having an epoxy equivalent weight of from 170 to 299, especially from 170 to 225, and at least one second diglycidyl ether of a polyhydric phenol, again preferably bisphenol-A or bisphenol-F, this one having an epoxy equivalent weight of at least 300, preferably from 310 to 600. The proportions of the two types of resins are preferably such that the mixture of the two resins has an average epoxy equivalent weight of from 225 to 400. The mixture optionally may also contain up to 20%, preferably up to 10%, of one or more other epoxy resins.

The epoxy resin constitutes at least about 10 weight percent of the adhesive, more preferably at least about 15 weight percent, and most preferably at least about 20 weight percent. The epoxy resin preferably constitutes up to about 70 weight percent of the

adhesive, more preferably up to about 60 weight percent, and most preferably up to about 50 weight percent.

The epoxy adhesive further contains an epoxy hardener. The hardener is a solid at room temperature has a melting temperature of at least 50°C and preferably at least 80°C. It contains functional groups, typically primary and/or secondary amino groups, which react with oxirane groups to form a bond thereto and extend the polymer chain. Suitable such hardeners include boron trichloride/amine and boron trifluoride/amine complexes, dicyandiamide, melamine, diallylmelamine, guanamines such as acetoguanamine and benzoguanamine, aminotriazoles such as 3-amino-1,2,4-triazole, hydrazides such as adipic dihydrazide, stearic dihydrazide, isophthalic dihydrazide, semicarbazide, cyanoacetamide, and aromatic polyamines such as diaminodiphenylsulphones. Dicyandiamide, isophthalic acid dihydrazide, adipic acid dihydrazide and 4,4'-diaminodiphenylsulphone are particularly preferred.

The curing agent is used in sufficient amount to cure the composition. The curing agent suitably constitutes at least about 1.5 weight percent of the adhesive, and more preferably at least about 2.5 weight percent. The curing agent preferably constitutes up to about 15 weight percent of the adhesive composition, more preferably up to about 10 weight percent, and most preferably up to about 6 weight percent.

Preferred epoxy adhesives of the invention contain at least one rubber. The rubber should have a glass transition temperature (T_g) of no greater than -25°C. Preferably, at least a portion of the rubber has a T_g of -40°C or lower, more preferably -50°C or lower and even more preferably -70°C or lower. The T_g of the rubber may be as low as -100°C or even lower.

The rubber is preferably present in the form of a rubber-modified epoxy resin, in the form of core-shell particles, or some combination of both.

A rubber-modified epoxy resin is an epoxy-terminated adduct of an epoxy resin and at least one liquid rubber that has epoxide-reactive groups, such as amino or preferably carboxyl groups. The rubber in this case is preferably a homopolymer or copolymer of a conjugated diene, especially a diene/nitrile copolymer. The conjugated diene rubber is preferably butadiene or isoprene, with butadiene being especially preferred. The preferred nitrile monomer is acrylonitrile. Preferred copolymers are butadiene-acrylonitrile

copolymers. The rubbers preferably contain, in the aggregate, no more than 30 weight percent polymerized unsaturated nitrile monomer, and preferably no more than about 26 weight percent polymerized unsaturated nitrile monomer.

The rubber preferably contains (prior to reaction with the epoxy resin to form the adduct) from about 1.5, more preferably from about 1.8, to about 2.5, more preferably to about 2.2, epoxide-reactive terminal groups per molecule, on average. Carboxyl-terminated rubbers are preferred. The molecular weight (M_n) of the rubber is suitably from about 2000 to about 6000, more preferably from about 3000 to about 5000.

Suitable carboxyl-functional butadiene and butadiene/acrylonitrile rubber starting materials are commercially available from Noveon under the tradenames Hycar® 2000X162 carboxyl-terminated butadiene homopolymer and Hycar® 1300X31 Hycar® 1300X8, Hycar® 1300X13, Hycar® 1300X9 and Hycar® 1300X18 carboxyl-terminated butadiene/acrylonitrile copolymers. A suitable amine-terminated butadiene/acrylonitrile copolymer is sold under the tradename Hycar® 1300X21.

The rubber is formed into an epoxy-terminated adduct by reaction with an excess of an epoxy resin. Enough of the epoxy resin is provided to react with all of the epoxide-reactive groups on the rubber and to provide free epoxide groups on the resulting adduct, without significantly advancing the adduct to form high molecular weight species. A ratio of at least two equivalents of epoxy resin per equivalent of epoxy-reactive groups on the rubber is preferred. More preferably, enough of the epoxy resin compound is used that the resulting product is a mixture of the adduct and some free epoxy resin compound. Typically, the rubber and an excess of the epoxy resin are mixed together with a polymerization catalyst and heated to a temperature of about 100 to about 250°C in order to form the adduct. Useful catalysts for conducting the reaction between the rubber and the epoxy resin include those described below. Preferred catalysts for forming the rubber-modified epoxy resin include phenyl dimethyl urea and triphenyl phosphine.

A wide variety of epoxy resins can be used to make the rubber-modified epoxy resin, including any of those described before. Preferred epoxy resins are liquid or solid glycidyl ethers of a bisphenol such as bisphenol A or bisphenol F. Halogenated, particularly brominated, resins can be used to impart flame retardant properties if desired. Liquid epoxy resins (such as DER 330 and DER 331 resins, which are diglycidyl ethers of

bisphenol A available from The Dow Chemical Company) are especially preferred for ease of handling.

When a rubber-modified epoxy resin is present, as just described, the rubber-modified epoxy resin will serve as all or part of each of components (A) (the epoxy resin) and (B) (the rubber) of the adhesive. Thus, if a rubber-modified epoxy resin is present, it is not necessary for the adhesive to include any additional rubber or any additional epoxy resin. However, one or more such additional epoxy resins may also be present, and one or more additional rubbers, notably a core-shell rubber as described below, may also be present together with a rubber-modified epoxy resin.

Another suitable type of rubber is a core-shell rubber. The core-shell rubber is a particulate material having a rubbery core. The rubbery core preferably has a T_g of less than -25°C , more preferably less than -50°C and even more preferably less than -70°C . The T_g of the rubbery core may be well below -100°C . The core-shell rubber also has at least one shell portion that preferably has a T_g of at least 50°C . By "core", it is meant an internal portion of the core-shell rubber. The core may form the center of the core-shell particle, or an internal shell or domain of the core-shell rubber. A shell is a portion of the core-shell rubber that is exterior to the rubbery core. The shell portion (or portions) typically forms the outermost portion of the core-shell rubber particle. The shell material is preferably grafted onto the core or is crosslinked. The rubbery core may constitute from 50 to 95%, especially from 60 to 90%, of the weight of the core-shell rubber particle.

The core of the core-shell rubber may be a polymer or copolymer of a conjugated diene such as butadiene, or a lower alkyl acrylate such as n-butyl-, ethyl-, isobutyl- or 2-ethylhexylacrylate. The core polymer may in addition contain up to 20% by weight of other copolymerized monounsaturated monomers such as styrene, vinyl acetate, vinyl chloride, methyl methacrylate, and the like. The core polymer is optionally crosslinked. The core polymer optionally contains up to 5% of a copolymerized graft-linking monomer having two or more sites of unsaturation of unequal reactivity, such as diallyl maleate, monoallyl fumarate, allyl methacrylate, and the like, at least one of the reactive sites being non-conjugated.

The core polymer may also be a silicone rubber. These materials often have glass transition temperatures below -100°C . Core-shell rubbers having a silicone rubber core

include those commercially available from Wacker Chemie, Munich, Germany, under the trade name Genioperl™.

The shell polymer, which is optionally chemically grafted or crosslinked to the rubber core, is preferably polymerized from at least one lower alkyl methacrylate such as methyl methacrylate, ethyl methacrylate or t-butyl methacrylate. Homopolymers of such methacrylate monomers can be used. Further, up to 40% by weight of the shell polymer can be formed from other monovinylidene monomers such as styrene, vinyl acetate, vinyl chloride, methyl acrylate, ethyl acrylate, butyl acrylate, and the like. The molecular weight of the grafted shell polymer is generally between 20,000 and 500,000.

A preferred type of core-shell rubber has reactive groups in the shell polymer which can react with an epoxy resin or an epoxy resin hardener. Glycidyl groups are suitable. These can be provided by monomers such as glycidyl methacrylate.

A particularly preferred type of core-shell rubber is of the type described in EP 1 632 533 A1. Core-shell rubber particles as described in EP 1 632 533 A1 include a crosslinked rubber core, in most cases being a crosslinked copolymer of butadiene, and a shell which is preferably a copolymer of styrene, methyl methacrylate, glycidyl methacrylate and optionally acrylonitrile. The core-shell rubber is preferably dispersed in a polymer or an epoxy resin, also as described in EP 1 632 533 A1.

Preferred core-shell rubbers include those sold by Kaneka Corporation under the designation Kaneka Kane Ace, including Kaneka Kane Ace MX 156 and Kaneka Kane Ace MX 120 core-shell rubber dispersions. The products contain the core-shell rubber particles pre-dispersed in an epoxy resin, at a concentration of approximately 25%. The epoxy resin contained in those products will form all or part of the epoxy resin component of the adhesive of the invention.

Amine epoxy adducts include, for example, reaction products of a diamine with a carboxylic anhydride and a polyphenol or an aminophenol as described in WO 01/94492. Fatty acid epoxy adducts include reaction products of fatty acids or oligomerized fatty acids (including dimer fatty acids) with epichlorohydrin, glycidol, diglycidyl ethers of polyphenols, and the like.

The adhesive of the invention preferably has a total rubber content, amine epoxy adduct and fatty acid epoxy adduct content of at least 1 weight percent, more preferably

from 3 to 15 weight percent and especially from 4 to 10 weight percent. Total rubber content is calculated for purposes of this invention by determining the weight of core-shell rubber particles (if any), plus the weight contributed by the liquid rubber portion of the rubber-modified epoxy resin(s) (if any), plus the weight of any other rubbers that may be present (if any). In each case, the weight of unreacted (non-rubber-modified) epoxy resins and/or other carriers, diluents, dispersants or other ingredients that may be contained in the core-shell rubber product or rubber-modified epoxy resin is not included. The weight of the shell portion of the core-shell rubber is counted as part of the total rubber content for purposes of this invention.

A preferred adhesive in accordance with the invention further contains at least one elastomeric toughener. The elastomeric toughener is a liquid or low-melting elastomeric material that contains capped or blocked isocyanate groups. The elastomeric portion of the elastomeric toughener includes one or more soft segments such as a polyether, a polybutadiene, or a polyester. Particularly preferred soft segments include poly(ethylene oxide) blocks, poly(propylene oxide) blocks, poly(ethylene oxide-co-propylene oxide) blocks, poly(butylene oxide) blocks, poly(tetrahydrofuran) blocks, poly(caprolactone) blocks and the like. These soft segments typically have a molecular weight of from 1000 to 10,000 daltons each, preferably from about 1500 to 5000 daltons. An especially preferred type of soft segment is a poly(tetrahydrofuran) block having a weight of from 2200 to 4500 daltons.

The elastomeric toughener contains at least one blocked or capped isocyanate group per molecule. It preferably contains an average of at least 2 such groups per molecule, but typically no more than 6 and preferably no more than about 4 blocked or capped isocyanate groups per molecule. Examples of capping or blocking groups are phenols or phenolamines, primary aliphatic, cycloaliphatic, heteroaromatic and araliphatic amines; secondary aliphatic, cycloaliphatic, aromatic, heteroaromatic and araliphatic amines, monothiols, alkylamides and hydroxyl functional epoxides, and benzyl alcohols. The capping or blocking group may contain functional groups such as phenol, aromatic amino, -OCN, epoxide, or it may comprise further polyurethane elastomers bound to it, but the capping or blocking group may instead be devoid of such groups. Preferred capping groups include a secondary aliphatic amine, a hydroxyalkylepoxy, or a phenol, aminophenol, polyphenol, allylphenol, or polyallylpolyphenol such as o,o-diallyl bisphenol A.

A convenient way to produce the elastomeric toughener is by forming an isocyanate-terminated prepolymer, and then reacting the remaining isocyanate groups with the capping or blocking agent. The isocyanate-terminated prepolymer is prepared by reacting a polyether polyol or polyester polyol, which corresponds to the structure of the soft segment of the reactive toughener, with an excess of a polyisocyanate. The polyisocyanate preferably contains aliphatic isocyanate groups. Preferred polyisocyanates are hexamethylene diisocyanate and isophorone diisocyanate.

The elastomeric toughener should be soluble or dispersible in the remainder of the components of the epoxy adhesive. The elastomeric toughener preferably has a viscosity at 45°C which is not greater than 1000 Pa·s and more preferably no more than about 800 Pa·s. Preferably, the weight average molecular weight of the toughener is about 8,000 or greater, and more preferably about 10,000 or greater. Preferably, the weight average molecular weight of the toughener is about 80,000 or less, and more preferably about 40,000 or less. Molecular weights as used herein are determined according to GPC analysis.

General methods for preparing these elastomeric tougheners are described, for example, in U. S. Patent No. 5,278,257, WO 2005/118734, U. S. Published Patent Application No. 2005/0070634, U. S. Published Patent Application No. 2005/0209401, U. S. Published Patent Application 2006/0276601, EP 1 602 702A and EP-A-0 308 664.

The elastomeric toughener may be linear, branched or lightly crosslinked.

The elastomeric toughener is present in sufficient amount to improve the performance of adhesive compositions containing it under dynamic load. The elastomeric toughener suitably constitutes at least about 10 weight percent, preferably at least about 14 weight percent and more preferably at least about 18 weight percent of the resin component A. Preferably, the elastomeric toughener constitutes up to about 38 weight percent of the adhesive, more preferably up to about 28 weight percent and even more preferably up to about 25 weight percent of the epoxy resin component A.

A one-component epoxy adhesive may contain other optional components. Once such optional component is a bisphenol compound that has two or more, preferably two, phenolic hydroxyl groups per molecule. Examples of suitable bisphenol compounds include, for example, resorcinol, catechol, hydroquinone, bisphenol, bisphenol A, bisphenol AP (1,1-bis(4-hydroxyphenyl)-1-phenyl ethane), bisphenol F, bisphenol K, tetramethylbiphenol

and the like. The bisphenol component can be dissolved into the adhesive composition or present in the form of finely divided particles. Preferably, the bisphenol component is pre-reacted with an epoxy resin (which may include a rubber-modified epoxy resin, if present) to advance the resin somewhat.

5 If used, the bisphenol component is preferably used in an amount from about 3 to about 35 parts by weight per 100 parts by weight of the rubber component. A preferred amount is from about 5 to about 25 parts by weight per 100 parts by weight of the rubber component. When the bisphenol component is added directly into the adhesive, it usually constitutes from 0.25 to 2 weight percent, especially 0.4 to 1.5 weight percent, of the
10 adhesive.

The one-component epoxy adhesive of the invention may contain various other optional components. Among these, fillers, rheology modifiers or pigments, one or more additional epoxy resins and a core-shell rubber are particularly preferred.

A filler, rheology modifier and/or pigment is preferably present in the one-
15 component epoxy adhesive. These can perform several functions, such as (1) modifying the rheology of the adhesive in a desirable way, (2) reducing overall cost, (3) absorbing moisture or oils from the adhesive or from a substrate to which it is applied, and/or (4) promoting cohesive, rather than adhesive, failure. Examples of these materials include calcium carbonate, calcium oxide, talc, coal tar, carbon black, textile fibers, glass particles
20 or fibers, aramid pulp, boron fibers, carbon fibers, mineral silicates, mica, powdered quartz, hydrated aluminum oxide, bentonite, wollastonite, kaolin, fumed silica, silica aerogel or metal powders such as aluminum powder or iron powder. Among these, calcium carbonate, talc, calcium oxide, fumed silica and wollastonite are preferred, either singly or in some combination, as these often promote the desired cohesive failure mode.

25 A filler of particular interest is a microballon having an average particle size of up to 200 microns and density of up to 0.2 g/cc. The particle size is preferably about 25 to 150 microns and the density is preferably from about 0.05 to about 0.15 g/cc. Expanded microballoons which are suitable include those commercially available from Dualite Corporation under the trade designation Dualite™, and also from Lehmann & Voss,
30 Hamburg, Germany. Specific examples of suitable polymeric microballoons include Dualite™ E065-135 and Dualite E130-40D microballoons. In addition, expandable

microballoons such as Expancel microspheres, which are available commercially from Akzo Nobel. Microballoons are conveniently present at a level of from about 1 to about 5 weight percent, preferably 1.5 to 3 weight percent, of the adhesive. Microballoons are preferably used in conjunction with one or more additional fillers, such as talc, calcium oxide, wollastonite, calcium carbonate, fumed silica or mixtures thereof.

The one-component epoxy adhesive can further contain other additives such as diluents, plasticizers, extenders, pigments and dyes, fire-retarding agents, thixotropic agents, flow control agents, thickeners such as thermoplastic polyesters, gelling agents such as polyvinylbutyral, adhesion promoters and antioxidants.

Fillers, rheology modifiers, gelling agents, thickeners and pigments preferably are used in an aggregate amount of about 5 parts per hundred parts of adhesive composition or greater, more preferably about 10 parts per hundred parts of adhesive composition or greater. They preferably are present in an amount of up to about 25 weight percent of the adhesive, more preferably up to about 20 weight percent. An advantage of this invention is that the adhesive retains good adhesive strength and impact strength, even when it contains as much as 15 to 25% by weight of fillers.

The adhesive is formed by mixing the epoxy resin, hardener, heat-activatable catalyst and optional ingredients, in any convenient order. Elevated temperatures may be used to soften the various materials in order to compound them more easily, but it is desirable to avoid using temperatures high enough to melt the hardener and/or activate the catalyst. Therefore, temperatures are generally kept to below 50°C during the adhesive-formulation process, when the hardener and/or the heat activatable catalyst are present.

The adhesive composition can be applied by any convenient technique. It can be applied cold or be applied warm if desired. It can be applied by extruding it from a robot into bead form on the substrate, it can be applied using manual application methods such as a caulking gun, or any other manual application means. The adhesive can also be applied using jet spraying methods such as a steaming method or a swirl technique. The swirl technique is applied using an apparatus well known to one skilled in the art such as pumps, control systems, dosing gun assemblies, remote dosing devices and application guns. The adhesive may be applied to the substrate using a streaming process. Generally,

the adhesive is applied to one or both substrates. The substrates are contacted such that the adhesive is located between the substrates to be bonded together.

After application, the adhesive is cured by heating to a temperature at which the curing agent initiates cure of the epoxy resin composition. Generally, this temperature is about 80°C or above, preferably 100°C or above. Preferably, the temperature is about 220°C or less, and more preferably about 180°C or less.

The adhesive of the invention can be used to bond a variety of substrates together including wood, metal, coated metal, aluminum, a variety of plastic and filled plastic-substrates, fiberglass and the like. In one preferred embodiment, the adhesive is used to bond parts of automobiles together or parts to automobiles. Such parts can be steel, coated steel, galvanized steel, aluminum, coated aluminum, plastic and filled plastic substrates.

An application of particular interest is bonding of automotive frame components to each other or to other components. The frame components are often metals such as cold rolled steel, galvanized metals, or aluminum. The components that are to be bonded to the frame components can also be metals as just described, or can be other metals, plastics, composite materials, and the like.

Adhesion to brittle metals such as galvaneal is of particular interest in the automotive industry. Galvaneal tends to have a zinc-iron surface that is somewhat rich in iron content and is brittle for that reason. A particular advantage of this invention is that the cured adhesive bonds well to brittle metals such as galvaneal. Another application of particular interest is the bonding of aerospace components, particularly exterior metal components or other metal components that are exposed to ambient atmospheric conditions during flight.

The adhesive composition once cured preferably has a Young's modulus of about 1000 MPa as measured according to DIN EN ISO 527-1. More preferably, the Young's modulus is about 1200 MPa or greater. Preferably, the cured adhesive demonstrates a tensile strength of about 25 MPa or greater, more preferably about 30 MPa or greater, and most preferably about 35 MPa or greater. Preferably, the lap shear strength of a 1.5 mm thick cured adhesive layer is about 15 MPa or greater, more preferably about 20 MPa or greater, and most preferably about 25 MPa or greater measured according to DIN EN 1465.

An epoxy adhesive of the composition has excellent storage stability. Storage stability refers to the extent to which the one-component epoxy adhesive resists curing under typical conditions under which it is stored and cured. An adhesive having good storage stability builds viscosity only slowly if at all under normal storage and transportation conditions, and thus remains usable for periods of weeks or months from the time it is packaged. Therefore, storage stability can be assessed by storing the material under defined conditions and periodically measuring viscosity. Smaller viscosity increases in a given period of time indicates better storage stability and, conversely, poorer storage stability is indicated by greater increases in viscosity.

In actual practice, transportation and storage conditions often are not stringently controlled, and can vary considerably. It is not unusual for adhesive products to encounter storage temperatures of 40°C or more during summer months, in uncooled warehouses and transportation vessels. Therefore, a preferred one-component epoxy adhesive of the invention also exhibits good storage stability at temperatures at least as high as 40°C.

Preferably, a one-component epoxy adhesive in accordance with the invention will exhibit a viscosity increase of no more than 30%, more preferably no more than 25%, after being stored under an inert atmosphere such as nitrogen for 24 weeks at a temperature of 23°C.

A one-component epoxy adhesive in accordance with the invention preferably exhibits a viscosity increase of no more than 70% (i.e., to 1.7 times its starting viscosity), still more preferably no more than 50% and even more preferably no more than 40%, after being stored under an inert atmosphere for 24 weeks at a temperature of 30°C.

A one-component epoxy adhesive in accordance with the invention preferably exhibits a viscosity increase of no more than 400% (i.e., to 3 times its starting viscosity), still more preferably no more than 350% after being stored under an inert atmosphere for 24 weeks at a temperature of 40°C.

Viscosity measurements are conveniently made using a Bohlin CS-50 or equivalent rheometer and a 4°/20mm plate/cone system. To measure the viscosity, the sample is heated to 45°C and equilibrated there for five minutes. The shear rate is ramped from 0.1/second to 20/second over five minutes at 45°C and then down to 0.1/second over another five minutes, again at 45°C. Viscosity is determined at 10/second.

The following examples are provided to illustrate the invention but are not intended to limit the scope thereof. All parts and percentages are by weight unless otherwise indicated.

5 **Examples 1-2**

44 parts of a 10,000 molecular weight phenol-formaldehyde novolac resin having a softening temperature of 130°C (Resicure 3057, from SI Group) are melted at 140°C. 56 parts of 2,4,6-tris(dimethylaminomethyl)phenol are added to the molten novolac resin, and the resulting mixture is stirred at 140°C for 30 minutes. A clear solution is obtained,
10 which is cooled to room temperature and ground to a powder. The resulting heat-activatable catalyst is designated Example 1.

Example 2 is prepared by dissolving 44 parts of a 24,000 molecular weight phenol-formaldehyde novolac resin (Resicure 5200, from SI Group) having a softening temperature of 180° into methanol. The resulting solution is combined with 56 parts of
15 2,4,6-tris(dimethylaminomethyl)phenol and brought to reflux for two hours to form a clear solution. The mixture is cooled to room temperature and the methanol is removed by evaporation. The resulting solid is dried and ground to a powder.

Example 3

20 A simple epoxy adhesive formulation is prepared to evaluate the curing activity of heat activatable catalyst Examples 1 and 2. The formulation contains DER™ 330 epoxy resin, dicyandiamide and various amounts of heat activatable catalyst Example 1. DER™ 331 is a liquid diglycidyl ether of bisphenol A, available from The Dow Chemical Company. It has an epoxy equivalent weight of approximately 187. Three samples, designated
25 Examples 3-A through 3-E, are prepared. The ratios of these ingredients are as given in Table 1.

Curing characteristics are evaluated by dynamic scanning calorimetry on a Q2000 instrument from TA Instruments. 5-15 mg of sample are tested under dry nitrogen. The samples are heated from 20°C to 250°C at 10°C/minute, held at 250°C for 30 minutes, then
30 cooled to room temperature at 10°C/minute and then reheated to 250°C at 10°C/minute.

The cure on-set temperature, peak exotherm temperature, T_g of the cured resin and enthalpy are all determined. Results are as indicated in Table 1.

Table 1

Ingredients	Parts by Weight				
	Ex. 3-A	Ex. 3-B	Ex. 3-C	Ex. 3-D	Ex. 3-E
Epoxy resin	93.49	92.31	89.94	93.7	91.8
Dicyandiamide	5.26	5.19	5.06	5.3	5.2
Catalyst Example 1	1.25	2.50	5.00	0	0
Catalyst Example 2	0	0	0	1	3
Test Results					
On-set temperature, °C	146	136	126	146	132
Peak temperature, °C	169	160	148	164	151
T_g , °C	123	123	123	134	125
Enthalpy, J/g	255	282	338	289	310

5

Example 4 and Comparative Sample A

A toughened crash-durable epoxy adhesive is prepared by mixing 54.65 parts of a mixture of liquid diglycidyl ethers of bisphenol-A, 13.22 parts of an adduct of a butadiene-acrylonitrile rubber and an epoxy resin, available commercially from Schill and Seilacher as Struktol™ 3914, 14 parts of a polyurethane toughener having capped terminal isocyanate groups, 1.49 parts of a wetting agent, 0.72 parts of an epoxy silane, 4.33 parts of dicyandiamide, 5.16 parts of fumed silica, 1 part of a heat activatable catalyst and 5.43 parts of fillers.

15 For Example 4, the heat activatable catalyst is the Example 1 catalyst. For Comparative Sample A, the heat activated catalyst is 2,4,6-

tris(dimethylaminomethyl)phenol in a poly(vinylphenol matrix). Active catalyst levels are the same in Example 4 and Comparative Sample A.

The storage stabilities of Example 4 and Comparative Sample A are evaluated at various temperatures as indicated in Table 2 below, by making viscosity measurements at the start of testing and after storing at the specified temperatures for the indicated periods of time. Testing is performed on a Bohlin CS-50 rheometer and a 4°/20mm plate/cone system. The samples are conditioned at 45°C for five minutes. While holding the sample at this temperature, the shear rate is increased from 0.1/second to 20/second over five minutes, and then decreased back to 0.1/second at the same rate. Viscosity at 10/second is measured. Results are as indicated in Table 2.

Table 2

Storage Conditions (Temperature, time)	Initial Viscosity, Pa·s (10/sec)	Final Viscosity, cP	Ratio, Final/Initial Viscosity	% Increase* *
23°C, 24 weeks				
Ex. 4	130	152	1.17	17%
Comp. Sample A*	126	174	1.38	38%
30°C, 24 weeks				
Ex. 4	130	176	1.35	35%
Comp. Sample A	126	235	1.86	86%
40°C, 24 weeks				
Ex. 4	130	402	3.1	210%
Comp. Sample A	126	561	4.4	340%

*Not an example of the invention. **Calculated as 100% X [(final viscosity – initial viscosity)/initial viscosity].

In all cases, significantly better storage stability is seen with the catalyst of the invention.

WHAT IS CLAIMED IS:

1. A heat-activatable catalyst composition comprising mixture of a solid or liquid tertiary amine compound that has a boiling temperature of at least 130°C and a novolac resin that has a weight average molecular weight of at least about 3000.
2. The heat-activatable catalyst composition of claim 1 wherein the tertiary amine compound includes at least one aminophenol.
3. The heat-activatable catalyst composition of claim 2 wherein the aminophenol is 2-(dimethylaminomethyl)phenol, 2,6-bis(dimethylaminomethyl)phenol, 2,4-bis(dimethylaminomethyl)phenol or 2,4,6-tris(dimethylaminomethyl)phenol.
4. The heat-activatable catalyst composition of any of claim 1-3 wherein the novolac resin has a weight average molecular weight of from 5000 to 20,000.
5. The heat-activatable catalyst composition of any of claims 1-4 wherein the novolac resin is a phenol novolac resin.
6. The heat-activatable catalyst composition of any of claims 1-5 wherein the weight ratio of the tertiary amine compound and the novolac resin is from 40:60 to 70:30.
7. A one-component epoxy adhesive, comprising:
 - A) one or more epoxy resins;
 - B) at least epoxy hardener having a melting temperature of at least 50°C; and
 - C) a heat activatable catalyst composition of any of claims 1-6.
8. A toughened one-component epoxy adhesive, comprising
 - A) one or more epoxy resins;
 - B) at least one epoxy hardener having a melting temperature of at least 50°C; and
 - C) a heat activatable catalyst composition of any of claims 1-6;

- D) at least one rubber, amine epoxy adduct or fatty acid-epoxy adduct; and
- B) at least one elastomeric toughener that has blocked or capped isocyanate groups.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2010/074701

A. CLASSIFICATION OF SUBJECT MATTER

See Extra Sheet

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)

IPC: C09J163/-, C08G59/-

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)

WPI, EPODOC, CNPAT, CNKI, CA, ISI Web of Knowledge, Elsevier Science Direct: tertiary, amine, novolac, resin, aminophenol, phenol+, epoxy, adhesive, hardener, toughen+, polymer+.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US4701378A (CIBA-GEIGY CORPORATION) 20 Oct. 1987 (20.10.1987) column 2, line 32-column 6, line 11	1-8
A	US4302373A (E. I. DU PONT DE NEMOURS AND COMPANY) 24 Nov. 1981 (24.11.1981) claims 1-28	1-8
A	CN1687229A (JIANG SU ZHONGDIAN HUAWEI ELECTRONIC CO. LTD.) 26 Oct. 2005 (26.10.2005) claim 2	1-8
A	CN1651542A (UNIV. WUHAN TECHNOLOGY) 10 Aug. 2005 (10.08.2005) claims 1-10	1-8

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

☒ See patent family annex.

* Special categories of cited documents:	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim (S) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 18 Mar. 2011 (18.03.2011)	Date of mailing of the international search report 31 Mar. 2011 (31.03.2011)
Name and mailing address of the ISA/CN The State Intellectual Property Office, the P.R.China 6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China 100088 Facsimile No. 86-10-62019451	Authorized officer SU, Min Telephone No. (86-10) 82245342

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2010/074701

Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
US4701378A	20.10.1987	EP0 197892A	15.10.1986
		JP61231024A	15.10.1986
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		EP0197892B	18.10.1989
		CA1259897A	26.09.1989
		DE3666442G	23.11.1989
		DE3674052G	18.10.1990
		JP6060231B	10.08.1994
US4302373A	24.11.1981	None	
CN1687229A	26.10.2005	CN100335541C	05.09.2007
CN1651542A	10.08.2005	None	

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2010/074701

Continuation of : A. CLASSIFICATION OF SUBJECT MATTER

C09J163/00 (2006.01) i

C08G59/50 (2006.01)i

C08G59/40 (2006.01)i