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(54) Title: NOVEL EPOXY RESIN CURE CATALYST

(57) Abstract

An epoxy resin catalyst and accelerator encompassed by the interreaction of a hydroxylated aromatic sulfone composition with a secondary amine. The resulting epoxy resin system containing the catalyst/accelerator may be used in applications such as adhesives, matrix resins for various composites, prepregs and coatings.

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Novel Epoxy Resin Cure Catalyst

Brief Description Of The Invention

An epoxy resin catalyst and accelerator composition containing the reaction product of a secondary amine and an organosulfonoxy compound and an epoxy resin composition containing the same.

Background To The Invention

According to *Kaelble, Noacanin and Gupta*, "Physical, Mechanical Properties of Cured Resins," Epoxy Resins, *Chemistry and Technology*, Second Edition (Clayton A. May, Ed.), publ. by Marcel Dekker, Inc., New York, N.Y., 1988, pp. 608-609, epoxy resins are a "three-dimensional network with a regular structure" when there is "optimum conditions of mixing cosolubility of epoxy and curing agent, and well-controlled curing." The authors go on to state at page 608:

> "However, these conditions are not always ideally achieved. Erath and Spurr reported on the occurrence of globular formations of 400- to 900Å diameter as a frequent problem in phenolic and epoxy resins [17]. These globular micelles are quite abundant in epoxies and apparently arise from crosslinking reactions that proceed most

rapidly at specific points in the resin. This type of structural inhomogeneity characterized by regions of higher and lower crosslinking density can logically be traced to nonoptimum cosolution and curing. Explanations of discrepancies between the theoretical and experimental values for properties like tensile strength may be traced to this heterogeniety of structure.

"Epoxy resins are noncrystalline, and the cured resins find structural applications normally below their heat-distortion or glass-transition temperature. In addition to the modulus or rigidity and strength, an important mechanical property of epoxy resin is toughness, or impact strength."

At page 609, they point out that the "idealized tensile strength" of an epoxy resin based on the cohesive-energy-density concept predicts $S_b=0.23\delta^2$ where S_b is the maximum tensile strength of a flawless sample in the absence of plastic deformation. The equation refers to the solid-state response of polymers. For epoxy resins, where δ = 9.7 to 10.9 $(cal/cm^3)^{\frac{1}{2}}$ and failure is of a brittle character, this relation predicts: S_b=940 to 1190kg/cm^2 = 13,300 to 16,900 psi. Values within these ranges can be obtained with a number of epoxy resins "when the tensile tests were conducted at high speed, such that failure occurred within 12 msec. and at a low temperature, -54°C, where stress relaxation processes were practically eliminated"

"Further experiments by Wegman et al. showed that increasing the temperature, lowering the speed of testing, or adding plasticizer, all of which introduce stress-relaxation processes and ductile response, lowered the tensile strength of epoxies below the range of the ... prediction."

In reality, industrial-characterized epoxy resins (free of reinforcement) give average tensile strengths ranging from about 9,000 to about 13,000psi.

It would be desirable to have cured epoxy resins that possess such homogeniety in the cured structure, that the tensile strength of the resin exceeds the idealized tensile strength range.

Organosulfonyl compounds range from relatively neutral materials to strong acids. The organosulfonyl compounds used in the invention are organosulfones. Such sulfones are not usually used as reactants where a reaction proceeds through the sulfone groups. These materials are typically used as solvents because of their polar nature and their inertness. When they are employed in a reaction, the reaction is effected by other groups that are present in the compounds. Sulfone moieties are known to affect the course of a chemical reaction, oftentimes by acting to withdraw electrons from a functional group at a different site in the molecule and this is known to enhance the occurrence of a nucleophilic reaction between the functional group and another functional reactant.

The reaction of organosulfonic compounds with amines is well known in the art. If the organosulfonic compound is the acid, then the amine salt is the usual product if amine hardeners are present. In this case, where a salt is formed, *Tanaka and Bauer,* "Curing Reactions," Epoxy Resins, *Chemistry and Technology,* Second Edition (Clayton A. May, Ed.), publ. by Marcel Dekker, Inc., New York, N.Y., 1988, page 299, suggest that the salt will retard epoxy cure. If it is the sulfonyl halide, then the sulfonamide is the usual product. In the instances where either the salt is formed or the sulfonamide, the bond forming these compounds is a strong one --- either an ionic or covalent bond. However, *Tanaka and Bauer, supra,* suggest that sulfonic acids and sulfonamides act as accelerators of epoxy cure. This suggests that the salt is a retarder of cure much as acetic acid was ineffective as a catalyst "because of salt formation with the amine. There is described in U.S. Patent No. 3,839,282, the formation of a complex (termed an adduct by the patentees) of an imidazole and sulfur dioxide (SO_2), a normally gaseous material, that ends up as a precipitated solid. The complex is capable of acting as a latent epoxy catalyst. According to the patent, the complex when mixed in an epoxy resin does not cause the epoxy resin to cure at room temperature, but at an elevated temperature the same epoxy formulation will undergo cure. A possible explanation could be that the SO_2 acts as a hydrogen bond acceptor in retarding the curing rate, see *Tanaka and Bauer, supra,* p.299. According to the patentee, latency exits when the epoxy resin containing the adduct has a shelf life of weeks or months (e.g., at least 6 months) and become non-latent

when heated to elevated temperatures (e.g., above 50°C.. preferably above 130°C.) and the cure is expeditious. An apparent deficiency of the catalyst is that upon cure, SO_2 is expected to be released, and one would anticipate at least a portion of it to be released to the atmosphere. This, of course, introduces an environmental problem.

Many amines are known to catalyze the cure of epoxy resins. Imidazoles are a class of amines that are well recognized amine epoxy resin catalysts. *Tanaka and Bauer, supra,* page 308, points out that "[C]ertain imidazoles and imidazolines are known to be good curing agents or catalysts." They state that some complexes of imidazole and imidazoline are efficient and low-exotherm latent curing agents for epoxy resins. Many amines are known hardeners of epoxy resins. In each instance, amines have fostered the polymerization of epoxy resins, even at low temperatures, such as temperatures lower than room temperature. The rate of polymerization increases with increased temperature. However, of the amines, imidazoles are a particular class that works effectively as a catalyst and a hardener, and in the terms of U.S. 3,839,282, it is best characterized as a curing agent.

Also, there are amines that contain sulfone groups that are hardeners for epoxy resins. One of the widely used hardener is bis(4,4'-diaminodiphenyl)sulfone ("DDS"). It is not generally used as a cure catalyst for epoxy resins. According to *Babayan*, U.S. 4,331,582, patented May 25, 1982, DDS

"has been added to high temperature epoxy formulations to provide humidity resistance. However, the DDS-epoxy reaction is extremely slow and the material never cures completely. The most widely utilized latent catalysts for promoting the reaction of DDS with epoxies are BF_3-complexes. However, the BF_3-complex is a much better accelerator of the epoxy to epoxy reaction and when used in conjunction with DDS, because of the sluggishness of the DDS-epoxy reaction, a substantial portion of the DDS remains unreacted, acting as a plasticizer in the cured product.

"Imidazoles and especially alkylated imidazoles are known to provide high temperature epoxies with excellent properties. However, these formulations gel in minutes and do not provide any latency."

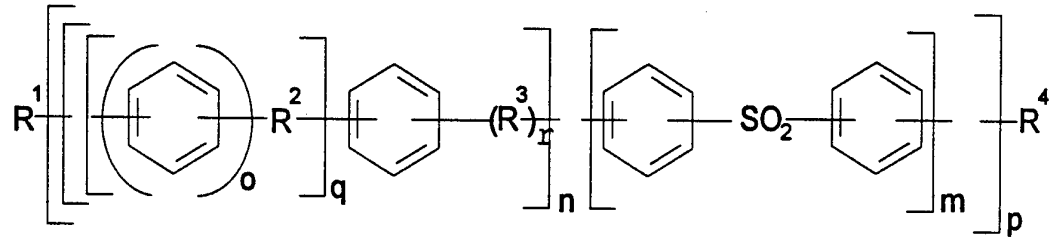
Babayan reacts an aromatic sulfonic acid with an imidazole to form a mono-salt structure. This mono-salt can be added to epoxy resins, according to the patentee, to introduce latency. The mono-salt is stable up to 200 °F. (93.3°C.) and can be combined with DDS when curing the epoxy resin.

The Invention

This invention depicts epoxy resin cure systems that rapidly homopolymerize or copolymerize epoxy resins without excessive exotherm, and that can be controlled to produce a thermoset having tensile strengths equal to or greater than the idealized tensile strength, *supra*. In addition, this invention encompasses curing agents

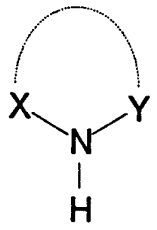
that accelerate the curing of epoxy resins to form thermosets that possess higher tensile strength, toughness and/or T_g.

This invention relates to a novel epoxy resin catalyst and accelerator encompassed by the interreaction of a sulfone composition of the formula:

I.) 

A B

with a secondary amine of the formula:

II.) 

wherein

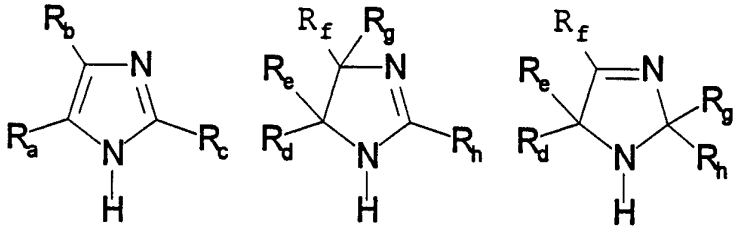
(a) X and Y, individually, are organic groups bondied to the nitrogen by a carbon to nitrogen bond, in which said carbon is bonded to oxygen to form a carbonyl moiety or is saturated;

(i) X and Y, individually, may be alkyl of 1 to about 14 carbon atoms, monocyclic aryl, monocyclic alkaryl in which the alkyl contains 1 to about 12 carbon atoms, monocyclic aralkyl in which the alkyl contains 1 to about 12 carbon atoms, cycloalkyl of about 5 to about 8 carbon atoms, or they may be joined

to form a heterocyclic ring containing the secondary amino group as a ring member;

(ii) preferred secondary amines are heterocyclic amines containing a secondary amino group are compounds such as (1) an imidazole or imidazoline encompassed by the formulae:

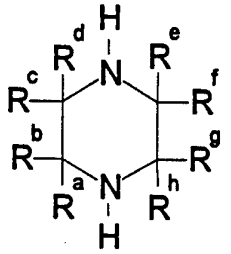
III.)



C D E

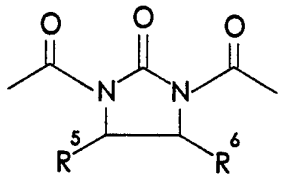
and (2) a piperazine encompassed by the formula:

IV.)



(b) m has a value of at least 1; n has a value of 0 or equal to or greater than ("≥") 1; the ratio of m to n, when n is ≥1, is from about 0.01 to 100, provided there is one unit B per molecule; p has a value of at least one; q has a value of 0 or ≥1; r has a value of 1 to about 4; o has a value of 0 or 1; g has a value of 0 or ≥1; R^1 and R^4 are (i) hydroxyl bonded to an aromatic carbon of an aromatic ring in units A and B or (ii) a monovalent hydroxyl substituted aliphatic organic group bonded through oxygen to an aromatic carbon of an aromatic ring in units A and B; R^2 is an

ether oxygen group, a carboxylic acid ester group, a sulfone group, a divalent aliphatic hydrocarbon group, a substituted divalent aliphatic hydrocarbon group wherein the substituent is hydroxyl, alkoxy, aroxy, alkaroxy, aralkoxy, and the like, a dioxy terminally-substituted divalent aliphatic hydrocarbon group, a substituted dioxy terminally-substituted divalent aliphatic hydrocarbon group wherein the substituent is carbon-bonded hydroxyl, alkoxy, aroxy, alkaroxy, aralkoxy, and the like, or a divalent unit of the formula:

V.) 

(c) R^5 and R^6 are hydrogen and an organo group bonded to the ring carbon by a carbon to carbon bond or an oxygen to carbon bond; R^3 is a carboxylic acid ester, a carbonate, a carbamate, an amide, an ether oxygen, the divalent unit of formula V.) above bonded to one of oxygen or an nitrogen to form an amide unit with the nitrogen, a divalent aliphatic hydrocarbon group, a substituted divalent aliphatic hydrocarbon group wherein the substituent is hydroxyl, alkoxy, aroxy, alkaroxy, aralkoxy, and the like; a dioxy terminally-substituted divalent aliphatic hydrocarbon group, a substituted dioxy terminally-substituted divalent aliphatic hydrocarbon group wherein the substituent is carbon-bonded hydroxyl, alkoxy, aroxy, alkaroxy, aralkoxy, and the like; R_{a-h} are each hydrogen, alkyl, aryl and, where bonded to adjacent carbons,

may be joined to form an aromatic fused ring group; one or more, preferably one, of R_{a-h} may be substituted by an azolyl such as an imidazolyl or an azolinyl such as imidazolinyl. R^a - R^h are individually hydrogen or an organo group bonded to the carbon of the heterocyclic ring by a carbon to carbon bond. Particularly desirable organo groups are alkyl, alkoxyalkyl, aryl, alkaryl, aralkyl, cycloalkyl, and the like. Generally, the organo groups contain not greater than about 10 carbon atoms.

A special embodiment of the invention includes a Brönsted or Lewis acid cationic catalyst as part of the catalyst composition of the invention. The Brönsted or Lewis acid cationic catalysts are especially preferred components of the catalyst system when the epoxy formulation that is being cured uses primary and/or secondary amines as hardeners.

In addition, the invention relates to the selective cure of epoxy resins by the copolymerization of a polyfunctional epoxy resin with a poly-p-amine, preferably one in which primary amino groups are bonded to carbon atoms of an aromatic ring. When such primary amines react with an epoxy group, the amino groups are converted to secondary amines. These are not the secondary amines that form part of the catalyst structure, but the secondary amines resulting from the reaction of the primary amino groups of polyamines with epoxy groups. In this case, the secondary amine hydrogens that are formed from the reaction of the primary amino groups with the epoxy groups, are retarded

from entering into the crosslinking reaction. This results in cured epoxy resins that have superior tensile strengths, ductility, elongation, and the like. Sacrificed by this reaction is the T_g of the thermoset polymer. However, an interesting aspect of the melting characteristics of these thermoset polymers is that many of them have bimodal T_gs, i.e., two glass transition temperatures. The invention allows for the control of the crosslinking reaction of the formed secondary amines so that one can select a combination of properties for the thermoset epoxy resins.

The sulfone molecule of formula I.) may be a monomer, dimer, oligomer or higher polymer and the secondary amine of formula II.) may be one or more s-amines. The proportion of secondary amine to the sulfone is minimally at least one secondary amine or mixture of secondary amines (averaging the equivalent of a molecule) for each sulfone group in the sulfone molecule of formula I.). Preferably, there is at least two such secondary amines (or mixtures averaging the equivalent of a molecule) associated with a sulfone group in the sulfone molecule. In the most preferred embodiment, every sulfone molecule contains two secondary amines complexed with it.

The novel epoxy resin catalyst of the invention is suitable for curing any of the available epoxy resins to produce cured products having one or more physical properties, such as tensile strength, flexural strength, flexural modulus, tensile modulus, elongation, lap shear strength, peel strength, and the like, that is superior or equivalent to that which is produced using any other

epoxy resin catalyst otherwise comparably formulated. In addition, the catalysts of the invention effect exceptionally rapid cure without damaging exothermic reaction and effect minimal to no shrinkage in the cured epoxy resin. The cure occurs quite rapidly, typically at least two times faster than other epoxy resin catalysts. This allows for rapid production of molded parts and substantial energy savings.

The invention also contemplates epoxy resin compositions in which the catalyst/accelerator of the invention achieves latent cure. Such latency is achieved when the epoxy resin is homopolymerized, or when copolymerized with a hardener that is free of primary amino groups, preferably free of amino groups.

The invention also includes an epoxy resin composition containing the catalyst of the invention.

Detailed Description Of The Invention

The invention relates to an improvement in epoxy resin catalyst and accelerator that yields unexpectedly superior performance in handling, mechanical properties, chemical properties, and the like. The resulting epoxy resins containing the epoxy resin catalyst and accelerator may be used for any of the applications in which epoxy resins are currently employed, such as, adhesives, matrix resins for composites of all sorts (reinforced by carbon fiber, glass fiber, aramide fibers, fabrics of them, fillers, and the like), prepregs, decorative or primer coatings, adhesive or

adhesive primers, structural adhesives and adhesive bonding primers, and the like.

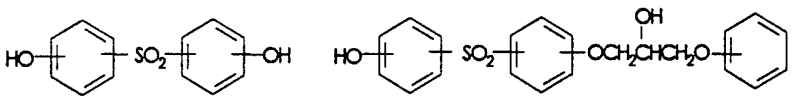
An optimal formulation of an epoxy resin attempts to take into account, for the ultimately cured resin, thermal and strength properties in general. Needless to say, there are many more specific properties that are evaluated, and a number of them are niche properties for a particular application. Curing of an epoxy resin involves the transformation of the thermoplastic uncured epoxy resin to the three-dimensional cured thermoset state. The function of an epoxy cure catalyst or curing agent is to facilitate the resin's cure and maximize the extent of the resin's cure, i.e., effect reaction of all of the epoxy groups and as much, for desired specific properties, of the other functional groups that are present in the formulation, thereby transforming the relatively low molecular weight epoxy resin into a highly crosslinked network. Facilitating the cure means effecting the cure in the shortest possible time without exothermic reaction occurring that causes the resin to blister or to undergo excessive shrinking.

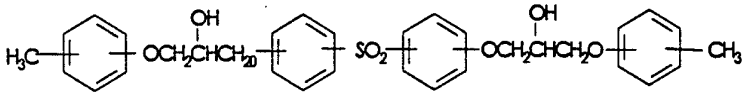
Thermal properties take into consideration the glass transition temperature (T_g) of the cured resin. That property is dependent upon the crosslinked density per unit of reactive epoxy, of the cured resin. The higher the crosslinked density coupled with amenable structural characteristics of the resin, the higher will be the resin's T_g. A high T_g means that the resin can be used in applications where the product is put to high use temperatures. However, the very nature of high crosslinked density suggests the resin will tend to be

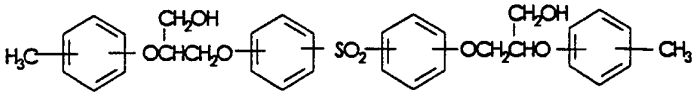
brittle, which means the resin will probably be deficient in tensile strength and elongation. The reason for not positively asserting a direct correlation between crosslink density and brittleness, with a deficiency in tensile strength and elongation, derives from the anomalies present in this field that dampens one's positive assertions on correlations of structure with properties.

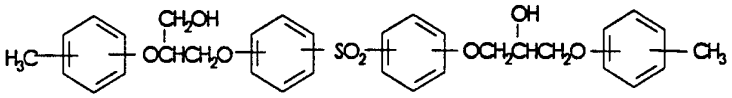
High ductility in an epoxy resin depends on a resin that is not overly crosslinked because the properties sought, e.g., unrecoverable deformation., plastic flow. i.e., elasticity, pliability, flexibility, etc., is the opposite of brittleness which is a product of high crosslinkage. Tensile strength is the resistance of the cured epoxy resin to a force tending to tear it apart. A truly ductile resin will exhibit a high tensile strength. This invention provides enormous variations in such properties essentially through the selection of the catalyst/accelerator of the invention in conjunction with the selection of the epoxy resin and/or hardeners.

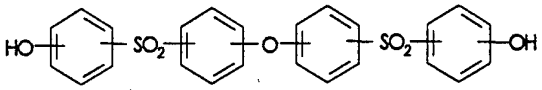
Suitable structures embodied by formula I.) above are the following:

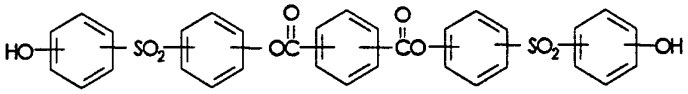


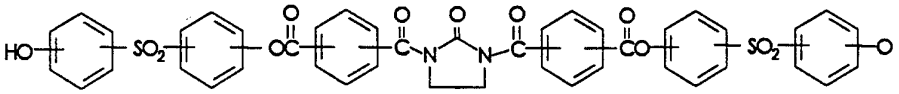


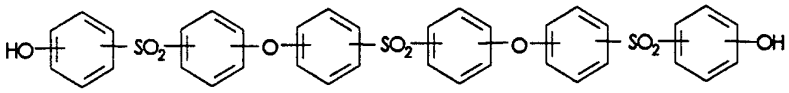


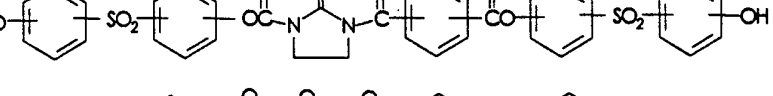




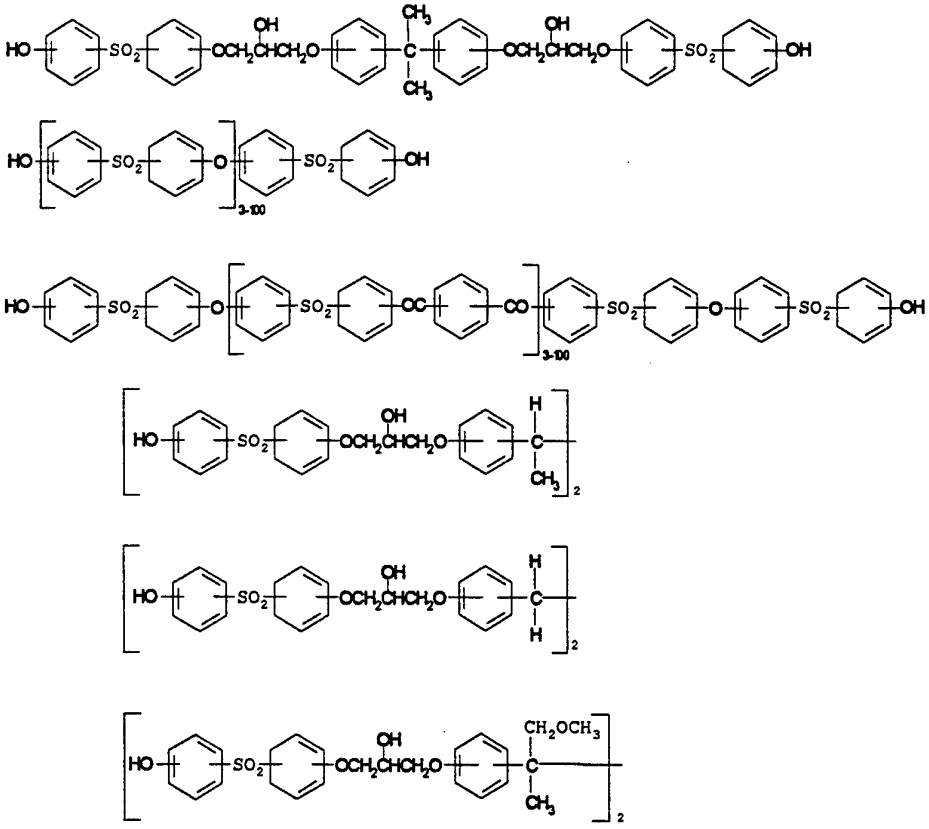


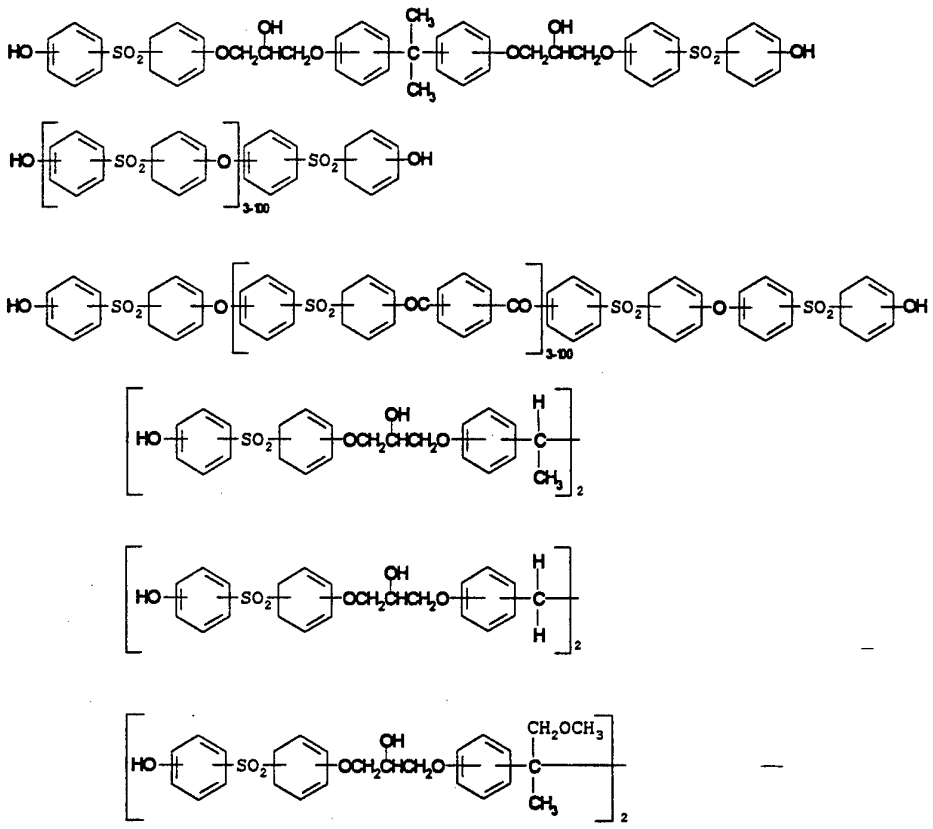




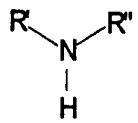






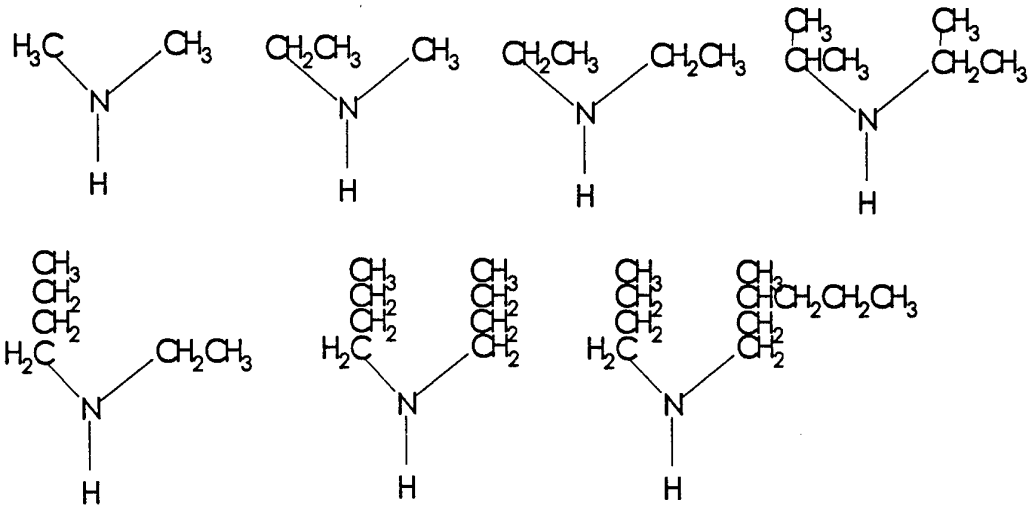


Illustrative of suitable secondary amines of formula II) are those encompassed by the formula:

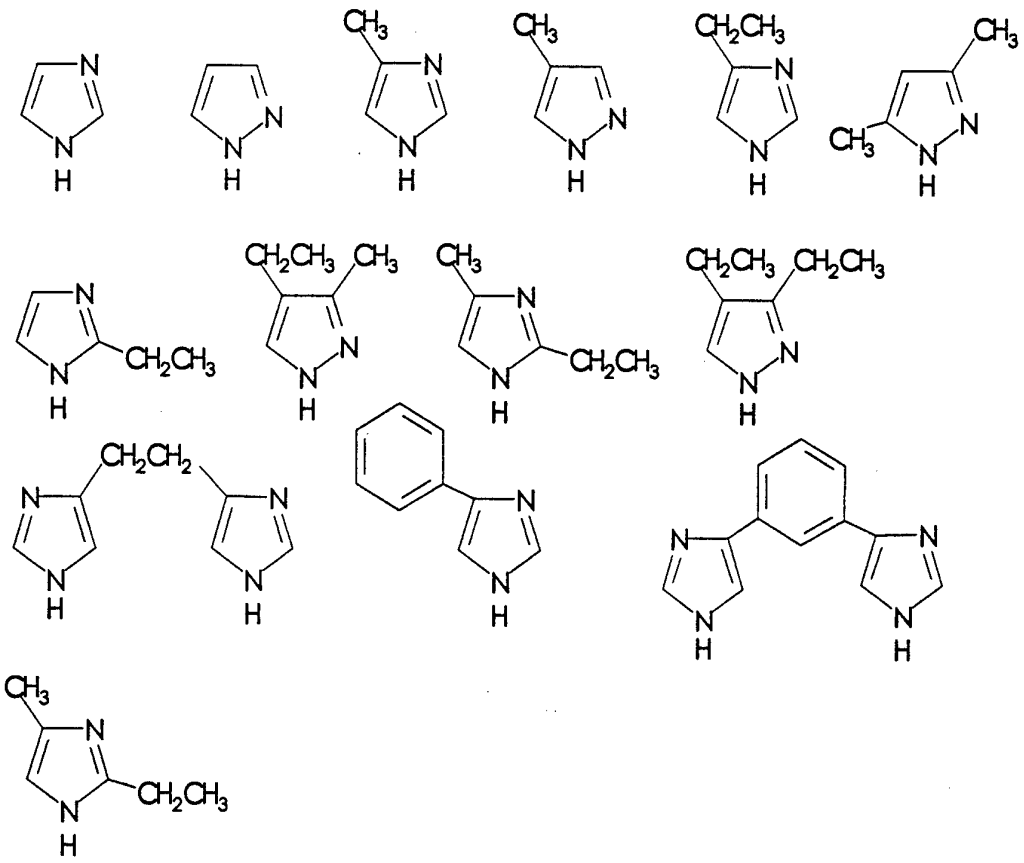


wherin R' and R' are alkyl containing 1 to about 8 carbon atoms, aryl of up to 2 rings, and cycloalkyl of about 5 to about 8 carbon atoms. Each of these may be subtituted. For example, the alkyl may be substituted by aryl and cycloalkyl, as defined above; the aryl substituted by alkyl and cycloalkyl, as defined above, and the cycloalkyl substituted by alkyl and aryl, as defined above. Preferably, the alkyl contain at least 3

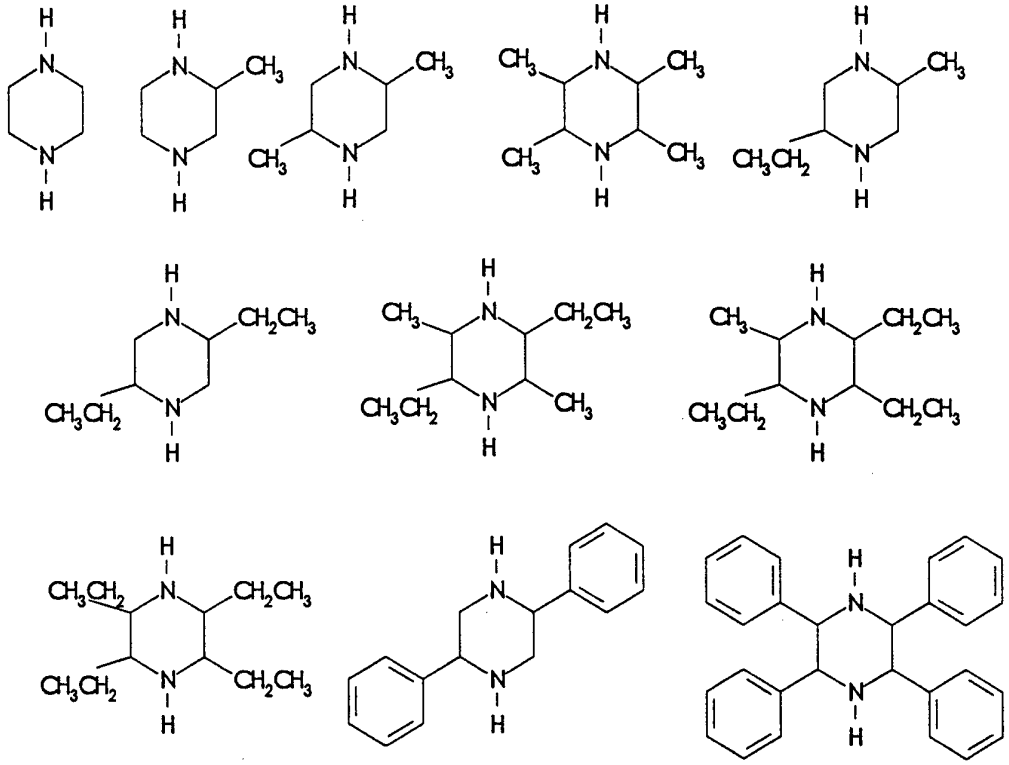
carbon atoms. Illustrative of such amines are the following:



Illustrative of suitable azoles and azolines of formula II) are the following compounds:



The piperazines are somewhat different from the azoles and azolines in that they more spontaneously react with the epoxy resin. In the typical case, they will be used as an adjunct with other secondary amines, though they may be used in the catalyst formulation to enhance reactivity and impart toughness to the epoxy formulation. For example, they may be used to assist in raising the viscosity of a premix or to A-stage or B-stage an epoxy resin. Suitable piperazines include the following:



Other components that may be added to the catalyst formulation to provide special properties to the cured epoxy resin include pyrrole, triazole, and piperidine, which while not active to the extent of the imidazoles, can be used to modify the catalyst activity, control cure rate, control pot life or alter solubility.

The catalyst formulation of the invention, and the epoxy resin formulation of the invention, may also contain acids, such as Brönsted and Lewis acids. Suitable acids include the acid halides, nitrates, sulfates, carboxylates, and the like, of metals such as Fe, Ni, Cu, Zn, Al, Ga, B, Sn, and the like. Also, suitable as a conjointly added component of the catalyst

composition of the invention are the carboxylic acids and the organosulfonic acids. Preferred acid salts are zinc chloride, boron trifluoride-etherate or amine salt, tin chloride, and the like. These additives are useful when using an amine hardener in the epoxy resin formulation. Absent the use of such hardeners, it is more desirable to practice the invention without the use of such acid additives. The acids are typically used, when employed, in the range of about 0.01 to about 5 weight percent of the weight of the resin formulation.

The reaction of the secondary amine and the organic sulfone of formula 1.) may be carried out at any temperature above the melting point of either of the reactants. In some instances, it will be desirable to dissolve each of the reactants in a separate solvent. One or more solvents are suitable so long as the mixture is homogeneous

Illustrative of suitable epoxy resin in which the catalysts of the invention may be employed include the following:

1. The epoxidized ester of the polyethylenically unsaturated monocarboxylic acids, such as epoxidized linseed, soybean, perilla, oiticica, tung, walnut and - dehydrated castor oil, methyl linoleate, butyl linoleate, ethyl 1,12-octadecadienoate, butyl 9, 12, 15 - octadecatrienoate, butyl oleostearate, monoglycerides of tung oil fatty acids, monoglycerides of soybean, sunflower, rapeseed, hempseed, sardine, or cottonseed oil. and the like.

2. The epoxidized esters of unsaturated monohydric alcohols and polycarboxylic acids, such as, for example, di (2, 3 - epoxybutyl) adipate, di (2, 3 - - epoxybutyl) oxalate, di (2, 3 - epoxyhexyl) succinate, di (3, 4 - epoxybutyl) maleate, di (2, 3 - epoxyoctyl) pimelate, di (2, 3 - epoxybutyl) phthalate, di (2, 3 - epoxyoctyl) tetrahydrophthalate, di (4, 5 - epoxydodecyl) maleate, di (2, 3 - epoxybutyl) terephthalate, di (2, 3 -epoxypentyl) thiodipropionate, di (5, 6 - epoxytetradecyl) diphenyldicaboxylate, di (3, 4 - epoxyheptyl) sulfonyl dibutyrate, tri (2, 3 - epoxybutyl) 1, 2, 4 - butanetricarboxylate, di (5, 6 - epoxypentadecyl) tartrate, di (4, 5 - epoxytetradecyl) maleate, di (2, 3 - epoxybutyl) azelate, di (3, 4 - epoxybutyl) citrate, di (5, 6 - epoxyoctyl) cyclohexane 1,2 - dicarboxylate, di (4, 5 - epoxyoctadecyl) malonate.

3. Epoxidized esters of unsaturated alcohols and unsaturated carboxylic acids, such as 2, 3 - epoxybutyl 3, 4 - epoxypentanoate, 3, 4 -epoxyhexyl 3, 4 - epoxypentanoate, 3, 4 - epoxycyclohexyl 3, 4 - epoxycyclohexanoate, 3, 4 - epoxycyclohexyl 4, 5 - epoxyoctanoate, 2, 3 -epoxycyclohexylmethyl epoxycyclohexane carboxylate.

4. Epoxidized derivatives of polyethylenically unsaturated polycarboxylic acids, such as, for example dimethyl 8, 9, 12, 13 - diepoxyeicosanedioate, dibutyl 7, 8, 11, 12 - diepoxyoctadecanedioate, dioctyl 10, 11 - diethyl - 8, 9, 12, 13 - diepoxy-eicosanedioate, dihexyl 6, 7, 10, 11 - diepoxyhexadecanedioate, didecyl 9 - epoxy - ethyl 10, 11 - epoxyoctadecanedioate, dibutyl 3

- butyl 3. 4, 5, 6 - diepoxycyclohexane 1, 2 - dicarboxylate, dicyclohexyl 3, 4, 5, 6-diepoxycyclohexane - 1, 2-dicarboxylate, dibenzyl 1, 2, 4, 5 - - diepoxycyclohexane -1, 2 - dicarboxylate and diethyl 5, 6, 10, 11 - diepoxyoctadecyl succinate.

5. Epoxidizcd polyesters obtained by reacting an unsaturated polyhydric alcohol and/or unsaturated polycarboxylic acid or anhydride groups, such as for example, the polyester obtained by reacting 8, 9, 12, 13 - eicosanedienedioic acid with ethylene glycol, the polyester obtained by reacting diethylene glycol with 2 - cyclohexene -1, 4 - dicarboxylic acid and the like, and mixtures thereof.

6. Epoxidized polyethylenically unsaturated hydrocarbons, such as epoxidized 2, 2 - bis (2 - cyclohexenyl) propane, epoxidized vinyl cyclohexene and cpoxidized dimer of cyclopentadiene.

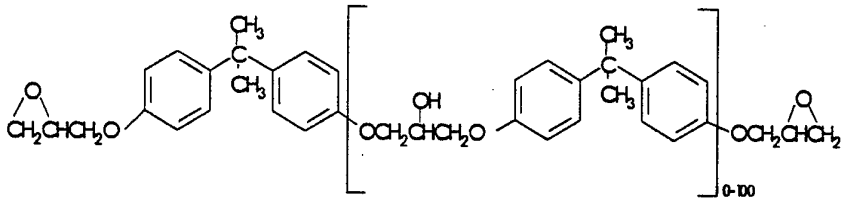
7. Epoxidizcd polymers and copolymers of diolefins, such as butadiene. Examples of this include, among others, butadiene-acrylonitrile copolymers (nitrile rubbers), butadiene-styrene copolymers and the like.

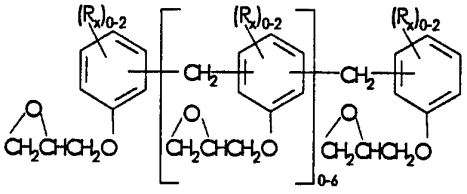
8. Glycidyl-containing nitrogen compounds, such as diglycidyl aniline and di- and triglycidylamine.

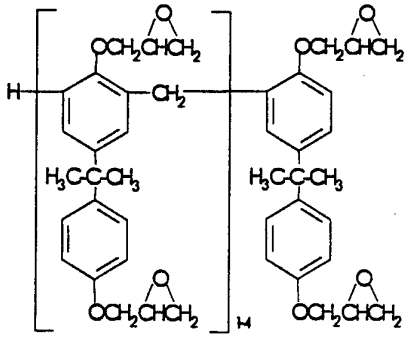
9. Particularly useful epoxy resins for utilizing the curing agents of the invention are the glycidyl ethers and particularly the glycidyl ethers of polyhydric phenols and polyhydric alcohols. The glydicyl ethers of polyhydric phenols are obtained by reacting

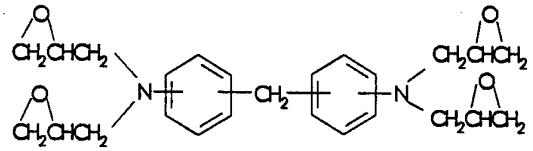
epichlorohydrin with the desired polyhydric phenols in the presence of alkali. Reaction products of epichlorohydrin with 2,2-bis(4-hydroxyphenyl)propane [bisphenol A] and bis(4-hydroxyphenyl)propane are good examples of polyepoxides of this type. Other cxamples include the polyglycidyl ethcr of 1, 1, 2, 2-tetrakis (4- hydroxyphenyl) ethane (epoxy value of 0.45 eq./100 g. and melting point 85°C.), polyglycidyl ether of 1, 1, 5, 5-tetrakis(hydroxyphenyl)pentane (epoxy value of 0.514 eq./100 g.) and the like, and mixtures thereof. Other examples include the glycidated novolacs as obtained by reacting epichlorohydrin with phenolic novolac resins obtained by condensation of formaldehyde with a molar excess of phenol or cresol.

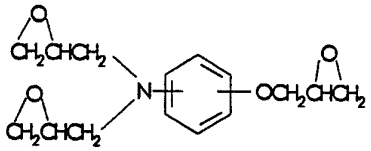
Illustrative of preferred epoxy resin are those listed below. They may be used alone, as the sole epoxy resin component, or they can be mixed with another epoxy resin. The epoxy resins containing aromatic and cycloaliphatic groups contribute to higher T_gs, tensile strengths, toughness, and the like properties. By mixing epoxy resins, with or without hardeners, and careful selection of the catalyst of the invention, resins with optimized properties for a variety of applications is possible.

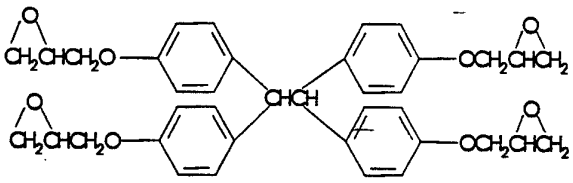


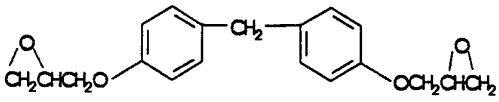


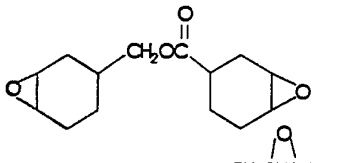


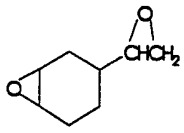


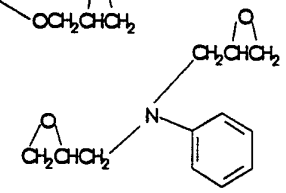


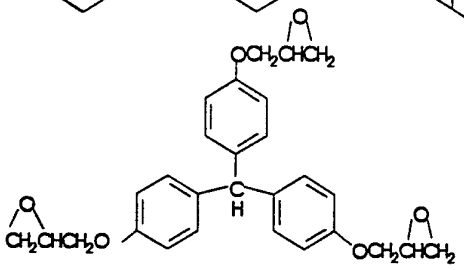


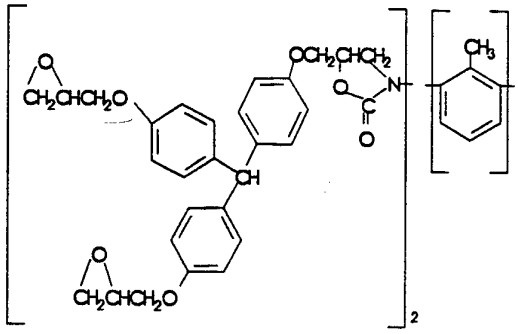












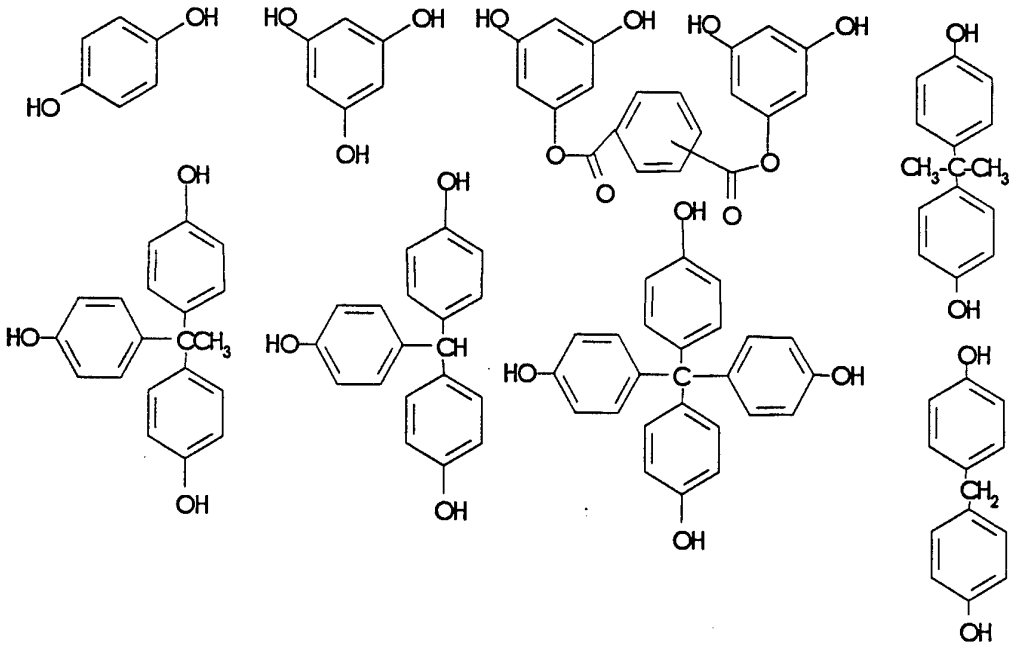
The epoxy catalyst and accelerator of the invention may be provided in an epoxy resin formulation in amounts that range quite broadly dependent upon the performance that is sought for the ultimate cured resin. The amount may be as little as 0.01 to as much as 20 weight percent based on the weight of the resin formulation. Preferably, the amount of the catalyst/accelerator ranges from about 0.05 to about 15 weight percent based on the weight of the resin formulation. Most preferably, the amount of the catalyst should be from about 0.1 to about 10 weight percent based on the weight of the resin formulation.

The epoxy resin formulation may comprise one or more epoxy resins *per se* and the catalyst/accelerator of the invention. It may also contain hardeners and other ingredients. The catalyst/accelerators of the invention are particular good homopolymerization catalysts because the homopolymer can have especially good cured resin properties. Homopolymerization, according to the terms of this invention, means the reaction of only epoxy resin in the presence of the catalyst/accelerator of the invention even though the hydroxy substituted sulfones are believed to react with the epoxy resins. Homopolymers may be made of one or more epoxy resins. Copolymers, according to the terms of this invention, means the reaction of one or more epoxy resins with one or more non-epoxy functional compounds, preferably polyfunctional compounds. Such polyfunctional compounds are typically called hardeners for the epoxy resin(s)

The copolymeric components cover a vast array of polyfunctional materials, ranging from polyhydroxy

compounds, polyamines, polysulfides, polyamides, polyurethanes, polycarboxylic acids, polyanhydrides, and the like. The copolymeric components may contain mixed functional groups.

The polyfunctional polyhydroxy compounds suitable for use in the practice of the invention include polyols and hydroxy-substituted aromatic compounds. The polyols include hydroxy-substituted alkanes, alkylethers, alkylamines (viz., trialkanolamines), alkylsulfides, alkyl esters, as well as polymers such as polyvinylalcohols, copolymers of vinylacetate and vinylalcohol, poly-2-hydroxyethylmethacrylate, copolymers of 2-hydroxyethylmethacrylate and styrene, and the like. The aromatic hydroxy compounds include the following:



as well as the aforementioned hydroxy substituted sulfones that are used in making the catalyst/accelerators of the invention. The latter serve as hardeners when used in amounts that are stoichiometrically in excess of the secondary amine.

The epoxy resins compositions of the invention may be used to impregnate continuous filament ribbons of fibers such as carbon, aramid, glass, nylon, polyester, polypropylene, and the like, fibers, to make prepregs and composite structures. The invention in epoxy resin composition may contain fillers, staple fibers, hollow microspheres, colorants, and other standard ingredients for epoxy resins. In addition, the epoxy resin composition of the invention may contain other thermosetting resins, such as phenolic resins, melamine-formaldehyde resins, and urea-formaldehyde resins, as well as thermoplastic resins, such as polyamides, polyurethanes, and the like.

In a further embodiment of the invention, it has been found that mixtures of 2,6-diaminopyridine (DAP) and various phenyl sulfones in the correct proportions form eutectic mixtures (and possible complexes) which are low melting, highly soluble epoxy hardeners and which produce cured epoxies having good physical and mechanical properties such as high tensile strength, high T_g high toughness and low cure shrinkage. Suitable partners for DAP have been found to be DHDS (di-4-hydroxydiphenylsulfone), DDS (4,4-diamino-diphenylsulfone), DHDS-Isophthalate and DHDS-Epoxy adducts. Procedures for the preparation of these complexes follow exactly the corresponding procedures

for the preparation of the analogous Imidazole-Sulfone complexes. The desired proportions are typically two molecules of DAP per sulfone group.

Preferred for the development of formulations based on diglycidyl bisphenol A resin ("DGEBA"), these epoxy hardeners and the Imidazole-Sulfone accelerators, the appropriate hardener should be mixed with the epoxy resin in the proportion of one active hydrogen per epoxide, ignoring any contribution from the accelerator and for optimizing rapid curing and optimum physical properties, one of the Imidazole-Sulfone accelerators should be used in a typical concentration in of about 2.5 - 5.0 phr. It should be appreciated that different formulations based on the choice of epoxide, hardener and accelerator will yield different results in terms of the T_g, tensile strength and toughness obtained.

Example 1

Preparation of (2:1 molar ratio) Imidazole ("Im")-di-4-hydroxydiphenylsulfone ("DHDS").

Ten grams of DHDS and 5.44 grams of Im were placed in a two-neck flask equipped with a condenser and magnetic stir bar. A small amount (5-10 ml.) of methyl ethyl ketone ("MEK") was added and the mixture heated to reflux until a clear, amber solution was obtained. The flask was then set up for distillation and the solvent was removed. The resulting pale amber liquid resin was then poured onto a stainless steel plate and allowed to cool. After about three hours, this material formed into soft crystals that were easily crushed with a flat

steel spatula. When melted, this material is converted into a viscous resin which remains in the resinous state for up to several hours before slowly crystallizing. The amorphous resinous form is very soluble in warm diglycidyl bisphenol A resin ("DGEBA"); and the crystalline form is sparingly soluble in the resin.

The solvent facilitates the generation of the resinous or crystalline complex and is desirable for shortening the preparation time. Preparation in the melt, though possible, is not favored because the rate of solution of DHDS in the mixture becomes very low near the end of its addition.

When a catalytic amount, in the range of about 0.05 to about 10 parts per weight of the catalyst per 100 parts by weight of the epoxy resin, of this material [such as 3-10 phr (parts per hundred of resin)] is dissolved in DGEBA and the mixture heated, it turns red at approximately 125°C. and solidifies in about ten seconds without the formation of a gel.

Example 2

Im_2·DHDS-Isophthalate (4:2:1 molar ratio)

DHDS-Isophthalate was prepared by adding 10.0 g. DHDS and 25 ml. MEK to a three-neck flask equipped with condenser and stir bar. Four grams of isophthaloyl chloride were dissolved in 15 ml. MEK and the solution placed in a small dropping funnel. The flask was flushed with dry N_2 and the DHDS-MEK mixture brought to reflux. The isophthaloyl chloride solution was then

added dropwise to the flask with stirring, the addition being completed in about thirty minutes. The solution was then cooled to room temperature, poured into a beaker and 4.0 g. powdered, anhydrous sodium carbonate was added. This mixture was stirred vigorously for five minutes, filtered to remove solids and the neutralized ester solution transferred to a clean flask. Im (5.20 g. of dry crystals) was then added, the flask was set up for distillation and the MEK removed. Im dissolved almost instantly. The product was a medium viscosity, amber resin, pourable at room temperature, having excellent solubility in DGEBA and having a catalytic activity for DGEBA comparable to the DHDS-Imidazole complex.

Example 3

Im-DHDS-Epoxy adduct.

This material was designed as a combination epoxy resin catalytic hardener/modifier intended to reduce the crosslink density in and improve toughness of the cured epoxy.

DHDS (10.0 g.) and 25 ml. MEK were placed in a three-neck flask equipped with a condenser and stir bar. Cresylglycidylether (14.6 g.) diluted with 15 ml. MEK was placed in a small dropping funnel. The DHDS-MEK mixture was brought to reflux and the dilute cresylglycidylether was added dropwise over a thirty minute period. When this addition had been completed, 5.44 g. of Im was added to the mixture and the flask set up for distillation. When the MEK had been distilled

off, a resinous product was obtained which was a pale amber, semi-solid at room temperature. This material had a low viscosity at approximately 100°C., was very soluble in warm DGEBA and, when mixed with the epoxy resin at a concentration of 5 - 10 phr, resulted in rapid hardening at 130 - 135°C.

The catalyst materials of Examples 1, 2 and 3 are very effective catalytic hardeners for epoxy resins which cure very rapidly with very low exotherm. When used as homopolymerization catalylsts, these materials give very high crosslink densities and produce brittle products. Catalyst materials of Examples 1 and 2 are also very effective accelerators for mixtures of epoxies and amines or polyphenols. Cure times can be dramatically reduced by the use of these materials without producing excessive exotherm. The catalyst of Example 3 is an extremely effective accelerator for epoxy-anhydride systems having all of the above cited advantages. With respect to the catalyst composition of Example 1, it was noted in the limited reactions tested that its concentration in DGEBA should be at least about 2.0 phr for rapid gelation. Excellent results have been obtained by using these accelerators at concentrations of 2.5 - 3.0 phr in combination with amines or polyphenols or, in the case of material Example 3, with anhydrides.

Example 4

In the following, of the DGEBA used in the following experiments, two equivalent forms of this

material were used: CIBA-Geigy® Araldite 6010 and Shell ® Epon 828.

Im_2·DHDS refers to the 2:1 molar ratio complex of Imidazole and dihydroxy diphenyl sulfone (sulfonyl diphenol). EMI2·DHDS refers to the similar complex formed from 2-ethyl,4-methyl Imidazole.

XU-205 is a CIBA-Geigy® product referred to in their data sheet as a modified methylenedianiline.

DHDS/epoxy adduct refers to the material formed by the slow addition of a solution of cresylglycidylether to a solution of DHDS. This is presumed to result in the replacement of the two phenolic OH groups by two secondary OH groups.

Components	1	2	3	4	5	6	7	8
DGEBA	3.0 g.	3.0 g.	6.0 g.	6.0 g.	15. g.	10. g.	15. g.	5.0 g.
Im_2·DHDS	0.15 g.	0.30 g.					1.5 g.	
IM/DHDS/THPE [1]			0.6 g.	0.6 g.				
Im_2·DHDS/ epoxy adduct					1.5 g.	0.5 g.		0.25 g.
epoxy novolac, CIBA-Geigy ECN-1280.							15. g.	
CIBA-Geigy HT-907[2]								4.25 g.
Molar Ratio of Reactants	—		1.6/1/.4	1.6/1/.4				

[1] THPE = 1,1,1-tris(4-hydroxyphenyl)ethane).

[2] Hexahydrophthalic anhydride

Weight Ratio of Reactants	0.05	0.1	—	—	—	—	—	—
Cure Conditions	250°F. 10 min	250°F. 10 min	200°F. 15 min. +250°F. 10 min. +300°F. 10 min. +350°F. 10 min.	200°F. 15 min. +250°F. 10 min. +300°F. 10 min. +350°F. 30 min.	200°F. 15 min. +250° F. 30 min.	200°F. 15 min. +250° F. 30 min.	175°F. 20 min. +200° F. 20 min. +250° F. 30 min.	250□F. 15 min. + 300°F. 15 min.
T_g	123°C.	116°C.	138°C.	157°C.	148°C.	122°C.	173°C.	136°C.

Components	9	10	11	12	13	14	15
DGEBA		40. g.	32. g.	32. g.	35 g	3.0 g	3.0 g
CIBA-Geigy CY-179[3]	5.0 g.						
cresol novolac	0.5 g.						
THPE	0.5 g.						
bis-phenol A	0.5 g.						
Im_2·DHDS	0.5 g.	2.0 g.	1.6 g.	1.6 g.	1.75 g		
XU-205[4]			10.24 g.	9.6 g.		0.96 g.	0.96 g.
Phenol		4.0 g.		1.6 g.	1.75		
2:1 molar ratio mixture of 2,6-diaminopyridine and diamino-diphenylsulfone (eutectic mixture)					6.5 g.		
EMI_2·DHDS						0.066 g	0.024 g
$ZnCl_2$						0.044 g.	0.016 g.
Weight Ratio of Reactants							
Molar Ratio of Reactants							
Cure Conditions	250°F. 30 min. +300°F. 30 min. + 350°F. I hr.	200°F. 15 min. + 250°F. 15 min.	200°F. 10 min. +250°F. 10 min. +300°F. 30 min.	175°F. 15 min. + 200°F. 15 min. + 250°F. 15 min. + 300°F. 2 hrs.	175°F. 20 min. + 200°F. 10 min. + 250°F. 15 min. +300°F. 30 min. +350°F. 1 hr.	250°F. 10 min. + 300°F. 30 min	250°F. 10 min. + 300°F. 30 min
T_g	160°C.	66.4°C.	82°C.	69.7°C.	77.1°C.	115°C.	133°C.
Tensile Modulus		531 ksi	568 ksi	498 ksi	698 ksi		
Ultimate Tensile Strength		24.9 ksi	28.2 ksi	29.1 ksi	30.9 ksi		
Ultimate Elongation		6.7%	6.9%	9.3%	7.9%		

[3] Cycloaliphatic diepoxy carboxylate

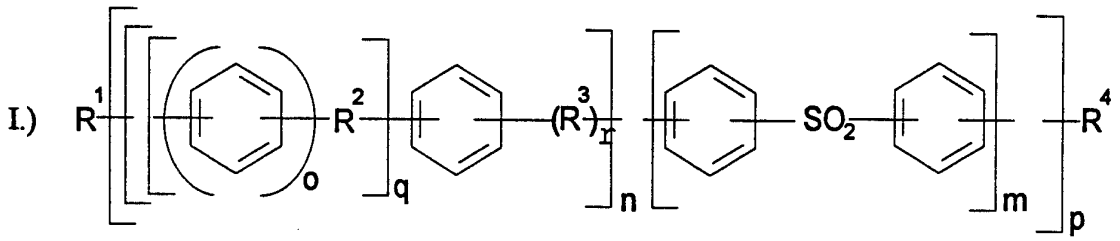
[4] Modified Methylene dianiline sold by CIBA Geigy, Hawthorne, NY.

Exotherm test.

100g. DGEBA and 5.0 g. Im_2.DHDS were mixed and placed in a metal container with a thermocouple imbedded in the center. This was placed in an air-circulating oven at 250°F. and the thermocouple temperature recorded as a function of time. The peak temperature was 574°F. after 11.5 minutes. There was no blistering or foaming but the sample cracked across the middle after 10 minutes.

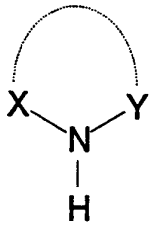
CLAIMS:

1. An epoxy resin catalyst and accelerator encompassed by the interreaction of a sulfone composition of the formula:

I.) 

A B

with a secondary amine of the formula:

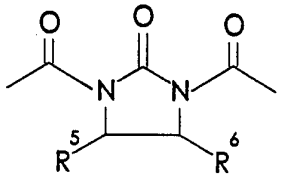
II.) 

wherein

X and Y, individually, are (i) organic groups bonded to the nitrogen by a carbon to nitrogen bond, in which said carbon is bonded to hydrogen or another carbon; R^1 and R^4 are (i) hydroxyl bonded to an aromatic carbon of an aromatic ring in units A and B or (ii) a monovalent hydroxyl substituted aliphatic organic group bonded through oxygen to an aromatic carbon of an aromatic ring in units A and B; R^2 is an ether oxygen group, a carboxylic acid ester group, a sulfone group, a divalent aliphatic hydrocarbon group, a substituted divalent aliphatic hydrocarbon group wherein the substituent is hydroxyl, alkoxy, aroxy, alkaroxy, aralkoxy, and the

like, a dioxy terminally-substituted divalent aliphatic hydrocarbon group, a substituted dioxy terminally-substituted divalent aliphatic hydrocarbon group wherein the substituent is carbon-bonded hydroxyl, alkoxy, aroxy, alkaroxy, or aralkoxy, or a divalent unit of the formula:

V.)



in which m has a value of at least 1; n has a value of 0 or equal to or greater than ("≥") 1; the ratio of m to n, when n is ≥1, is from about 0.01 to 100, provided there is one unit B per molecule; p has a value of at least one; q has a value of 0 or ≥1; r has a value of 1 to about 4; o has a value of 0 or 1; g has a value of 0 or ≥ 1; R^5 and R^6 are hydrogen and an organo group bonded to the ring carbon by a carbon to carbon bond or an oxygen to carbon bond; R^3 is a carboxylic acid ester, a carbonate, a carbamate, an amide, an ether oxygen, the divalent unit of formula V.) above bonded to one of oxygen or a nitrogen to form an amide unit with the nitrogen, a divalent aliphatic hydrocarbon group, a substituted divalent aliphatic hydrocarbon group wherein the substituent is hydroxyl, alkoxy, aroxy, alkaroxy, or aralkoxy; a dioxy terminally-substituted divalent aliphatic hydrocarbon group, a substituted dioxy terminally-substituted divalent aliphatic hydrocarbon group wherein the substituent is carbon-bonded hydroxyl, alkoxy, aroxy, alkaroxy, aralkoxy; R^{a-h} are each hydrogen, alkyl, aryl and, where bonded to adjacent

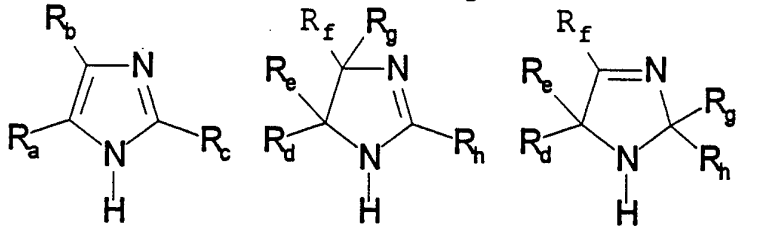
carbons, may be joined to form an aromatic fused ring group; and one or more of R^{a-h} are optionally substituted by an azolyl or an azolinyl.

2. The epoxy resin catalyst and accelerator of claim 1 wherein X and Y are (i) alkyl of 1 to about 14 carbon atoms, (ii) monocyclic aryl, (iii) monocyclic alkaryl in which the alkyl contains 1 to about 12 carbon atoms, (iv) monocyclic aralkyl in which the alkyl contains 1 to about 12 carbon atoms, (v) cycloalkyl of about 5 to about 8 carbon atoms, or (vi) joined to form a heterocyclic ring containing the secondary amino group as a ring member.

3. The epoxy resin catalyst and accelerator of claim 2 wherein X and Y are joined to form a heterocyclic amine containing a secondary amino group.

4. The epoxy resin catalyst and accelerator of claim 3 wherein the heterocyclic amines are (1) an imidazole or imidazoline encompassed by the formulae:

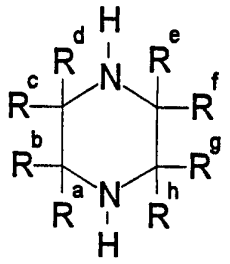
III.)



C D E ,

or (2) a piperazine encompassed by the formula:

IV.)



in which R_{a-h} are each hydrogen, alkyl, aryl and, where bonded to adjacent carbons, may be joined to form an aromatic fused ring group; one or more of R_{a-h} may be substituted by an azolyl; R^a - R^h are individually hydrogen or an organo group bonded to the carbon of the heterocyclic ring by a carbon to carbon bond.

5. The epoxy resin catalyst and accelerator of claim 4 wherein the composition includes a Brönsted or Lewis acid.

6. The epoxy resin catalyst and accelerator of claim 5 wherein the acid catalyst is zinc chloride.

7. The epoxy resin catalyst and accelerator of claim 4 wherein the sulfone is DHDS.

8. The epoxy resin catalyst and accelerator of claim 7 wherein the secondary amine is imidazole.

9. The epoxy resin catalyst and accelerator of claim 7 wherein the secondary amine is 2-ethyl-4-methyl imidazole.

10. The epoxy resin catalyst and accelerator of claim 7 wherein the secondary amine is piperazine.

11. The epoxy resin catalyst of claim 7 wherein the composition contains DAP.

12. The epoxy resin catalyst of claim 11 wherein the DAP is in combination with DDS.

13. An epoxy resin formulation containing an epoxy resin and the catalyst and accelerator of claim 1.

14. A eutectic mixture of DAP and DDS.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/07721

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C08F 283/10; C08G 75/20
US CL :525/534
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)

U.S. : 525/534

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)

US PAT APS
IMIDAZOLE AND DIHYDROXYDIPHENYL-
SULFONE WITH EPOXY AND CURING.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,189,548 (SAKASHITA) 19 FEBRUARY 1980. See column 19 lines 36-43; column 20, line 63; column 21, line 1; column 21, lines 16-22.	1-9
Y	US, A, 4,892,134 (SAKAMOTO) 09 MAY 1989, SEE COLUMN 3, LINE 16; COLUMN 4, LINES 1-2.	1-9
A	US, A, 3,839,282 (SWEENY) 01 OCTOBER 1974	1-14
A	US, A, 4,331,582 (BABAYAN) 25 MAY 1982	1-14
A	US, A, 4,390,664 (KANAYAMA) 28 JUNE 1983	1-14
A	US, A, 4,499,246 (TESSON) 12 FEBRUARY 1985	1-14

[X] 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 part 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 document 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	Date of mailing of the international search report
05 OCTOBER 1993	02 DEC 1993
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer HELEN F. LEE
Facsimile No. NOT APPLICABLE	Telephone No. (703) 308-2351

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/07721

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4,661,559 (GARDNER) 28 APRIL 1987	1-14