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(54) Title: STORAGE STABLE COMPATIBLE CURING AGENT COMPOSITIONS FOR EPOXY RESINS SELF CURABLE AT SUB–AMBIENT TEMPERATURES

(57) Abstract

There is provided a curing agent composition for epoxy resins and two component curable epoxy resin compositions. The curing agent is made by reacting at least a b) substituted aryl amidopolyamine with a c) monoglycidyl capping agent, where the substituted aryl amidopolyamine is made by reacting at least; bi) a phenolic compound substituted with at least one carboxyl group and at least one hydrocarbyl group having at least 1 carbon atom, and bii) an aliphatic polyamine compound having at least two primary amine groups. The curing agent is storage stable for at least 6 months. There is also provided a two component epoxy resin composition, which advantageously can be made in the absence of external catalysts/accelerators, and can cure within 24 hours at the low temperature of 4.4 °C. The two component epoxy resin composition also exhibits excellent compatibility between the curing agent and the epoxy resin, thus reducing or eliminating the need for an induction time.

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STORAGE STABLE COMPATIBLE CURING AGENT COMPOSITIONS FOR EPOXY RESINS SELF CURABLE AT SUB-AMBIENT TEMPERATURES

This invention is related to a storage stable curing agent composition for epoxy resins, and to two component solvent borne or solventless systems having enhanced compatibility between the epoxy resin and the curing agent, which are rapidly heat curable at ambient and sub-ambient temperatures in the absence of external catalysts/accelerators. The invention is also directed to methods of application and manufacture, as well as to the cured products made thereby.

There has long been a desire to formulate a curing agent which is simultaneously storage stable, is immediately compatible with conventional epoxy resins, and is sufficiently reactive with epoxy resins that the system will cure in a wide range of temperatures, even as low as 4.4 °C, within a 24 hour period in the absence of external accelerators if possible. Conventional amine curing agents have primary amine groups, and stored or used in low temperature curing conditions or in high humidity environments, produce in the final cured product the undesired side effect of blooming or hazing. This phenomena is thought to result from the reaction between the highly reactive primary amine groups with atmospheric carbon dioxide and moisture to produce carbamates, resulting in scission of the curing agent polymer chain. Another problem that can occur with conventional primary amine curing agents in storage is that they may oligomerize, especially in hot environments. Thus, many amine curing agents have a problem with storage

stability. To some extent, this problem can be ameliorated by reacting out many of the primary amine hydrogens. The drawback to this approach in the past has been that the reactivity of the curing agent was impaired because secondary amines are less reactive that the primary amines, such that accelerators had to be used to obtain adequate cure times, especially at low curing temperatures. Furthermore, many of the amine curing agent adducts formed to eliminate the presence of primary amine groups are poorly compatible with the epoxy resin such that induction times of 10 minutes to two hours were needed to compatibilize the epoxy resin composition with the curing agent composition.

It would be desirable to have a curing agent composition which for curing epoxy resins, whose primary amine groups have been converted to secondary amine groups, and which composition is storage stable and yet reactive enough to cure epoxy resins without external catalysts/accelerators in a wide range of curing temperatures and which can be applied to a substrate immediately upon mixing with the epoxy resin rather than waiting for an induction time to compatibilize the two components.

There is provided a curing agent composition, a method for making a curing agent composition, two component curable epoxy resin compositions and methods of their application, and the different cured products thereof. The curing agent comprises the reaction product of a b) substituted aryl amidopolymine with a c) monoglycidyl capping agent, where the substituted aryl amidopolyamine comprises the reaction product of:

bi) a phenolic compound substituted with at least one carboxyl group and at least one hydrocarbyl group having at least 1 carbon atom, preferably 8 or more, and

bii) an aliphatic polyamine compound having at least two primary amine groups.

The bi) a phenolic compound is more preferably substituted with at least one carboxyl group and at least one hydrocarbyl group having more than 12 carbon atoms, and the bii) aliphatic polyamine compound preferably has at least two primary amine groups and a secondary amine group.

Preferably the curing agent comprises the reaction product of a bi) a phenolic compound substituted with at least one carboxyl group and at least one hydrocarbyl group having at least 1 carbon atom; and preferably 8 or more and more preferably 14 or more carbon atoms a) a polyepoxide compound; bii) a polyamine compound having at least two primary amine groups; and c) a monoglycidyl capping agent. These compounds produced by this reaction can be characterized by having a β-hydroxy ester group and a β-hydroxy secondary amine group, terminated with moieties unreactive towards epoxide groups at room temperature in the absence of catalysts, and having one or more epoxide reactive secondary amine sites throughout the compound.

More preferably, the phenolic acid compound is reacted with the polyepoxide compound to produce a substituted aromatic glycidyl ester compound, which ester is combined and reacted with the polyamine compound and the monoglycidyl capping agent. Preferable phenolic acid compounds are those having an 8 to 36 carbon branched or unbranched alkyl group.

Most preferably, the substituted aromatic glycidyl ester is reacted first with the total amount of the polyamine compound used in the manufacture of the curing agent to make a glycidyl ester-amine adduct, followed by addition of the monoglycidyl capping agent with the adduct.

In another embodiment of the preferred ones, however, one may first react the monoglycidyl capping agent with the polyamine compound to convert one of the primary amine groups to a secondary amine group, followed by reaction of the polyepoxide compound onto the free primary amine group, and finishing the reaction with addition of the phenolic acid compound onto the free epoxide linkage.

The most preferred embodiment is the former described method, where the polyepoxide compound is reacted with the phenolic acid to make a substituted aromatic glycidyl ester composition, followed by combining and reacting onto the substituted aromatic glycidyl ester composition the polyamine and monoglycidyl capping agent in the stated sequence or as a mixture, more preferably in the stated sequence.

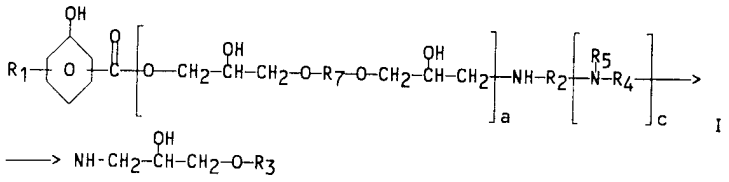
There is also provided a two component epoxy resin composition comprising an epoxy resin component and the above described curing agent component. Preferably, the two component epoxy resin composition is in the absence of external catalysts/accelerators, and can cure within 24 hours, and preferably within 15 hours at 4.4 °C.

While not being limited to a theory, it is believed that the compositions can self cure without external accelerators, even at low temperatures, because the curing agent adduct contains phenolic hydroxyl groups, which self catalyze reactions between the epoxy resins

and the amine nitrogens. Yet, quite unexpectedly, storage stability tests revealed that the amine curing agent retained a substantially constant viscosity over a 6 month period, which is a good indicator that the phenolic hydroxyl groups and amine hydrogens on the curing agent molecules did not autocatalyze with each other and oligomerize, and did not cleave through carbamate formation, leading to the retention of its curing reactivity.

The curing agents also have the advantage of enhanced compatibility with epoxy resins as evidenced by clear draw down films as soon as the epoxy resin and the curing agent components are mixed together and drawn. This enhanced compatibility leads to very short, or the complete elimination of, induction times. Typical epoxy resin compositions need an induction period ranging from 15 minutes to 1 hour to compatibilize the epoxy and curing agent components prior to curing. The curing agents of the invention, however, can be mixed with the epoxy resin and immediately cured without waiting for an induction period to compatibilize the components.

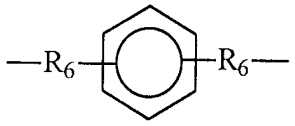
According to a specific embodiment of the present invention, the curing agent composition is represented by the following structural formula



I

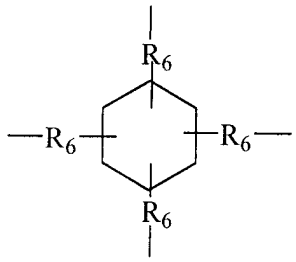
wherein R_1 is a branched or unbranched, substituted or unsubstituted, monovalent hydrocarbyl group having at least one carbon atom, preferably an alkyl group having at least an average of at least 14 carbon atoms; R_2 and

R_4 each independently represent a branched or unbranched, substituted or unsubstituted, divalent hydrocarbyl group having 2-24 carbon atoms, preferably 2-6 carbon atoms, or



II

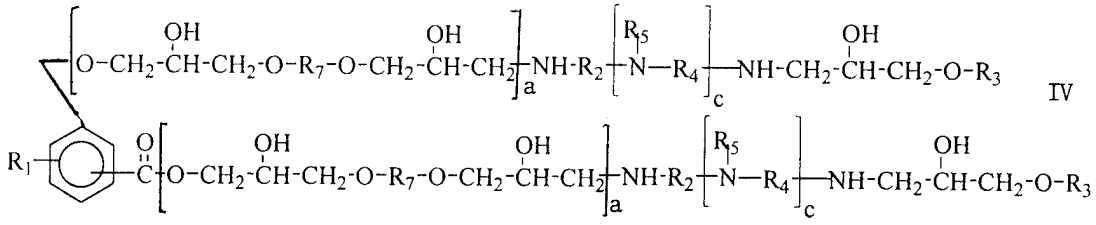
or



III

wherein R_6 represents a branched or unbranched, substituted or unsubstituted, divalent hydrocarbyl group having 2-24 carbon atoms; R_3 is a branched or unbranched, substituted or unsubstituted, monovalent hydrocarbyl having 1-24 carbon atoms, a polyoxyalkylene group, an aryl group, an alkaryl group, or an aralkyl group; R_5 is hydrogen or a branched or unbranched, substituted or unsubstituted, monovalent hydrocarbyl having 1-24 carbon atoms, preferably hydrogen; R_7 is the residue of said polyepoxide compound; a represents an integer equal to 0 or 1, and c represents an integer from 0-10, preferably from 1-10.

Other species may be present in the curing agent composition, such as:



IV

wherein each R group and a and c are as described above.

The structure of the phenolic acid is an aromatic ring to which is covalently bonded at least one hydroxyl group, at least one hydrocarbyl group, and at least one carboxyl group. Usually and preferably, the structure of the phenolic acid will contain only one hydroxyl group and one carboxyl group bonded to the aromatic ring. However, it is rare if not impossible to commercially acquire a phenolic compound which is so pure that it contains only one species. Commercially available phenolic compounds usually contain a mixture of species, such as mono and di carboxyl substituted phenolics. Thus, while the preferable embodiment is one in which the phenolic acid contains only one of each group bonded to the aromatic ring, this embodiment includes a phenolic which contains a mixture of species in which the predominant (>70 mole percent) species has only one carboxy group and one hydroxyl group bonded to the aromatic ring.

One of the substituents on the aromatic ring of the phenolic acid is the hydrocarbyl group. While the hydrocarbyl group can comprise a wide variety of structures and atoms, it must have a predominantly hydrocarbon character. Included within the meaning of a hydrocarbyl group are the alkyl or alkenyl groups, the aliphatic substituted aromatic or alicyclics, or the aromatic or alicyclic substituted alkyls or alkenyls. Each of these groups may be branched or unbranched. The

phenolic acid preferably contains at least 50 mole% species which have only one hydrocarbyl substituent.

The substituent on the substituted aryl amidopolyamine is at least one hydrocarbyl group having at least one carbon atom. Longer chain hydrocarbyl groups are preferred. All else remaining equal, a curing agent having longer chain hydrocarbyl substituents, i.e. 8 or more, preferably greater than 12, and most preferably 14 or more, tend to be more hydrophobic than the curing agents having short chain hydrocarbyl groups on the order of 1-7 carbon atoms. In many applications, the hydrophobic character of the hydrocarbyl substituent is desirable to improve the compatibility of the curing agent with the epoxy resin component. Further, long chain hydrocarbyl substituents are somewhat more flexible than their shorter chain counterparts, thus lowering the glass transition temperature of the curing agent. It is desirable to have a curing agent with a lowered glass transition temperature to improve its flow properties in low temperature curing conditions. Thus, the most preferred hydrocarbyl groups are those having 14 or more carbon atoms. Although there is no particular upper limit on number of carbon atoms, the most common number of carbon atoms used within this invention will be 14-24, more typically from 14-18, although hydrocarbons with up to 36 carbon atoms are also available.

Of the types of hydrocarbyl substituents, the alkyls are preferred. These can be branched or unbranched, preferably unbranched or having no more than 1 branch per 6 backbone carbon atoms. Examples of alkyl substituents having at least about 8 carbon atoms include octyl, nonyl, decyl, isodecyl, dodecyl, pentadecyl, eicosyl, triacontyl and the like, as well as radicals derived from

substantially saturated petroleum fractions, olefin polymers and highly refined white oils or synthetic alkanes.

Other types of hydrocarbyl groups which are suitable include substituted hydrocarbyl groups; that is, groups containing non-hydrocarbon substituents which do not alter the predominantly hydrocarbon character of the group. Examples are halo, nitro, cyano, ether, carbonyl, and sulfonyl groups. Also included are hetero atoms which are atoms other than carbon present within a chain or ring otherwise composed of carbon atoms. Suitable hetero atoms include, for example, nitrogen, oxygen, and sulphur. Further included within the meaning of the hydrocarbyl group are the alkoxy compounds.

Preferably, no more than an average of one substituent or hetero atom will be present for each 10 carbon atoms in the hydrocarbyl group, and most preferably, the hydrocarbyl group does not contain any hetero atoms or substituents.

The phenolic acid may contain more than one hydrocarbyl substituent on the aromatic ring. The dihydrocarbyl substituted phenolic acids may have a long chain hydrocarbyl of 14 or more carbon atoms and a short chain hydrocarbyl of from 1 to 4 carbon atoms attached to the aromatic ring, or both of the hydrocarbyls may be long chain. As noted above, however, preferably greater than 50 mole% of the species contain only one hydrocarbyl substituent.

The phenols on which the hydrocarbyl and carboxyl groups are situated are aromatic compounds containing at least one, and preferably one, hydroxyl group. Examples are phenol, α- or β- naphthols, resorcinol, hydroquinone, 4,4'-dioxydiphenyl, 4,4'-dioxydiphenylether,

4,4'-dioxydiphenylsulfone, 4,4'-dioxydiphenylmethane, the condensation products of phenol and formaldehyde known as novolacs, and bis(4-hydroxyphenyl) alkyls or ethers or sulfones optionally substituted with alkyl groups on the aromatic rings. Phenol is preferred.

To substitute the hydroxyl aromatic compound with the hydrocarbyl group, a hydrocarbon-based compound of the hydrocarbyl group as mentioned above is reacted with the hydroxyl aromatic compound at a temperature of from 50 °C to 200 °C in the presence of a suitable catalyst such as aluminum chloride, boron trifluoride or zinc chloride.

The phenolic acid also contains at least one carboxyl group as a substituent, and preferably only one carboxyl group per aromatic ring. The carboxyl group is bonded directly to the aromatic phenolic ring, or indirectly to the ring through an aliphatic chain. Preferred, however, is a carboxyl group bonded directly to the aromatic ring of the phenolic acid at the ortho or para positions to the phenolic hydroxyl group. Further, within the meaning of a carboxyl group are the alkyl esters and anhydrides of the carboxyl substituents.

Examples of the carboxyl groups bonded to the phenolic aromatic ring are those derived from carboxylic acids containing from 0 to 24 carbon atoms, not counting the carboxyl group carbon. The carboxylic acids from which the substituents are derived include -formic acid (a-carboxy acid), -acetic acid, -propionic acid, or -stearic acid substituents. A particularly preferred carboxyl group is a carboxy acid in view of its high reactivity with amines.

The phenolic acid containing the carboxyl and the hydrocarbyl groups can be prepared by methods which are

known in the art as the "Kolbe-Schmitt reaction," which comprises reacting a salt, preferably an alkali metal salt, of the hydrocarbyl substituted phenol with carbon dioxide and subsequently acidifying the salt thus obtained. The conditions of the carbonation reaction are likewise well known to those skilled in the art. It may be carried out at atmospheric or superatmospheric pressure in a substantially inert, non-polar liquid diluent.

A particularly preferred phenolic acid is a hydrocarbyl substituted salicyclic acid. This phenolic acid is a good building block toward producing a curing agent which has good flow, reactivity, and compatibility with epoxy resins at low cure temperatures in the absence of external accelerators/catalysts, and a good balance of mechanical properties and weatherability.

In a more preferred embodiment, the phenolic compound used in the invention is a salicylic acid substituted with a from 14 to 18 linear carbon alkyl group located at the o- or p- position to the phenolic hydroxyl group. The preparation of alkyl substituted salicyclic acids is described in US Patent No. 3,013,868.

To manufacture the substituted aryl amidopolyamine, the phenolic compound described above is reacted with an aliphatic polyamine compound having at least two primary amine groups at an elevated temperature, typically at a temperature from 140 °C to 180 °C and preferably from 150 °C to 160 °C for a time sufficient to substantially complete the reaction, usually from 1 to 12 hours and preferably from 4 to 12 hours, if curing agents of e.g. the formula I, wherein a = 0 are prepared. For the preparation of curing agents of e.g. formula I wherein a = 0, the ingredients can be mixed together and reacted,

but preferably, the phenolic compound should be added to the polyamine compound so as to reduce the possibility of reacting both of the primary amine groups on the polyamine compound with the phenolic compound. This reaction may be carried out in the presence of absence of solvents or catalysts, typically in the presence of a solvent and in the absence of a catalyst. If a catalyst is employed, one could use triphenylphosphite. It is advisable not to let the reaction temperature rise too much above 170 °C for an extended period of time in order to avoid de-carboxylation of the phenolic compound and the resultant production of free phenolic compounds in the reaction mixture. To drive the reaction to completion, vacuum may be applied during the course of the reaction or towards the tail end of the reaction.

Preferably, at least one primary nitrogen group equivalent of polyamine is reacted per carboxyl group equivalent on the phenolic compound, and more preferably the polyamine is reacted with the phenolic compound at a molar excess, such as at a molar ratio of 1.25:1 or more, in order to react out the all the carboxyl groups to form amide groups wherever carboxyl groups appear on the phenolic compound. While molar ratios of less than 1:1 are tolerable, the object of providing a reactive curing agent at low temperature cure conditions which is storage stable and compatible with epoxy resins is best achieved if an molar equivalent or excess of the polyamine is used. Once the amine reaction onto the phenolic compound and the reaction is complete, the excess amine, if any, should be vacuum distilled off, typically at 20in.Hg to 30in.Hg for 30 to 480 minutes.

To manufacture e.g. curing agents according to the formula I, wherein a = 1, the phenolic acid described

above is reacted with a polyepoxide at an elevated temperature, typically from 140 °C to 180 °C, and preferably from 150 °C to 160 °C for a time sufficient to substantially complete the reaction, usually from 1 to 12 hours and preferably from 1 to 8 hours for curing agents of e.g. formula I, wherein a = 1. It is advisable not to let the reaction temperature rise too much above 170 °C-180 °C for an extended period of time in order to avoid the possibility of de-carboxylation of the phenolic compound, which would result in the production of free phenolic compounds in the reaction mixture. The reaction for the preparation of curing agents of e.g. according to formula I, wherein a = 1 can be conducted at any pressure ranging from a partial vacuum to superatmospheric pressure. To drive the esterification reaction between the carboxyl group on the phenolic compound and the polyepoxide compound to completion, it is preferred to apply a partial vacuum either during the course of the reaction or towards the tail end of the reaction. The reaction is substantially completed when free acid can no longer be detected in the composition. The ingredients can be mixed together and subsequently reacted, but preferably, the phenolic acid is added to the polyepoxide compound so as to reduce the possibility of reacting both of the oxirane groups on the polyepoxide compound with the phenolic acid.

The reaction between the polyepoxide compound and the phenolic acid are suitably carried out at molar ratios of at least 1:1, preferably greater than 1:1 such as at least 2:1, and even 3:1 on up. It is desirable to use a molar excess of the polyepoxide compound so that one of the oxirane groups on the polyepoxide compound is free to react with the polyamine compound and does not react with

further phenolic acids. If a stoichiometric amount of the phenolic acid is added to the polyepoxide compound such as at a molar ratio of polyepoxide to phenolic acid of 0.5:1 or less (the stoichiometry proceeding upon the assumption that the phenolic acid has only one functional group, the acid group, and a diepoxide is used), then both of the oxirane groups will be consumed by the acid group on the phenolic compound. Therefore, a stoichiometric excess of oxirane groups (>0.5:1) is desired to ensure that the substituted aromatic glycidyl ester compound has free oxirane groups available for reaction with the polyamine compound.

The reaction between the phenolic acid and the polyepoxide compound may be carried out in the presence or absence of solvents or catalysts, typically in the presence of both. Suitable solvents include alcohols, ketones, esters, ethers of hydrocarbons. Examples of suitable solvents are butanol, methyl isobutyl ketone, toluene, ethylglycol acetate, xylene, benzyl alcohol, phthalic acid esters of monohydric alcohols, e.g. n-butanol, amylalcohol, 2-ethylhexanol, nonanol, benzyl alcohol, gamma -butyrolactone, delta -valerolactone, epsilon -caprolactone, lower and higher molecular weight polyols, e.g. glycerol trimethylol-ethane or -propane, ethyleneglycol, and ethoxylated or propoxylated polyhydric alcohols, either individually or in admixture.

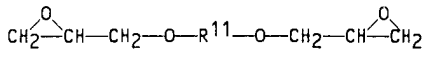
If a catalyst is employed, one could use a Lewis acid, metal salts, and bases. Examples include trimethylamine, triethylamine, benzyldimethylamine, tris(dimethylaminomethyl)phenol, dimethylethanolamine, n-methymorpholine, benzyl trimethyl ammonium chloride, ethyl triphenyl phosphonium salts, tetrabutyl phosphonium

salts, and stannous salts of carboxylic acids. Typical amounts of catalyst used range from 0.1 to 100 ppm.

The polyepoxide used in the invention is any polyepoxide having an average of 1.5 or more oxirane groups per molecule, preferably 1.7 or more oxirane groups. The polyepoxide compounds can be monomeric or polymeric, saturated or unsaturated, aliphatic, cycloaliphatic, aromatic or heteroaromatic and may be substituted, if desired, with other substituents in addition to the epoxy groups with, for example, hydroxyl groups or halogen atoms such as bromine.

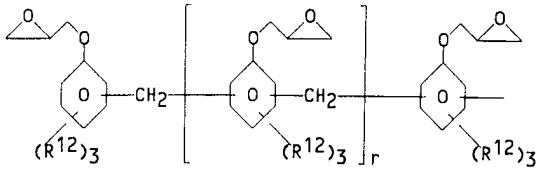
Suitable polyepoxide compounds are the reaction products of polyphenols and epihalohydrins, polyalcohols and epihalohydrins, amines and epihalohydrins, sulphur containing compounds and epihalohydrins, polycarboxylic acids and epihalohydrins or mixtures thereof.

Preferred polyepoxide compounds include, but are not limited to, any one of those represented by the formulas:



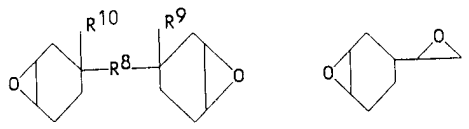
V

or



VI

or

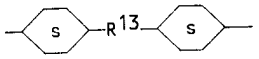


VII

wherein r is a real number from about 0 to about 6, R^{11} is a divalent aliphatic group, a divalent cycloaliphatic

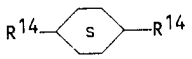
group, a divalent aryl group, a polyoxyalkylene group, or a divalent arylaliphatic group, R^{12} is independently a hydrogen or a C_1-C_{10} alkyl group, R^8 is a divalent aliphatic group optionally containing ether or ester group(s) or together with R^9 or R^{10} form a spiro ring optionally containing heteroatoms, and R^9 and R^{10} are independently hydrogen or R^9 or R^{10} together with R^8 form a spiro ring optionally containing heteroatoms such as oxygen.

R^{11} can be a divalent cycloaliphatic group having the formula:



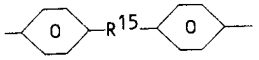
VIII

or



IX

wherein R^{13} and R^{14} are each independently an alkylene group, or a divalent arylaliphatic group having the formula



X

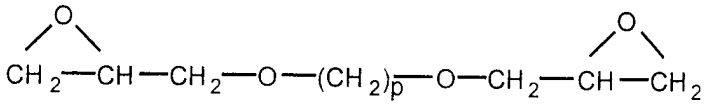
wherein R^{15} is an alkylene group.

For the polyepoxide compound having a nominal functionality of two or more, the epoxy compound is preferably a diglycidyl ether of a dihydric phenol, diglycidyl ether of a hydrogenated dihydric phenol, an aliphatic glycidyl ether, epoxy novolac or a cycloaliphatic epoxy.

Diglycidyl ethers of dihydric phenols can be produced, for example, by reacting an epihalohydrin with a dihydric phenol in the presence of an alkali. Examples

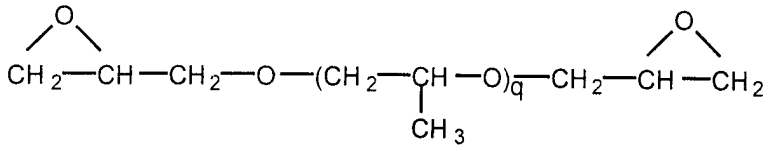
of suitable dihydric phenols include: 2,2-bis(4-hydroxyphenyl) propane (bisphenol-A); 2,2-bis(4-hydroxy-3-tert-butylphenyl) propane; 1,1-bis(4-hydroxyphenyl) ethane; 1,1-bis(4-hydroxyphenyl) isobutane; bis(2-hydroxy-1-naphthyl) methane; 1,5-dihydroxynaphthalene; 1,1-bis (4-hydroxy-3-alkylphenyl) ethane and the like. Suitable dihydric phenols can also be obtained from the reaction of phenol with aldehydes such as formaldehyde (bisphenol-F). Diglycidyl ethers of dihydric phenols includes advancement products of the above diglycidyl ethers of dihydric phenols with phenolic compounds such as bisphenol-A, such as those described in U.S. Patent Nos. 3,477,990 and 4,734,468.

Diglycidyl ethers of hydrogenated dihydric phenols can be produced, for example, by hydrogenation of dihydric phenols followed by glycidation with epihalohydrin in the presence of a Lewis acid catalyst and subsequent formation of the glycidyl ether by reaction with sodium hydroxide. Examples of suitable dihydric phenols are listed above.



XI

Aliphatic glycidyl ethers can be produced, for example, by reacting an epihalohydrin with an aliphatic diol in the presence of a Lewis acid catalyst followed by conversion of the halohydrin intermediate to the glycidyl ether by reaction with sodium hydroxide. A representative formula is:



XII

wherein p is an integer from 2 to 12, preferably from 2 to 6; and q is an integer from 4 to 24, preferably from 4 to 12.

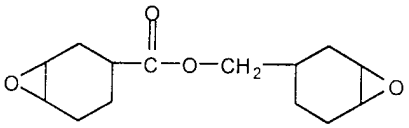
Examples of suitable aliphatic glycidyl ethers include for example, diglycidyl ethers of 1,4 butanediol, neopentyl glycol, cyclohexane dimethanol, hexanediol, polypropylene glycol, and like diols and glycols; and triglycidyl ethers of trimethylol ethane and trimethylol propane.

Epoxy novolacs can be produced by condensation of formaldehyde and a phenol followed by glycidation by epihalohydrin in the presence of an alkali. The phenol can be for example, phenol, cresol, nonylphenol and t-butylphenol. Examples of the preferred epoxy novolacs include those corresponding to the formula VI above. Epoxy novolacs generally contain a distribution of compounds with a varying number of glycidated phenoxymethylene units, r. Generally, the quoted number of units is the number closest to the statistical average, and the peak of the distribution.

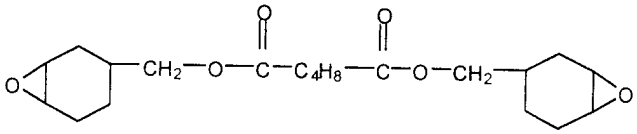
Cycloaliphatic epoxies can be produced by epoxidizing a cycloalkene-containing compound with greater than one olefinic bond with peracetic acid. Examples of the preferred cycloaliphatic epoxies include those corresponding to the formula VII above. Examples of cycloaliphatic epoxies include, for example, 3,4-epoxycyclo-hexylmethyl-(3,4-epoxy)cyclohexane carboxylate, dicycloaliphatic diether diepoxy

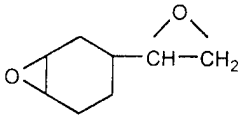
[2-(3,4-epoxy)cyclohexyl-5,5-spiro(3,4-epoxy)cyclohexane-m-dioxane], bis(3,4-epoxycyclohexylmethyl)adipate, bis(3,4-epoxycyclohexyl)adipate and vinylcyclohexene dioxide [4-(1,2-epoxyethyl)-1,2-epoxycyclohexane]. Cycloaliphatic epoxies include compounds of the formulas:

XIII

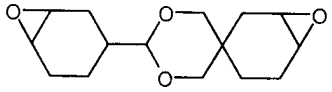


XIV





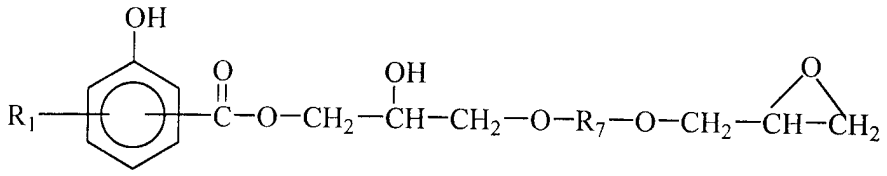
XV



XVI

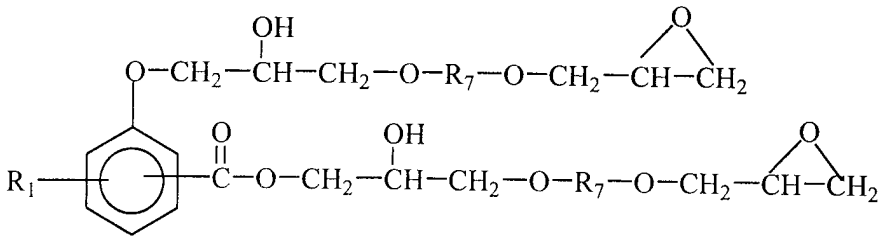
Commercial examples of the preferred epoxy compounds having a nominal functionality of two or more include, for example, EPON Resins DPL-862, 828, 826, 825, 1001, EPONEX Resin 1510, HELOXY Modifiers 107, 67, 68, and 32 (EPON, EPONEX and HELOXY are trade marks); and Epoxy Resins ERL-4221, -4289, -4299, -4234 and -4206.

The reaction between the phenolic acid compound and the polyepoxide compound will produce a variety of species depending upon the particular phenolic acid functional sites which undergo reaction. The following reaction scheme represents two species produced between phenolic acid - polyepoxide reaction, where all of the carboxylic acid groups on the phenolic acid compound have been reacted:



XVII

and



XVIII

wherein R_1 is the hydrocarbyl substituent on the phenolic acid compound, and R_7 is the polyepoxide residue.

Once the substituted aromatic glycidyl ester composition is made, it is reacted with the bii) polyamine compound and the c) monoglycidyl capping agent in the stated sequence or simultaneously in mixture, preferably sequentially to increase the number of species having the polyamine compound reacted into the molecule. However, adding the polyamine and monoglycidyl capping agent in mixture is also suitable for the purposes of the invention.

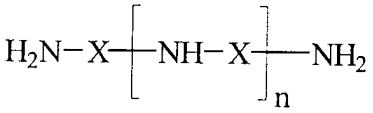
Preferably, at least one mole of the polyamine compound is reacted per mole of the substituted aromatic glycidyl esters, and more preferably the polyamine is reacted with the substituted aromatic glycidyl esters at a molar excess, such as at a molar ratio of 1.25:1 or more, more preferably 2:1 or more, in order to react out the all the oxirane groups and provide primary amino group termination. The reaction conditions are much like

those described above with relation to the phenolic acid and the polyepoxide compound, except that typically no catalysts are needed. The temperature can range from 100 °C to 230 °C, with the higher end of the temperature range initiated when vacuum distillation is applied. The substituted aromatic glycidyl ester composition is preferably added to the polyamine compound to ensure that the polyamine compound, once reacted, will have a free unreacted primary amine site available for reaction with the monoglycidyl capping agent. Once the amine reaction onto the substituted aromatic glycidyl ester composition is complete, the excess amine, if any, should be vacuum distilled off, typically at 20 in.Hg to 30 in.Hg for 30 to 480 minutes.

The aliphatic polyamines useful for the manufacture of the aryl amidopolyamines (e.g. curing agents according to formula I wherein a = 0), are those, which have at least two primary amine groups, one primary amine group for reaction with the carboxyl group of the phenolic compound and the other primary amine group for reaction with the monoglycidyl compound.

The polyamines useful for reaction onto the substituted aromatic glycidyl ester composition (e.g. curing agents according to formula I, wherein a = 1), are those which have at least two primary amine groups, one primary amine group used for reaction with the oxirane groups in the substituted aromatic glycidyl ester composition, and the other primary amine available for reaction with the monoglycidyl capping agent.

Examples of polyamines useful in the practice of the invention are those represented by the formula:



XIX

wherein n is an average of integers between about 0 and 10, preferably between 1 and 4; and X is a divalent branched or unbranched hydrocarbon radical having about 1-18 carbons, one or more aryl or alkaryl groups, or one or more alicyclic groups. Preferably, X is a lower alkylene radical having 1-10, preferably 2-6, carbon atoms.

Such alkylene polyamines include methylene polyamines, ethylene polyamines, butylene polyamines, propylene polyamines, pentylene polyamines, hexylene polyamines, heptylene polyamines, etc. The higher homologs of such amines and related aminoalkyl-substituted piperazines are also included. Specific examples of such polyamines include ethylene diamine, triethylene tetramine, tris(2-aminoethyl)-amine, 1,2- and 1,3-propylene diamine, trimethylene diamine, 1,2- and 1,4-butanediamine, hexamethylene diamine, decamethylene diamine, octamethylene diamine, diethylene triamine, triethylene tetramine, di(heptamethylene)triamine, tripropylene tetramine, tetraethylene pentamine, trimethylene diamine, pentaethylene hexamine, di(tri-methylene)triamine, p- and m-xylylene diamine, methylene dianiline, 2,4-toluenediamine, 2,6-toluenediamine, poly-methylene polyphenylpolyamine, and mixtures thereof. Higher homologs, obtained by condensing two or more of the above-illustrated alkylene amines, are also useful. More preferred are those polyamines containing at least one secondary amino group in addition to the at least two primary amino groups, and multiple divalent hydrocarbon radicals having 2-4 carbon atoms.

The ethylene type polyamines, examples of which are mentioned above, are especially useful for reasons of cost and effectiveness. Such polyamines are described in detail under the heading "Diamines and Higher Amines" in Kirk-Othmer, Encyclopedia of Chemical Technology, Second Edition, Vol. 7, pp. 22-39. They are prepared most conveniently by the reaction of an alkylene chloride with ammonia or by reaction of an ethylene imine with a ring-opening reagent such as ammonia. These reactions result in the production of the somewhat complex mixtures of alkylene polyamines, including cyclic condensation products such as piperazines. These mixtures are satisfactory in preparing the compositions of this invention.

Hydroxy polyamines, e.g., alkylene polyamines having one or more hydroxyalkyl substituents on the nitrogen atoms, are also useful in preparing amides of this invention. Preferred hydroxyalkyl-substituted alkylene polyamines are those in which the hydroxyalkyl group has less than about 10 carbon atoms. Examples of such hydroxyalkyl-substituted polyamines include N-(2-hydroxy-ethyl)-ethylene diamine, N,N'-bis(2-hydroxyethyl)ethylene diamine, monohydroxypropyl-substituted diethylene triamine, dihydroxypropyltetraethylene pentamine and N-(3-hydroxybutyl)tetramethylene diamine. Higher homologs obtained by condensation of the above-illustrated hydroxyalkyl-substituted alkylene amines through amino radicals or through hydroxy radicals are likewise useful.

Other types of polyamines which are useful include those in which one of the above described polyamines are reacted in stoichiometric excess with polyepoxide compounds or polycarboxylic acids to produce a primary amine terminated amine adduct having either aminealkyl

hydroxy linkages or amide linkages along the adduct chain. This primary amine terminated polyamine adduct can then be used to react with the phenolic compound described above.

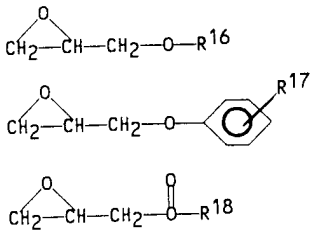
Once the polyamine compound is reacted onto the substituted aromatic glycidyl ester composition, the monoglycidyl capping agent reacts onto the free primary amine groups. As noted above, a larger number of the desired species are obtained if the polyamine compounds and the monoglycidyl capping agents are added sequentially, the latter being added after the polyamine is reacted and excess polyamine is preferably distilled off.

Typically, a solvent is added at this point if one has not already been added in prior steps. The monoglycidyl capping agent adds onto the primary amine functionality relatively easy, in that no catalysts are needed, and the reaction temperature is fairly low, in the range of 80 °C to 110 °C. There is no particular pressure limitation, and the reaction proceeds well at atmospheric pressures.

The capping agent is reacted with the adduct of the polyamine-substituted aromatic glycidyl ester adduct at a molar ratio of preferably 0.5:1 to preferably not more than 2:1. While one can go much higher than a 2:1 ratio, it is not necessary to do so in order to convert the primary amine groups present on the polyamine-substituted aromatic glycidyl ester adduct into secondary amine groups through reaction with the capping agent. With respect to the preferable lower limit, not all of the free primary amine groups present in the adduct need to be reacted and converted into secondary amine groups. One will notice a some reduction in blush even if the

adduct is only partially capped with the monoglycidyl capping agent.

The monoglycidyl capping agent can be an aliphatic, alicyclic, or aromatic compound attached to a monoglycidyl functional group. Non-limiting examples of monoglycidyl capping agents which are suitable for use in the invention include:



XX

XXI

XXII

wherein R^{16} and R^{18} are the same or different and are a branched or linear alkyl, an alkalicyclic, polyoxyalkyl, or alkenyl group having 2-100 carbon atoms, optionally branched,; and R^{17} is hydrogen or a branched or unbranched alkyl having 1-18 carbon atoms. There may be more than one type of R^{17} group attached to the aromatic ring.

These categories would include the unsaturated epoxy hydrocarbons of butylene, cyclohexene and styrene oxide; epoxy ethers of monovalent alcohols such as methyl, ethyl, butyl, 2-ethylhexyl, dodecyl alcohol and others; epoxides of the alkylene oxide adducts of alcohols having at least 8 carbon atoms by the sequential addition of alkylene oxide to the corresponding alkanol (ROH), such as those marketed under the NEODOL name (NEODOL is a trade mark); epoxy ethers of monovalent phenols such as phenol, cresol, and other phenols substituted in the o- or p- positions with C_1-C_{21} branched or unbranched alkyl,

aralkyl, alkaryl, or alkoxy groups such as nonylphenol; glycidyl esters of mono-carboxylic acids such as the glycidyl ester of caprylic acid, the glycidyl ester of capric acid, the glycidyl ester of lauric acid, the glycidyl ester of stearic acid, the glycidyl ester of arachidic acid and the glycidyl esters of alpha, alpha-dialkyl monocarboxylic acids described in U.S. Pat. No. 3,178,454, epoxy esters of unsaturated alcohols or unsaturated carboxylic acids such as the glycidyl ester of neodecanoic acid, epoxidized methyl oleate, epoxidized n-butyl oleate, epoxidized methyl palmitoleate, epoxidized ethyl linoleate and the like; phenyl glycidyl ether; allyl glycidyl ethers, and acetals of glycidaldehyde.

Specific examples of monoglycidyl capping agents useful to the practice of the invention include alkyl glycidyl ethers with 1-18 linear carbon atoms in the alkyl chain such as butyl glycidyl ether or a mixture of C_8-C_{14} alkyls, cresyl glycidyl ether, phenyl glycidyl ether, nonylglycidyl ether, p-tert-butylphenyl glycidyl ether, 2-ethylhexyl glycidyl ether, and the glycidyl ester of neodecanoic acid.

The aliphatic based capping agents are usually hydrophobic in character, which tends to improve the flow properties of the epoxy-curing agent mixture at low temperatures, and tends to lower the glass transition temperature of the film or coating. The lower glass transition temperature improves the impact strength of the cured film. Aromatic based monoglycidyl capping agents, however, have the advantage of rendering the cured film more rigid, chemically resistant, and resistant to stresses at high temperatures. Any one of these types of capping agents may be used, and mixtures

thereof are also advantageous to attain an overall balance of mechanical strength and chemical resistance.

The capping agent is reacted with the amidopolyamine compound to prepare curing agents of e.g. formula I wherein a = 0, in an amount effective to render the curing agent storage stable for 6 months and compatible with bisphenol A and bisphenol F type liquid diglycidyl ether epoxy resins as well as epoxidized phenolic novolac resins. Usually, the monoglycidyl capping agent is reacted with the amidopolyamine compound at a molar ratio of 0.5:1 to 2:1. While one can go much higher than a 2:1 ratio, it is not necessary to do so in order to convert the primary amine groups into secondary amine groups. Further, the curing agent can be only partially capped with the monoglycidyl capping agent, because even a partial capping will have some effect on blush reduction and increasing storage stability.

In addition to reducing the effect of blushing by reacting out some or all of the primary amine groups on the amidopolyamine, reacting the amidopolyamine with a monoglycidyl functional group has the advantage of leaving the one free amine hydrogen active for reaction with epoxy groups. It is desirable to avoid reacting the amidopolyamine with functional groups which would yield the structure -NH-CO-, since the carboxy group tends to deactivate the amine hydrogen. Reacting the primary amine on the amidopolyamine compound with a glycidyl functionality, however, leaves the secondary amine hydrogen more active for reaction with an epoxy resin. Thus, one can achieve the dual advantage of reducing blush without destroying the reactivity of the curing agent toward the epoxy resin.

As to the order of reaction, it is desired to first make the amidopolyamine compound followed by reaction with the monoglycidyl capping agent to ensure that the polyamine compounds react onto the phenolic compounds. Reacting all ingredients together in situ would result in competing reactions where monoglycidyl functionalities undesirably react with the acid groups on the phenolic compound or with both primary amine functionalities on the polyamine compound, thereby effectively reducing the number of species having amidopolyamine linkages between the phenolic compound and the polyamine compound, end capped with the monoglycidyl capping agent.

The curing agents of the invention can optionally be mixed with other conventional curing agents. The amount of other conventional curing agents mixed in will depend upon the requirements placed upon the end product and the efficiencies one desires to achieve. If the end use does not require a product which has high end physical properties and/or it is not important to have lowered processing times, and/or the product is not stored for lengthy time periods, then greater amount of an inexpensive conventional curing agent can be mixed with the curing agent composition of the invention. The amount of the curing agent of the invention can range in the low end of from 1 to 50 wt% based on the weight of all curing agents, but is preferably from 50 wt% to 100 wt%.

Conventional curing agents are usually polyamines with at least 2 nitrogen atoms per molecule and at least two reactive amine hydrogen atoms per molecule. The nitrogen atoms are linked by divalent hydrocarbyl groups. Other hydrocarbyl groups such as aliphatic, cycloaliphatic or aromatic groups may also be singly

linked to some of the nitrogen atoms. These polyamines contain at least 2 carbon atoms per molecule. Preferably polyamines contain about 2 to 6 amine nitrogen atoms per molecule, 2 to 8 amine hydrogen atoms per molecule, and 2 to 50 carbon atoms.

Examples of the polyamines useful as conventional curing agents for epoxy resins include aliphatic polyamines such as ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, dipropylene triamine, tributylene tetramine, hexamethylene diamine, dihexamethylene triamine, 1,2-propane diamine, 1,3-propane diamine, 1,2-butane diamine, 1,3-butane diamine, 1,4-butane diamine, 1,5-pentane diamine, 1,6-hexane diamine, 2-methyl-1,5-pentanediamine, 2,5-dimethyl-2,5-hexane-diamine and the like; cycloaliphatic polyamines such as isophoronediamine, 4,4'-diaminodicyclohexylmethane, menthane diamine, 1,2-diaminocyclohexane, 1,4-diamino-cyclohexane, and diamines derived from "dimer acids" (dimerized fatty acids) which are produced by condensing the dimer acids with ammonia and then dehydrating and hydrogenating; adducts of amines with epoxy resins such as an adduct of isophoronediamine with a diglycidyl ether of a dihydric phenol, or corresponding adducts with ethylenediamine or m-xylylenediamine; araliphatic polyamines such as 1,3-bis(aminomethyl)benzene; aromatic polyamines such as 4,4'-methylenedianiline, 1,3-phenylenediamine and 3,5-diethyl-2,4-toluenediamine; amidoamines such as condensates of fatty acids with diethylenetriamine, triethylenetetramine, etc; and polyamides such as condensates of dimer acids with diethylenetriamine, triethylenetetramine, etc. Some commercial examples of polyamines include EPI-CURE Curing

Agent 3140 (a dimer acid-aliphatic polyamine adduct)(EPI-CURE is a trade mark), EPI-CURE Curing Agent 3270 (a modified aliphatic polyamine), EPI-CURE Curing Agent 3274 (a modified aliphatic polyamine), EPI-CURE Curing Agent 3295 (an aliphatic amine adduct), EPI-CURE Curing Agent 3282 (an aliphatic amine adduct), EPI-CURE Curing Agent 3055 (an amidoamine), EPI-CURE Curing Agent 3046 (an amidoamine) and EPI-CURE Curing Agent 3072 (modified amidoamine), and EPI-CURE Curing Agent 3483 (an aromatic polyamine) available from Shell Chemical Company. Mixtures of polyamines can also be used.

The invention is also directed to two component epoxy compositions having an epoxy resin component (A) and a curing agent component (B).

The epoxy resin component (A) has at least one 1,2-epoxy group per molecule. Mixtures of epoxy compounds having one epoxy functionality and two or more epoxy groups are also suitable. The epoxy compounds having two or more epoxy groups per molecule means that the nominal functionality is two or more. Generally epoxy resins contain a distribution of compounds with a varying number of 1,2-epoxy equivalency. The actual average functionality of these epoxy compounds is 1.5 or more. Any of the epoxy compounds can be saturated or unsaturated, linear or branched, aliphatic, cycloaliphatic, aromatic or heterocyclic, and may bear substituents. Such substituents can include bromine or fluorine. They may be monomeric or polymeric, liquid or solid, but are preferably liquid or a low melting solid at room temperature.

The epoxy compounds can be of the glycidyl ether type prepared by reacting epichlorohydrin with a compound containing at least one aromatic hydroxyl group carried

out under alkaline reaction conditions. Examples of other epoxy resins suitable for use in the invention include diglycidyl ethers of dihydric compounds, epoxy novolacs and cycloaliphatic epoxies. Specific examples of the epoxy resins useful in the epoxy resin component A are described hereinbefore with reference to the reaction between the phenolic acid and the polyepoxide compound.

Preferred epoxy resins include, but are not limited to, any one of those represented by the hereinbefore specified formulas V, VI and VII.

The two component epoxy resin composition is either solvent borne or solventless. Suitable solvents are described above, with preference given to ketones, alcohols, and xylene. Solventless epoxy resin compositions are those compositions which are applied in the absence of a solvent and in the absence of an aqueous medium.

The two component compositions of the invention are mixed and cured, preferably in the absence of external accelerators, in a wide range of temperatures ranging from -25 °C to 100 °C. One advantage of the invention is that the curing agent composition of the invention and the epoxy resin can cure, once mixed, within 24 hours at 4.4 °C, and even in as short a time as within 15 hours at 4.4 °C in the absence of external accelerators. This is unexpected since many, if not all, of the primary amine groups are reacted out with the monoglycidyl capping agent, thus otherwise lowering the reactivity of the curing agent. For measurement purposes, the two component mixture is "cured" or "curable" when it cures or has the capacity to cure to a hard gel (cotton free) at the designated temperature in the absence of external accelerators and at 50% relative humidity. At 25 °C, the

curing agent composition of the invention can cure an epoxy resin in as quick as 5 hours. At lower temperatures, the amount of time required for cure naturally increases, although due to the excellent compatibility between the curing agent composition and the epoxy resin used in the invention, the overall time to cure at any given temperature is dramatically reduced compared to epoxy resins mixed with other types of curing agents.

Advantageously, the curable epoxy resin composition is cured in the absence of catalyst compounds which accelerate the reaction between the curing agent and the epoxy resin, commonly known as accelerators. An accelerator, however, can be included, if desired, to increase the cure rate of the epoxy resin-curing agent system beyond that already achieved in its absence. Various amine-compatible accelerators can be used as long as they are soluble in the amine curing agents. Examples of accelerators include metal salts such as, for example, sulfonates, phosphonates, sulfates, tetrafluoroborates, carboxylates and nitrates of Groups IA, IIA and transition metal series of the Periodic Table (CAS version), preferably Mg, Ca, Zn and Sn salts, and complexes thereof; inorganic acids such as, for example, HBF_4, H_2SO_4, H_2NSO_3H and H_3PO_4; carboxylic acids, preferably hydroxy-substituted carboxylic acids such as, for example, salicylic, lactic, glycolic and resorcylic; phenolic compounds such as, for example, phenol, t-butylphenol, nonylphenol and bisphenol A; imidazoles; cyanamide compounds such as dicyandiamide and cyanamide; sulfonamides such as, for example p-toluenesulfonamide, methanesulfonamide, N-methylbenzenesulfonamide and sulfamide; and imides such as, for example, phthalimide,

succinimide, perylenetetracarboxylic diimide and saccharin.

When the cure rate at the desired temperature is suboptimal, it is sometimes desirable to include the accelerator. For example, for adhesive applications and civil engineering applications where application at low temperature is desired, it may be desirable to include the accelerator. The accelerators are typically present in an amount of from 0.1 weight percent to 10 weight percent, preferably to 5 weight percent, based on the epoxy resin, if used at all.

The storage stable composition of the invention may include other additives, such as fillers, elastomers, uv-stabilizers, extenders, plasticizers, accelerators, pigments, reinforcing agents, flow control agents and flame retardants depending on the application.

For coating applications, the curable two component epoxy resin composition can also contain pigments of the conventional type such as iron oxides, lead oxides, strontium chromate, carbon black, titanium dioxide, talc, barium sulfate, phthalocyanine blue and green, cadmium red, iron blue, chromic green, lead silicate, silica and silicates. Such pigments can be added to the polyamine curing agent component or the epoxy resin component prior to mixing them together. Their amounts usually range from 20 to 100 pbw based on the weight of the epoxy resin and the curing agent composition.

For floor topping application, the curable epoxy resin composition can also contain a filler such as sand, other siliceous materials, iron or other metals. Small amounts of thixotropic agents, colouring agents, inert plasticizers, and levelling agents can also be incorporated in the curable epoxy resin composition if

desired. These curable flooring compositions can be trowelled, sprayed or brushed on to a floor substrate.

The curing agent composition of the invention contains no added solvents or water when used in powder coating applications. In applications where the curing agent composition is applied wet to a substrate, the curing agent composition is non-aqueous and is either dissolved in solvents or is applied neat, or solventless. Preferably, some amount of solvent is used in the curing agent composition and in the two component epoxy resin composition to reduce the viscosity of the curing agent and/or the epoxy resin compositions, especially in cold temperature applications. The reduction in viscosity facilitates the handling and application of the composition in various environments. Suitable solvents include alcohols, ketones, esters, ethers of hydrocarbons. Examples of suitable solvents are butanol, methyl isobutyl ketone, toluene, ethylglycol acetate, xylene, benzyl alcohol, phthalic acid esters of monohydric alcohols, e.g. n-butanol, amylalcohol, 2-ethylhexanol, nonanol, benzyl alcohol, gamma - butyrolactone, delta -valerolactone, epsilon - caprolactone, lower and higher molecular weight polyols, e.g. glycerol trimethylol-ethane or -propane, ethyleneglycol, and ethoxylated or propoxylated polyhydric alcohols, either individually or in admixture. The amount of solvent can range from 0 to 80 wt%. The solids concentration can range from 20 wt% to 100 wt%, preferably from 65 wt% to 85 wt%.

Defoamers, tints, slip agents, thixotropes, etc., are common auxiliary components to most coatings and may be employed in the composition of the present invention. Flow control agents are typically used in amounts ranging

from 0.05 to 5 wt%, based on the combined weight of the epoxy resin and the curing agent composition.

Re-inforcing agents may be added to either of the components, and include natural and synthetic fibers in the form of woven, mat, monofilament, chopped fibers and the like. Other materials for re-inforcing include glass, ceramics, nylon, rayon, cotton, aramid, graphite and combinations thereof. Suitable fillers include inorganic oxides, inorganic carbonates, ceramic microspheres, plastic microspheres, glass microspheres, clays, sand, gravel and combinations thereof. The fillers can be used in amounts suitably from 0 to 100 pbw of the combined epoxy/curing agent components.

Aside from coating applications, the curing agent compositions of the invention and the two component compositions utilizing the curing agents compositions can be used in such applications as flooring, casting, crack or defect repair, moulding, adhesives, potting, filament winding, encapsulation, structural and electrical laminates, composites and the like.

A typical use for the two component compositions of the invention is in coatings. The heat-curable coating composition can be applied to a substrate by brush, spray, or rollers. Alternatively, the curing agent compositions can be mixed and dried to a powder for powder coating applications. In the case where the coating is applied wet, the epoxy resin composition is preferably a liquid resin, a semi-solid resin, or in solution, at the application temperature. The same is true for the curing agent composition.

The two component compositions of the invention comprising curing agents derived from components (bi) (bii) and c, e.g. those according to formula I wherein

a = 0, are mixed and cured, preferably in the absence of external accelerators, in a wide range of temperatures ranging from -25 °C to 100 °C. One advantage of the invention is that the curing agent composition of the invention and the epoxy resin can cure, once mixed, within 24 hours at 4.4 °C. This is unexpected since many, if not all, of the primary amine groups are reacted out with the monoglycidyl capping agent, thus otherwise lowering the reactivity of the curing agent. For measurement purposes, the two component mixture is "cured" when it cures to a hard gel (cotton free) at the designated temperature in the absence of external accelerators and at 50% or more relative humidity. At 25 °C, the curing agent composition of the invention can cure an epoxy resin as quick as 10 hours, even as soon as within 7 hours, depending upon the particular species of curing agent, epoxy resin, and humidity conditions. At lower temperatures, the amount of time required for cure naturally increases, although due to the excellent compatibility between the curing agent composition and the epoxy resin used in the invention, the overall time to cure at any given temperature is dramatically reduced compared to epoxy resins mixed with other types of curing agents.

In general the curing agent compositions of the invention can also be used in thermosetting powder coating compositions prepared by the various methods known to the powder coating industry: dry blending, melt compounding by two roll mill or extruder and spray drying. Typically the process used is the melt compounding process: dry blending solid ingredients in a planetary mixer and then melt blending the admixture in an extruder at a temperature within the range of 80 °C to

130 °C. The extrudate is then cooled and pulverized into a particulate blend.

The thermosetting powder composition can generally be applied directly to a substrate of, e.g., a metal such as steel or aluminum. Non-metallic substrates such as plastics and composites can also be used. Application can be by electrostatic spraying or by use of a fluidized bed. Electrostatic spraying is the preferred method. The coating powder can be applied in a single sweep or in several passes to provide a film thickness after cure of 2.0 to 15.0 mils.

The substrate can optionally be preheated prior to application of a powder composition to promote uniform and thicker powder deposition. After application of the powder, the powder-coated substrate is baked, typically at 120 °C, preferably from 150 °C to 205 °C for a time sufficient to cure the powder coating composition, typically from 1 minute to 60 minutes, preferably from 10 minutes to 30 minutes.

The following examples illustrate an embodiment of the invention and are not intended to limit the scope of the invention.

SSA is about 63 wt% salicyclic acid mono substituted with C_{14}-C_{18} alkyl groups dissolved in xylene and containing less than 15 mole% of C_{14}-C_{18} alkyl phenols and less than 5 mole% of dicarboxylic acid species, having an acid value of 92 mg KOH/g in solution and 146 mg KOH/g based on the solids.

TETA is triethylene tetramine commercially available from Union Carbide having a typical amine value of 1436 mg KOH/g.

HELOXY Modifier 62 is a commercial grade of ortho-cresyl glycidyl ether manufactured by Shell Chemical Company, that is produced by treatment of ortho-cresol with epichlorohydrin and sodium hydroxide. HELOXY Modifier is a thin liquid having a viscosity at 25 °C of 7 centipoise and an epoxide equivalent weight of 175 to 195.

EPON 828 is a diglycidyl ether liquid epoxy resin commercially available from Shell Chemical Company and Shell Chemical Europe Ltd.

EXAMPLES 1-4, relating to curing agents according to formula I, wherein a = 0

Example 1

This example illustrates the synthesis of the substituted aryl amidopolyamine compound based on a substituted salicyclic acid and triethylene tetramine, which is subsequently reacted with a monoglycidyl ether.

A 4 necked round-bottomed glass flask was equipped with a condenser having a water trap, a nitrogen inlet, an acid inlet, and the TETA inlet. The flask was flushed with nitrogen. 1529.4 G of SSA was charged to the flask, after which a total of 390.42 grams of TETA was charged over a period of time to the flask, for a total of 1919.8 grams of reaction ingredients. The amount of SSA and TETA added were reacted in a ratio of one amine equivalent to one acid equivalent, or a 1:1 mole ratio. During the course of the reaction through completion, approximately 613 grams of water and xylene were distilled off. In this reaction scheme, the total amount of ingredients were mixed together prior to reaction.

After addition of the SSA to the flask, TETA was added dropwise at about 23 °C initial, with the contents of the flask being stirred at about 60 rpm under a nitrogen pad, for a period of two hours, during which the exotherm raised the temperature of the reaction mixture to 50 °C. Once addition of the TETA was complete, the temperature of the reactants in the flask was raised to 150 °C slowly over a 55 minute period, and then raised to 160 °C over the next one and a half hours. The reaction was left overnight at room temperature. The next day, the reaction was again heated to 160 °C for the first two hours, and subsequently warmed to 170 °C over the next 7 hours. To drive the reaction to full completion and the desired acid value, the reactants were again heated to 145 °C - 150 °C over a 5 hour period under vacuum at about 20 in.Hg. The acid value was measured at 10.3 mg KOH/g, and the amine value was measured to be 345.4 mg KOH/g.

Once this product was made, 514.82 grams of it was used to react with 198.25 g of the monoglycidyl ether HELOXY 62. The amounts of each ingredient used were based on reacting them in stoichiometric ratios of one primary amine equivalent to one epoxide equivalent.

The product was charged to a 4 necked round bottomed flask equipped with a condenser. The flask was purged with nitrogen, and agitation was initiated. Once the product was heated to 93 °C, the HELOXY 62 was added dropwise over a period of about 3 hours. The reaction temperature was held at 90-96 °C for the next 30 minutes, after which the final end capped amidopolyamine curing agent was isolated under nitrogen purge using a coarse grade Gardner filter cup. The acid and amine values of

the final end capped amidopolyamine product were measured to be 7.6 and 246.4 mg KOH/g, respectively. This curing agent was mixed with solvents to arrive at a curing agent solution having 80 g of the end capped amidopolyamine, 5 g of n-butanol, and 15.64 g of xylene. The percent solids was calculated to be 79.5.

Example 2

This example demonstrates the storage stability of the product made in Example 1. A 120 g sample of the curing agent made in Example 1, without being mixed in solvents, was set in a glass container at ambient temperature for a period of six months without being disturbed except when sampled intermittently for viscosity. The viscosity of the curing agent was measured at one month intervals using a Brookfield viscometer with a spindle 6 and again using a spindle 7 at 20 rpm. For comparison purposes, a 120 g sample of CARDOLITE NC-541, a commercially available low temperature phenalkamine curing agent having aliphatic polyamines attached to an aromatic backbone with aliphatic sidechains, from The Cardolite Corporation, was also sampled monthly over a six month period for changes in viscosity, using a spindle 7 at 20 rpm (CARDOLITE is a trade mark). The results are tabulated in Table 1 below. The results show a dramatic increase in the viscosity of the CARDOLITE sample at one month, with a steady increase thereafter. By contrast, the viscosity of the end capped amidopolyamine curing agent made in Example 1 were fairly constant throughout the six month period, indicating that the product was storage stable, and was not self reacting to form the more viscous higher molecular weight oligomeric species. The results are also a good indicator that the curing agent was resistant

to reaction with carbon dioxide and atmospheric water, which often produces the undesirable side effect of blush and soft film formation. By end capping the primary amine groups with the monoglycidyl compound, this undesirable effect can be substantially avoided, and as shown in further examples, the reactivity of the amidopolyamine is quite good even though the primary amine groups have been substantially reacted out with the monoglycidyl compound.

TABLE 1

Month	Example 1	CARDOLITE NC-541
Initial	38,800	53,800
1 month	35,950	113,800
2 months	38,150	117,000
3 months	40,250	137,400
4 months	45,450	138,200
5 months	55,800	151,600
6 months	39,400	158,600

Example 3

This example demonstrates the properties of end capped amidopolyamine curing agent solution made in Example 1 when mixed and reacted with an epoxy resin.

6 g of EPON 828 epoxy resin were reacted in a 1:1 stoichiometric ratio with 8.54 g of the curing agent solution. Upon mixing, the end capped amidopolyamine was immediately compatible with the epoxy resin as evidenced by the formation of a clear solution upon mixing. Thus, there existed no need for an induction time after mixing the ingredients.

A formula for coating was made consisting of 6.0 g of the EPON 828 resin, 8.54 g of the end capped

amidopolyamine final product in solution made in Example 1, and 0.006 g of BYK 348 flow control agent. Upon mixing, the mixture was dropped onto 4 inch by 6 inch cold roll steel panels, and allowed to cure over 7 days. The film thickness was 1-2 mils, initial specular gloss was 104 at 60 ° and 102.7 at 20 °. On glass panels with cure conditions set at 7 days, 25 °C, and 50 RH, the gloss at 60 ° was 146 and at 20 ° was 165. On glass panels with cure conditions set at 7 days, 4.4 °C, and 50-60% RH, the gloss at 60 °C was 124 and at 20 °C was 118. The impact strength on films cast onto the cold rolled steel was 32 in/lb (direct) and 28 in/lb (indirect), MEK resistance was 35 double rubs, and adhesion was 4A by X-Cut method.

The results indicate that films made with the curing agent of the invention had good impact resistance at ambient cure temperatures, and had good glossy film characteristics. Thus, even though the primary amine groups in the curing agent were capped with a monoglycidyl compound, the curing agent had good reactivity and resulted in films with good impact resistance.

Example 4

In this example, the amidopolyamine capped curing agent solution was mixed with an epoxy resin for examination of the film properties.

33.18 Pbw of EPON Resin 828 was mixed with 33.18 pbw of the curing agent solution made in Example 1 at a stoichiometric ratio of 1:0.707, respectively. The mixture was pigmented with a white pigment and given a 30 minute induction time, although this time was not necessary. The mixture was drawn down with a # 50 wire-wound bar on bonderite 1000 steel panel at an average

thickness of 2.5 mils. The curing conditions were set for 14 days at 25 °C and 50% RH. The pot life of the mixture was about 6 hours, and the initial mix viscosity was 600 cP. The film became a soft gel (set to touch) at 2 hours, a hard gel (cotton free) at 6.5 hours, and mar resistant (through dry) at 10 hours. At a 24 hour cure, the film had a hardness of 2B; and after 14 days, a hardness of F. Also after the 14 day cure, the direct impact was p16, f20; adhesion X-cut was 5A, flexibility on Mandrel test was 6.35% elongation, specular gloss was 98.4 at 60 ° and 85.6 at 20 °, and the MEK resistance was 85. The coatings showed very good water resistance properties as evidenced by the maintenance of coating integrity in water immersion tests under ambient (25 °C) and elevated temperatures (60 °C) for 2000 hours.

When cured at 4.4 °C and 70%RH for 14 days, the film had a hardness of 3B. Its cure rate was 6 hours to soft gel, 24 hours to hard gel, and 42 hours to mar resistance.

The results indicate that coatings made with the curing agent of the invention had good reactivity as indicated by their reasonable cure rates, and produced films having excellent hardness at room temperature and good hardness when cured at temperatures as low as 4.4 °C. The reactivity of the epoxy resin composition was good in that it cured to a hard gel within 24 hours at the low temperature of 4.4 °C, even in the absence of an external accelerator/catalyst. The coating composition exhibited a pot life of about 6 hours even with a highly functional resin such, as EPON Resin 828, and relatively low coating application viscosity under ambient

conditions, thus satisfying two basic requirements for ambient-cure coatings known to those skilled in the art.

EXAMPLES 5-9 relating to curing agents according to formula I, wherein a = 1

Example 5

This example illustrates the synthesis of the substituted aromatic glycidyl ester composition. 500 Grams of EPIKOTE 828 in xylene, which is a bisphenol A based epoxy resin available from Shell Chemicals Europe; 327 grams of a 63 wt.% 3-alkyl substituted salicyclic acid mixture in xylene (corresponding to about 20 mole % per epoxy group), in which the alkyl group contains from 14 to 18 carbon atoms and the mixture contains less than 15 mole% of C_{14}-C_{18} alkyl phenols and less than 5 mole% of dicarboxylic acid species; and 0.15 grams of ethyltripenylphosphonium iodide were mixed together in a vessel equipped with a condenser. The reaction temperature was increased to 175 °C (heating up to 110 ° C in 30 minutes, holding for another 30 minutes at 110 °C and then heating to 175 °C within the next 60 minutes), and holding the temperature at 175 °C for the next 30 minutes, for a total reaction time of 2.5 hours. Water and xylene were stripped off. Subsequently, the substituted aromatic glycidyl ester composition was allowed to cool. Once cooled, the product was dissolved in xylene to 85 wt% solids. The product had an acid number of zero (theoretical) in solution and an acid number of zero (theoretical) based on solids. This product was designated as SSA-1. The same product was further reduced in concentration to an 80 wt% solids by adding more xylene to SSA-1. The more diluted product having 80 wt% solids was designated as SSA-2.

Example 6

In this example, a substituted aromatic glycidyl ester composition was also made using the same ingredients and procedure as in Example 1, except that only the amount of the substituted salicyclic acid having 14 to 18 carbon atom substitution corresponded to 5 mole % per epoxy group instead of 20 mole %. The product was dissolved in xylene to give a solution having 95 wt% solids. This product was designated as SSA-3. This product was dissolved with more xylene to give a solution with 85 wt% solids. This more diluted product was designated as SSA-4.

Example 7

This example demonstrates the synthesis of the curing agent of the invention based on SSA-2.

A 2000 ml.4necked round-bottomed flask was equipped with a condenser having a water trap, a nitrogen inlet, an acid inlet, and the TETA inlet. The flask was flushed with nitrogen. 468.54 G of TETA was charged to a flask and warmed to 93 °C over a fifteen minute period. Then, 471.00 g of SSA-2 was added slowly over a period of 1 hour, 25 minutes, and held at 93 °C for 1 more hour. Subsequently, the temperature was increased to 230 °C for the remainder of the reaction, which lasted for another 6 hours, during which a vacuum was pulled to about 25 in.Hg - 27 in.Hg to distill off unreacted TETA and xylene. About 91.52 g of xylene and 312.36 g of TETA were collected. After that, the reaction was allowed to cool overnight. The amine value was measured at 421 mg KOH/g.

The next day, the reaction product was heated to 230 °C to confirm that no more TETA would distill, and then cooled to 115 °C, at which time 118.76 g of n-

butanol was added. At about 93 °C, 176.91 g of HELOXY 62 capping agent was added dropwise over a 40 minute period and reacted for about another 40 minutes at that temperature. Then, 356.28 g of xylene was added to produce a curing agent solution (CA-2) having about 65 wt% solids, an amine value of 189 mg KOH/g based on the solution, and an amine value of 291 mg KOH/g based on solids.

Example 8

This example demonstrates the synthesis of the curing agent of the invention based on SSA-4.

A 2000 ml 4-necked flask was equipped with a condenser having a water trap, a nitrogen inlet, an acid inlet, and the TETA inlet. The flask was flushed with nitrogen. 468.54 g of TETA was charged to a flask and warmed to 93 °C over a half hour period. 262.65 g of SSA-4 was added to the TETA over a 1 hour, 5 minute period, and held at about 94 °C for 1 more hour, after which the temperature was slowly increased to a maximum of 230 °C under a vacuum of about 28.5 in.Hg to distill off unreacted TETA and xylene. The resulting product had an amine value of 580 mg KOH/g. About 39.9 g of xylene and 312.36 g of TETA were distilled off and recovered.

The product was cooled to 106 °C, at which time 59.55 g of n-butanol was added, further reducing the temperature to 92 °C. Subsequently, 176.91 g of HELOXY 62 modifier was added over a 25 minute period, after which 178.66 g of xylene was added and the product allowed to cool. This product had a 78.42 wt.% solids concentration, which was subsequently reduced to a 67.48 wt.% solids concentration as the final curing agent (CA-4) by addition of more xylene and butanol in a

3:1 weight ratio. The amine value in solution was 237 mg KOH/g, and on solids basis was 352 mg KOH/g.

Example 9

This example demonstrates the physical and chemical properties of the curing agent and films made with the curing agent of the invention. To the curing agent of CA-2 was added 0.37g of BYK 346 flow control agent, and to CA-4 was added 0.39 g of BYK-346 flow control agent. Each of the curing agents were reacted in a 1:1 stoichiometric calculated ratio with the epoxy resin. The cured films were made at room temperature and at 4.4 °C for the designated amount of time, and tested for their physical properties. For compatibility between the epoxy resin and the curing agent, the two were combined in mass rather than as a film, and inspected by eye for haziness.

The following ASTM test methods were employed for the corresponding tests:

Test	ASTM
Pencil Hardness	D3363
Direct Impact	D2794
Reverse Impact	D2794
Adhesion X-cut	D3359
Flexibility, Conical Mandril	D522

TABLE I

Curing Agent	CA-2	CA-4
Amount (g)	58.48	52.89
EPON 828 (g)	41.15	46.72
Compatibility, at 4.4 and 25 °C		
Initial	Clear	Clear
t=30 min.	Clear	Clear
CURE CONDITIONS: 14 DAYS AT 25 ± 2 °C, 50 ± 5% RH, COLD ROLLED STEEL		
% binder solids, calc.	75.01	77.74
After 24 Hour Cure		
Soft gel, set to touch (h)	2.25	2.5
Hard gel, cotton free (h)	4	4
Mar resistant (h)	5.75	5
Film Hardness	H	H
After 7 Day Cure		
Film Hardness	H	H
After 14 Day Cure		
Film Hardness	2H	H
Direct Impact, in/lb	p64,f68	p68,f72
Reverse impact, in/lb	p8,f12	p68,f72
Adhesion, X-cut	5A	5A
Flexibility, Mandrel Test	pass 1/8in	pass 1/8in
%Elongation	32	32
MIBK Resistance, Min, spot test	50 (#F)	>60 (#HB)
MEK Resistance, (#double rubs)	>200	>200

TABLE I (Cont'd)

CURE CONDITIONS: 14 DAYS AT 4.4 °C, 60%RH, DETERGENT WASHED GLASS PANELS		
% Binder Solids	75.01	77.74
After 24 Hour Cure		
Soft gel, set to touch (h)	5	4.5
Hard gel, cotton free (h)	11	9
Mar resistance, through dry (h)	18.5	13.5
Film Hardness	5B	5B
After 7 Day Cure		
Film Hardness	HB	HB
After 14 Day Cure		
Film Hardness	HB	HB
MIBK Resistance, min (spot test)	15 (#2B)	45(#2B)
MEK Resistance, (#double rubs)	>200	>200

The results indicate that the curing agents of the invention have good compatibility immediately upon mixing with the epoxy resin both at room temperature and at sub-ambient temperatures, such as 4.4 °C. The cure rates at room temperature and sub-ambient temperature are quick even in the absence of external accelerators/catalysts. Further, the cured films had good hardness.

C L A I M S

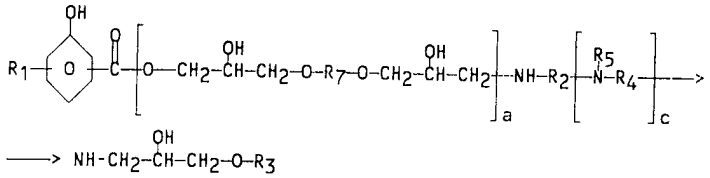
1. A curing agent composition comprising the reaction product of a b) substituted aryl amidopolyamine with a c) monoglycidyl capping agent, said substituted aryl amidopolyamine comprising the reaction product of:

bi) a phenolic compound substituted with at least one carboxyl group and at least one hydrocarbyl group having at least 1 carbon atom, and

bii) an aliphatic polyamine compound having at least two primary amine groups.

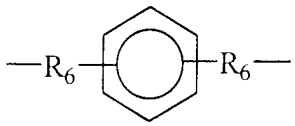
2. A curing agent composition according to claim 1, characterized in that it comprises a polyepoxide compound in addition to components c), bi), bii).

3. A curing agent composition according to claim 1, characterized in that it comprises a compound represented in the formula:

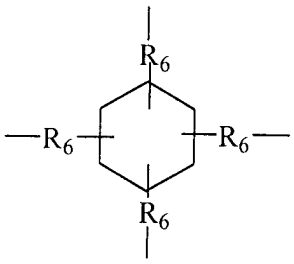


I

wherein R_1 is a branched or unbranched, substituted or unsubstituted, monovalent hydrocarbyl group having at least one carbon atom; R_2 and R_4 each independently represent a branched or unbranched, substituted or unsubstituted, divalent hydrocarbyl group having 2-24 carbon atoms, or



II



wherein R_6 represents a branched or unbranched, substituted or unsubstituted, divalent hydrocarbyl group having 2-24 carbon atoms; R_3 is a branched or unbranched, substituted or unsubstituted, monovalent hydrocarbyl having 1-24 carbon atoms, a polyoxyalkylene group, an aryl group, an alkaryl group, or an aralkyl group; R_5 is hydrogen or a branched or unbranched, substituted or unsubstituted, monovalent hydrocarbyl having 1-24 carbon atoms, R_7 is the residue of said polyepoxide compound; a represents an integer equal to 0 or 1; and c represents an integer from 0-10.

4. The composition of claim 1, wherein the composition comprises the reaction product of the phenolic acid compound with the polyepoxide compound to produce a substituted aromatic glycidyl ester compound, and subsequently combining and reacting said polyamine compound and said monoglycidyl capping agent with said aromatic glycidyl ester compound.

5. The composition of claim 1, wherein the phenolic compound comprises salicyclic acid substituted with an 8 to 36 carbon alkyl group.

6. The composition of claims 1-5, wherein the salicyclic acid is substituted with a branched or unbranched 14 to 24 carbon alkyl group.

7. The composition of claims 1-6, wherein at least one mole of polyamine is reacted per carboxyl group equivalent on the phenolic compound.

8. The composition of claim 1, wherein said composition is non-aqueous.

9. The composition of claim 3, wherein a = 1 and wherein said phenolic acid compound and said polyepoxide compound are reacted to substantial completion prior to reaction with the polyamine compound.

10. The composition of claim 2, wherein the reaction between the polyepoxide compound and the phenolic acid are carried out at molar ratios of greater than 2:1, respectively.

11. The composition according to claim 2, wherein the substituted aryl amidopolyamine comprises the reaction product of:

bi) a phenolic compound substituted with at least one carboxyl group and at least one hydrocarbyl group having more than 12 carbon atoms, and

bii) an aliphatic polyamine compound having at least two primary amine groups and a secondary amine group, and

biii) a polyepoxy compound which is first reacted in substoichiometric amounts with the polyamine compound prior to reacting the polyamine compound with the phenolic compound.

12. The curing agent composition of claim 1, wherein the carboxyl group on the phenolic compound comprises a -carboxy acid, an -acetic acid, a - propionic acid, or a -stearic acid.

13. The curing agent composition of claim 1, wherein the phenolic compound comprises an 8-24 carbon alkyl substituted salicyclic acid, the polyamine compound

comprises at least two primary amine nitrogens and at least on secondary amine nitrogen, and the monoglycidyl ether comprises an alkyl glycidyl ether having 2-18 carbon atoms or an alkaryl glycidyl ether wherein the alkyl has 1-24 carbon atoms.

14. The composition of claims 1-13, wherein the polyamine compound further contains at least one secondary amine group, and the salicyclic acid is substituted with a 14 to 24 carbon alkyl group.

15. The composition of claims 1-14, wherein the polyamine compound comprises diethylene triamine, triethylene tetramine, tetraethylenepentamine, or m-xylylene diamine.

16. The composition of claims 2-15, wherein the monoglycidyl capping agent is reacted with the said adduct at a molar ratio of 0.5:1 to 2:1.

17. The composition of claims 1-16, wherein the monoglycidyl capping agent comprises an alkyl glycidyl ether having 1-24 branched or unbranched carbon atoms in the alkyl chain, an alkaryl glycidyl ether, an aryl glycidyl ether, an allyl glycidyl ether, an alicyclic alkyl glycidyl ether, or a glycidyl ester of a monocarboxylic acid.

18. A two component solventborne or solventless epoxy composition comprising an epoxy resin component and a curing agent component, said curing agent component comprising the reaction product of:

b) a substituted aryl amidopolyamine comprising the reaction product of:

bi) a phenolic compound substituted with at least one carboxyl group and at least one hydrocarbyl group having at least 8 carbon atoms, and

bii) an aliphatic polyamine compound having at least two primary amine group, and

c) a monoglycidyl capping agent.

19. Composition of claim 18, which is curable within 24 hours at 4.4 °C in the absence of external accelerator compounds.

20. The composition of claim 18, which is in the absence of external accelerators.

INTERNATIONAL SEARCH REPORT

Int ational Application No
PCT/EP 97/07299

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G59/54

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 6 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 229 563 A (FOSCANTE ET AL) 21 October 1980 see column 2, line 9 - column 7, line 25; claims 1,7; examples	1,18
A	US 4 264 758 A (WADDILL) 28 April 1981 see column 1, line 31 - column 2, line 12; claims 1,2; examples	1,18
A	EP 0 545 354 A (KANSAI PAINT) 9 June 1993 see page 2, line 22 - page 4, line 7 see page 5, line 50 - page 6, line 34; claims 1-7	1,18
A	US 2 938 004 A (DE HOFF ET AL) 24 May 1960 see column 1, line 41 - column 3, line 58; claim 1	1,18

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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

"E" earlier document but published on or after the international filing date

"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)

"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

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 June 1998	23/06/1998

Name and mailing address of the ISA	Authorized officer
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Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 97/07299

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 879 957 A (CIBA) 11 October 1961 see page 1, line 8 - page 4, line 13; claims 1-9; examples VI-XI,XIV -----	1,18

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 97/07299

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