

1

2,980,601

COAL TAR MODIFIED AMINE TYPE CURING AGENT FOR POLYEPOXIDES

Archibald V. Meigs, Houston, Tex., assignor to Coast Paint and Lacquer Company, Houston, Tex., a corporation of Texas

No Drawing. Filed June 12, 1958, Ser. No. 741,451

11 Claims. (Cl. 208—44)

This invention relates to a process for producing coal tar modified amine type curing agent for polyepoxides which comprises the use of the well known reaction of primary amino groups of aliphatic polyamines with the ketone group of aliphatic and aromatic ketones to form aliphatic and aromatic polyamine-ketone condensation products, then further utilizing the well known reaction of hydroxyl groups with the hydrogen of secondary amino groups by combining the aliphatic polyfunctional amine-ketone condensation product with coal tar in stoichiometric proportions so that all the amino hydrogens combine with the hydroxyl groups of the phenols, xylenols and the like present in the coal tar to form tertiary amino groups. More particularly, the invention relates to a process by which liquid coal tar, a complex mixture of organic chemicals, useful in thermoplastic coal tar protective coatings is chemically combined with a polyfunctional, aliphatic amine to produce a coal tar modified polyfunctional aliphatic amine compound having a plurality of tertiary amino groups for use in curing polyepoxide coating compositions to hard, flexible heat and solvent resistant coal tar-polyepoxide protective coating for steel and concrete surfaces, although not limited to such uses.

The present application is a continuation-in-part of a prior application Serial No. 700,562, filed December 4, 1957, now abandoned, by the same applicant.

It is an object of this invention to provide a new complex liquid coal tar modified polyfunctional aliphatic amine type curing agent having a plurality of tertiary amino groups for cold or air curing polyepoxides in coating compositions to a hard, flexible corrosion resistant tough sealing coal tar-polyepoxide film on pipe line joints or any clean steel or concrete surfaces. Specifically, the object of producing the new modified polyfunctional aliphatic, amine type curing agent for polyepoxides is to provide a method by which liquid coal tar may be applied to pipes and metal surfaces without the use of heating kettles and the attendant personnel.

A further object is to provide a coal tar modified polyfunctional aliphatic amine curing agent for cold applied air curing of polyepoxide ethers or resins in coating compositions to hard flexible coal tar-polyepoxide films impermeable to water, resistant to acids and alkali, with excellent resistance to organic solvents, and which retain their hardness and strength at elevated temperatures. The coal tar-polyepoxide films formed by curing polyepoxides in coating compositions with the coal tar modified polyfunctional aliphatic amine give hard flexible films that provide excellent protection against corrosion of surfaces of steel structures and metal pipes above ground or underground, and give hard tough flexible films

2

on sections of pipes which do not require the use of strong wrappings such as cloth fabric, burlap, jute, asbestos felt, impregnated glass fiber tapes, paper or other materials to prevent damage to the cured coal tar-polyepoxide film on sections of pipe in transit or during installations or to prevent damage to the film after installation due to soil stresses or damage to the film by the acid or alkaline condition of the soil.

Other important objects and advantages of the invention will be evident from the following detailed description constituting a specification of the invention.

In general the products used to make the coal tar modified polyfunctional aliphatic amine curing agent of the invention are (1) refined coal tar, (2) a polyfunctional aliphatic amine, and (3) an aliphatic or aromatic ketone.

The refined coal tar used in this invention is a black viscous liquid mixture of tars produced by the destructive distillation of coal without admixture of petroleum. Crude coal tar is a very complex mixture of organic chemical compounds chiefly of the aromatic series. The composition and the physical properties of coal tar are greatly influenced by the nature of the coal, the method of production and the temperature of carbonization.

The coal tar component of this invention may be obtained from one, or a mixture of more than one, or a mixture of all of the following types of coal tar:

- (1) Gas works coal tar from (a) horizontal retorts, (b) vertical retorts, and (c) inclined retorts.
- (2) Coke oven coal tar.
- (3) Blast furnace coal tar.
- (4) Producer gas coal tar.

The crude coal tar from each of these sources is a black more or less viscous liquid containing water, ammonia, free carbon or particles of coal or other foreign materials. When these crude coal tars are dehydrated by any one of the several methods to remove water and ammonia, and light oil, a dark-brown to a black thin liquid is obtained which is a grade of refined coal tar, and when this first refined coal tar is heated in a still at 110–170° C. the light oil is removed yielding a dark-brown to black viscous liquid also known as refined coal tar. Upon heating this second grade of refined coal tar to 170°–235° C. to remove a part or all the middle oil, a dark-brown to black very viscous to semi-solid product remains which is also known to the trade as refined coal tar. The preferred coal tar of this invention is the refined coal tar obtained after removing water, ammonia, and the light oil.

The refined coal tar component of this invention is a product of the destructive distillation of bituminous coal but is not limited to this type of coal. The refined coal tar from one or more than one of the following types of coal may be used: Anthracite coal tar (water gas tar), cannel coal tar, lignite tar, and peat tar.

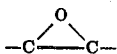
The refined coal tar of this invention is not analogous to coal tar pitch, the residue obtained from coal tar after removing water, ammonia, light oil, and middle oil, and anthracene oil and other higher boiling organic chemical compounds. Coal tar pitch is classified as soft pitch, melting point 60° C. medium pitch, melting at 100° C. and hard pitch, melting at 150°–200° C. The coal tar pitch employed in the Whittier and Lawn U.S. Patent Number 2,765,288 is described as mainly hydrocarbon in nature, and practically insoluble in aqueous alkali, ethanol, and isopropanol which properties corre-

3

spond closely to that of hard pitch or in part medium pitch, and consequently, is not analogous to the refined coal tar of this invention.

The refined coal tar employed in this invention is not analogous to the phenolic pitch employed in the Bradley Patent Number 2,528,417, which is described as a higher boiling aqueous alkali extract of cracked petroleum oil or coal tar distillate containing higher boiling alkyl phenols or the very high boiling or residuum which boils at 250° C. and upward.

The polyepoxides suitable for use with the coal tar modified amine type curing agent of this invention comprises those organic compounds possessing at least two reactive epoxy groups.



in their molecule. The polyepoxides may be saturated or unsaturated, aliphatic cycloaliphatic, aromatic or heterocyclic and be substituted if desired with non-interfering substances. The polyepoxides may be monomeric or polymeric and preferably have a molecular weight between 125 and 3000.

For clarity, many of the polyepoxides will be referred to hereinafter in terms of their epoxy equivalency. The term epoxy "epoxy equivalency" refers to the number of epoxy groups contained in the average molecular weight of the desired material. The epoxy equivalency is obtained by dividing the average molecular weight of the polyepoxides by the epoxide equivalent weight. The epoxy equivalent weight is determined by heating one-gram-sample of the polyepoxide with an excess of pyridinium chloride dissolved in pyridine at the boiling point for twenty minutes. The excess pyridinium chloride is then back titrated with 0.1 N sodium hydroxide to phenolphthaleum end point. The epoxy value is calculated by considering one HCl as an equivalent of one epoxide. This method is used to obtain all epoxides values reported herein.

If the polyepoxide material consist of a single compound and all of the epoxy groups are intact, the epoxy equivalency will be integers, such as 2, 3, 4 and the like. However, in the case of polymeric-type polyepoxides many of the materials may contain some of the monomeric monoepoxides or have some of their epoxy groups hydrated or otherwise reacted and/or contain macromolecules of somewhat different molecular weight so the epoxy equivalency may be quite low and contain fractional values. The polymeric material may, for example, have an epoxy equivalency of 1.5, 1.8, 2.5, and the like.

The polyepoxides may be exemplified by the following: vinyl cyclohexane dioxide, epoxidized mono-, di-, and triglycerides, butadiene dioxide, 1,4-bis (2,3-epoxy propoxy) benzene, 1,3-bis (2,3-epoxy propoxy)-benzene, 4,4'-bis (2,3-epoxypropoxy) diphenyl ether, 1,8-bis (2,3-epoxy propoxy) octane, 1,4-bis (2,3-epoxy propoxy) cyclohexane, 4,4'-bis (2-hydroxy - 3,4 - epoxybutoxy) diphenyl dimethylmethane, 1,3-bis (4,5-epoxypentoxo)-5-chlorobenzene, 1,4-bis (3,4-epoxybutoxy) 2-chlorocyclohexane, diglycidyl thioether, diglycidyl ether, ethylene glycol diglycidyl ether, resorcinol diglycidyl ether, 1,2,5,6-diepoxyphexyne-3, 1,2,5,6-diepoxyhexane and 1,2,3,4-tetra (2-hydroxy-3,4-epoxybutoxy) butane.

Other examples include the glycidyl polyethers of polyhydric phenols obtained by reacting a polyhydric phenol with an excess, e.g. 4 to 8 mol excess of a chlorohydrin such as epichlorohydrin and diglycerol chlorohydrin. The polyether 2,2-bis (2,3-epoxy propoxyphenyl) propane is obtained by reacting bisphenol 2,2-bis (4-hydroxyphenyl) propane with an excess of epichlorohydrin in an alkaline medium. Other polyhydric phenols that can be used for this purpose include resorcinol, catechol, hydroqui-

4

none, methyl resorcinol, or polynuclear phenols, such as 2,2-bis (4-hydroxyphenyl) butane, 4,4'-dihydroxybenzophenone, bis (4-hydroxyphenyl) ethane, and 1,5-dihydronaphthalene.

Still a further group of the polyepoxides comprises the polyepoxy polyethers obtained by reacting, preferably in the presence of an acid-acting compound, such as hydrofluoric acid, one of the afore-described halogen containing epoxides with polyhydric alcohols and subsequently treating the resulting product with an alkaline component. Polyhydric alcohols that may be used for this purpose include glycerol, propylene glycol, ethylene glycol, diethylene glycol, hexanetriol, sorbitol, mannitol, pentanetriol, pentaerythritol, di- and tripentaerythritol, polyglycerol, dulcitol, inositol, carbohydrates, methyl trimethylolpropane, 2,6-octane-diol, 1,2,4,5-tetrahydroxy-cyclohexane, 2-ethyl hexanetriol-1,2,6, glycerol methyl ether, glycerol allyl ether, polyvinyl alcohol and polyallyl alcohol, and mixtures thereof. Such polyepoxides may be exemplified by glycerol triglycidyl ether, mannitol tetraglycidyl ether, pentaerythritol tetraglycidyl ether and sorbitol tetraglycidyl ether.

A further group of the polyepoxides comprises the polyepoxy polyesters obtained by esterifying a polycarboxylic acid with an epoxy-containing alcohol, such as, for example, the glycidyl ester of adipic acid, diglycidyl ester of malonic acid, and the diglycidyl ester of succinic acid.

Other polyepoxides include the polyepoxypolyhydroxy to polyethers obtained by reacting preferably in an alkaline medium, a polyhydric alcohol or polyhydric phenol with a polyepoxide such as the reaction product of glycerol and bis (2,3-epoxypropyl) ether, the reaction product of sorbitol and bis (2,3-epoxy-2-methyl propyl) ether, the reaction product of pentaerythritol and 1,2-epoxy-4,5-epoxypentane and the product of bis phenol and bis (2,3-epoxy-2-methyl propyl) ether, the reaction product of resorcinol and bis (2,3-epoxypropyl) ether and the reaction product of catechol and bis (2,3-epoxypropyl) ether.

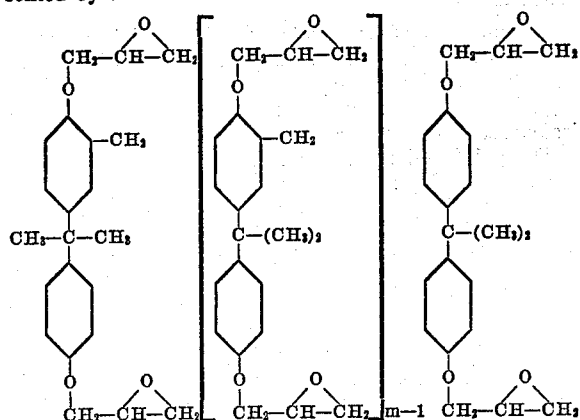
A group of polymeric-type polyepoxides comprises the hydroxy substituted polyepoxy polyethers obtained by reacting, preferably in an alkaline medium, a slight excess e.g., 0.5 to 3 mol excess, of a halogen-containing epoxide as described above, with any of the afore-described polyhydric phenols, such as resorcinol, catechol, bis-phenol, bis [4-(2'-hydroxynaphth-1-yl)-2-hydroxynaphth - 1 - yl] methane and the like.

Other polymeric polyepoxides include polymers and copolymers of the epoxy-containing monomers possessing at least one polymerizable ethylenic linkage. When this type of monomer is polymerized in the substantial absence of alkaline or acidic catalyst such as in the presence of heat, oxygen, peroxy compounds, actinic light, and the like, they undergo additional polymerization at the multiple bond leaving the epoxy group unaffected. These monomers may be polymerized with themselves or with other ethylenically unsaturated monomers such as styrene, vinyl acetate, methacrylonitrile, acrylonitrile, vinyl chloride, vinylidene chloride, methyl acrylate, methyl methacrylate, diallyl phthalate, vinyl allyl phthalate, divinyl allyl phthalate, divinyl adipate, 2-chloroallyl acetate, and vinyl methylallyl pimelate. Illustrative examples of these polymers include poly (allyl 2,3-epoxypropyl ether), poly (2,3-epoxypropyl crotonate), allyl 2,3-epoxypropyl ether-styrene, copolymer, methallyl 3,4-epoxybutyl ether-allyl benzoate copolymer, poly (vinyl 2,3-epoxypropyl) ether, allyl glycidyl ether-vinyl acetate copolymer and poly [4-(2',3'-glycidylloxy)-styrene].

Another group of polyepoxides that may be used with the coal tar modified amine type curing agent in polyepoxide in coating compositions are the glycidyl ethers of novolac resins which resins are obtained by condensing an aldehyde with a polyhydric phenol. A typical member of this class is the epoxy resin from formaldehyde 2,2-bis (4-hydroxyphenyl) propane novolac resin which

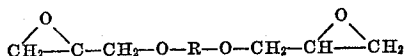
5

contains as predominant constituent the substance represented by the formula

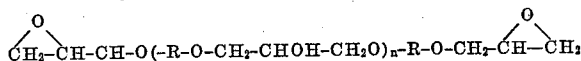


wherein m is a value of at least 1.

Particularly preferred polyepoxides suitable for use with the coal tar modified polyamine type curing agent of the present invention comprises the glycidyl polyethers of dihydric phenols obtained by reacting epichlorohydrin with polyhydric phenols in an alkaline medium. The monomeric products of this type may be represented by the general formula



wherein R represents a divalent hydrocarbon radical of dihydric phenol. The polymeric products will generally not be a single simple molecule but will be a complex mixture of glycidyl polyethers of the general formula



wherein R is a divalent hydrocarbon radical of the dihydric phenol and n is an integer of the series 0, 2, 3, etc. While for any single molecule of the polyether n is an integer, the fact that the obtained polyether is a mixture of compounds causes the determined value of n to be an average which is not necessarily zero or a whole number.

The afore-described preferred glycidyl polyethers of the dihydric phenols may be prepared by reacting the required proportions of the dihydric phenol and the epichlorohydrin in an alkaline medium. The desired alkalinity is obtained by adding basic substances, such as sodium or potassium hydroxide preferably in stoichiometric excess to the epichlorohydrin. The reaction is preferably accomplished at temperatures within the range of from 50° C. to 150 C. The heating is continued for several hours to effect the reaction and the product is then washed free of salt and base.

The preparation of some of the glycidyl polyethers of the dihydric phenols are given in detail in U.S. Patent 2,826,562.

Particularly preferred members of the described group of polyepoxides are the glycidyl polyethers of the dihydric phenols, and, especially 2,2-bis (4-hydroxyphenyl) propane having an epoxy equivalency between 1.1 and 2.0 and a molecular weight of 300-900. Particularly preferred are those having Durrans mercury method melting point below about 60° C.

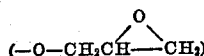
The glycidyl polyethers of polyhydric phenols with epichlorohydrin are also referred to as ethoxline resins. See Chemical Week, vol. 69, page 27, Sept. 8, 1951.

Also particularly preferred are the glycidyl polyethers of polyhydric alcohols which are obtained by reacting the polyhydric alcohol with epichlorohydrin, preferably in the presence of 0.1% to 5% by weight of an acid acting compound, such as boron trifluoride, hydrofluoric acid or stannic chloride. The reaction is affected at about 50-125° C. with the proportion of the reactants being such that there is about one mol of epichlorohydrin for

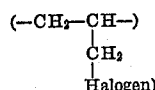
6

every equivalent of hydroxyl group in the polyhydric alcohol. The resulting chlorohydrin ether is then dehydrochlorinated by heating at about 50° C. to 125° C. with a small, e.g., 10% stoichiometrical excess of a base, such as sodium aluminate.

The products obtained by the method shown in the preceding paragraph may be described as halogen-containing ether epoxide reaction mixtures and products are polyether polyepoxide reaction products which in general contain at least three non-cyclic ether ($-O-$) linkages, terminal epoxide-containing ether

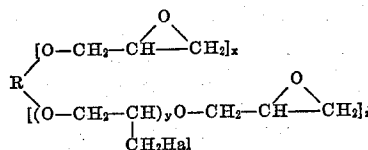


groups and halogen attached to a carbon of an intermediate



group.

These halogen-containing polyether polyepoxide reaction products, obtainable by partial dehydrohalogenation of polyhalohydrin alcohols may be considered to have the following general formula



in which R is the residue of the polyhydric alcohol which may contain unreacted hydroxyl groups, x indicates one or more of the epoxy groups attached to the alcohol residue, y may be one or may vary in different reaction products of the reaction mixture from zero to more than one, and z is one or more, and $x+z$, in the case of products derived from polyhydric alcohols containing three or more hydroxyl groups, averages around two or more than two terminal epoxide groups per molecule.

Particularly preferred members of this group comprise glycidyl polyethers of aliphatic polyhydric alcohols containing from 2 to 10 carbon atoms and having from 2 to 6 hydroxyl groups and more preferably the alkane polyols containing from 2 to 8 carbon atoms and having from 2 to 6 hydroxyl groups. Such products preferably have an epoxy equivalency greater than 1.0, and still more preferably between 1.1 and 4 and a molecular weight between 170 and 900.

Also preferred are the glycidyl ethers of novolac resins as described above. These novolac resin epoxides are obtained by condensing the novolac resin with at least three moles of epichlorohydrin per phenolic hydroxide equivalent of novolac resin and then adding about one mole of alkali metal hydroxide per hydroxy-equivalent of novolac resin.

Also preferred are the polymers and copolymers of the unsaturated epoxy-containing monomers, such as allyl glycidyl ether. These polymers are preferably prepared by heating the monomer or monomers in bulk or in the presence of an inert solvent such as benzene in the presence of air or a peroxy catalyst, such as di-tertiary-butyl peroxides, at temperatures ranging generally from 75° C. to 200° C.

A mixture of the polyepoxides and refined coal tar upon standing at ambient temperature or when heated to 120° C. to 150° C., the epoxy groups of the polyepoxide resins are cleaved by the reactive groups such as the hydroxyl groups of phenols, xylenols, and the like present in the coal tar resulting in the formation of non-curing resins of simple or complex composition. To prevent the formation of non-curing compounds of polyepoxide

resins in coal tar-polyepoxide coating compositions, the process of this invention is designed to utilize the advantages of thermoplastic coal tar protective coating in a heat resistant coal tar-polyepoxide resin coating by combining the reactive hydroxyl groups of the complex organic chemical compounds in refined coal tar with a poly-functional aliphatic amine to produce a coal tar modified poly-functional aliphatic amine curing agent for polyepoxide resin coating compositions.

The coal tar modified polyfunctional amine-type curing agent of this invention containing a plurality of tertiary amino groups may be prepared by first forming a polyfunctional amine condensation by mixing one molecule of a polyfunctional aliphatic amine with two molecules of an aliphatic or aromatic ketone and heating to 60° C. to 70° C. and holding at this temperature until the ketonic oxygen combines with the two hydrogens of the terminal primary amino groups of the polyfunctional aliphatic amine to form two molecules of water and one molecule of the polyfunctional aliphatic amine condensation product containing two tertiary amino groups. This condensation product is then added to the coal tar in such stoichiometric proportions that the secondary amino hydrogens will react, when heated to 60° C. to 70° C. with the hydroxyl groups of the phenols, xylenols and the like present in the coal tar. The mixture may be heated slowly to 150° C. for the purpose of removing the water formed during the reaction.

The aliphatic ketones that may be used to produce the aliphatic amine-aliphatic ketone condensation product are acetone, di-ethyl ketone, di-isopropyl ketone, methyl ethyl ketone, methyl isopropyl ketone, methyl isobutyl ketone, phorone, di-isobutyl ketone, and the like. Because of its relatively low boiling point acetone and other low boiling point ketones are less preferable for use in forming the polyamine condensation product.

The preferred ketone is methyl isobutyl ketone because of the reactivity with primary amino groups and availability.

Similarly aromatic ketones such as acetophenone, benzophenone, benzyl ethyl ketone, benzyl acetone, 2-furyl phenyl ketone, and the like may be used to form an aromatic ketone polyfunctional aliphatic amine condensation product that may be used to produce a coal tar modified polyfunctional aliphatic amine-aromatic ketone condensation product curing agent for polyepoxides. Two alternative methods for the preparation of the coal tar modified aliphatic amine curing agent of this invention are: (1) the formation of a polyfunctional aliphatic amine condensation product with a commercial grade of tar acids using the stoichiometric quantity of tar acids, hydroxyl containing compounds from coal tar such as phenols and xylenols and the like to react with the primary amino groups to form tertiary amino groups; then adding this polyfunctional aliphatic amine tar acid product to the coal tar in stoichiometric proportions determined by the secondary amino groups in the tar acid polyfunctional aliphatic amine condensation product and the number of available hydroxyl groups in the coal tar and heating to 60° C. to 70° C. thus forming the second form of coal tar modified polyfunctional aliphatic amine curing agent having a plurality of tertiary amino groups, and (2) preparation of the coal tar modified polyfunctional aliphatic amine curing agent by adding a polyfunctional aliphatic amine in such stoichiometric proportions that the amino hydrogens will react with all the hydroxyl groups of the phenols, xylenols and the like present in the coal tar.

The object of these procedures in the preparation of the curing agent for this invention is to produce coal tar modified polyfunctional amine compound in which there are a plurality of tertiary amino groups or a plurality of secondary and tertiary amino groups. Polyfunctional amines having plurality of tertiary amino groups when used as curing agents may promote chain propagation

and/or complex cross linkage in the polyepoxide resin giving cured films having thermal stability and chemical resistance.

The methods of preparation are designed to combine the reactive organic compounds of the refined coal tar with the polyfunctional aliphatic amine making these organic chemical compounds a part of the complex chemical structure of the cured polyepoxide protective coating.

The polyfunctional aliphatic amines preferred for the preparation of the coal tar modified amine type curing agent for polyepoxides are diethylene triamine, triethylene tetramine, tetraethylene pentamine, and such other polyfunctional aliphatic amines containing two primary amino groups and one or more secondary amino groups.

The complex coal tar modified polyfunctional aliphatic amine curing agent of this invention may be used with or without filler and vehicle, forming one component of a two component system, and the other, the polyepoxy resin component, may also be used with or without vehicle. The two components are to be kept separate until just before application of the coating composition to the metal, or concrete surface or pipe joints to be coated.

The polyepoxide may be mixed in varying ratios from one part by volume of the polyepoxide resin composition with or without vehicle with one volume of the refined coal tar-modified polyfunctional aliphatic amine curing agent component, with or without filler and vehicle to two parts by volume of the polyepoxide resin coating composition with or without vehicle with one part by volume of the refined coal tar modified polyfunctional aliphatic amine curing agent component with or without filler, thus, varying widely the quantity of epoxy ether resin from 30% to 70% by weight with from 70% to 30% by weight of the complex coal tar modified polyfunctional total resin coal tar content. The quantity of the polyepoxide resin used may be increased to 80 or 90% of the epoxy ether resin-refined coal tar content without increasing the ratio of the refined coal tar modified polyfunctional aliphatic amine curing agent per 100 parts epoxy ether resins.

Aromatic hydrocarbon vehicles such as toluene, toluol or high flash naphtha may be added to the refined coal tar-polyfunctional aliphatic amine curing agent component and to the polyepoxide resin component in amounts sufficient to reduce the viscosity to a workable consistency. If a workable viscosity is obtained in a given formulation, the aromatic hydrocarbon vehicle may be omitted.

The application of the coal tar modified polyfunctional aliphatic amine curing agent of this invention for curing polyepoxide resins or ethers is illustrated in detail but not limited by the following examples given in parts by weight.

EXAMPLE I

The following two component product was prepared by mixing the first two ingredients of component A and heating to 60 to 70° C. then adding the refined coal tar and thoroughly mixing and heating to 140°-145° C. to dehydrate, then cooling to 80°-90° C. adding solvent and mixing, then adding filler and grinding.

Component A

	Parts
Diethylene triamine	4.0
Methyl isobutyl ketone	8.0
Refined coal tar	52.0
Toluene	15.0
Filler	21.0

Component B

Polyepoxide resin from Bis-phenol A and epichlorohydrin (melting point 25° C. and epoxy value of 0.35)	85
Toluene	15

Components A and B were mixed by volume in the ratio of 1 to 2 just before application and the resulting mixture sprayed onto a clean steel surface at ambient

9

temperature of 20–30° C. A hard, tough, high-gloss, enamel-like film was obtained in 16 to 24 hours.

A second mixture was made mixing one part by volume of component A to one part by volume of component B.

The resulting mixture was sprayed onto a clean steel surface at ambient temperature of 20–30° C. A hard, gloss enamel-like film was obtained in 16 to 24 hours.

EXAMPLE II

As in Example I, the following two component product was made without filler.

Component A

Methyl isobutyl ketone	12.0
Diethylene triamine	6.0
Refined coal tar	67.0
Toluene	15.0

Component B

Polyepoxide resin from Bis-phenol A and epichlorohydrin (melting point 25° C., epoxy value 0.35)	85.0
Toluene	15.0

Components A and B were mixed in the ratio of 1 part by volume of A to 2 parts by volume of B and also in the ratio of 1 to 1 by volume. Each of the resulting mixtures was sprayed immediately onto separate clean steel surfaces at ambient temperature of 20 to 30° C. A hard, tough, flexible, high gloss enamel-like film was obtained with each mixture in 16 to 24 hours at an ambient temperature of 20 to 30° C.

EXAMPLE III

As in Example I the following two component product was made.

Component A

Refined coal tar	67
Diethylene triamine	12
Filler	21

Component B

Polyepoxide resin from Bis-phenol A and epichlorohydrin (liquid at 25° C. and epoxy value 0.50)	100.0
---	-------

Components A and B were mixed in the ratio by volume of 1 to 1 and sprayed immediately onto a clean steel surface at a temperature of 25° C. and cured at 25° C. in a closed container. A hard, tough, flexible, high gloss enamel-like film was obtained in 6 to 8 hours.

Example III is applicable to coating interior of closed tanks, pipes, and other surfaces where volatile solvents are not tolerated or are prohibited.

EXAMPLE IV

As in Example I, the following two component product was made.

Component A

Methyl isobutyl ketone	8.0
Diethylene triamine	4.0
Refined coal tar	48.0
Toluene	15.0
Filler	25.0

Component B

Polyepoxide resin from Bis-phenol A and epichlorohydrin (melting point 65° C. and an epoxy value of .22)	70
Toluene	30

Components A and B were mixed in the ratio by volume of 1 part of component A to 2 parts of component B and also, in the ratio, by volume of 1 to 1 of each component. The resulting mixtures were each sprayed separately onto a clean steel surface. A hard, tough, flexible, high gloss enamel-like film was obtained in 16 to 24 hours at ambient temperature of 20 to 30° C.

10

EXAMPLE V

As in Example I, the following two component product was made.

Component A

Diethylene triamine	1
Coal tar acids (100%)	4
Refined coal tar	58
Toluene	15
Filler	22

Component B

Polyepoxide resin from Bis-phenol A and epichlorohydrin (melting point at 30° C. and an epoxy value of 0.35)	85
Toluene	15

Components A and B were mixed by volume in the ratio of 1 of component A and 2 of component B and, also, mixed in the ratio of 1 volume of component A to 1 by volume of component B. The resulting mixtures were immediately sprayed onto clean steel panels. A hard, tough, flexible high gloss enamel-like film was obtained at ambient temperature of 20° to 30° C. in 16 to 24 hours.

EXAMPLE VI

As in Example I, the following two component product was made.

Component A

Phorone	6.0
Tetrathylene pentamine	4.0
Refined coal tar	48.0
Filler	15.0
Toluene	25.0

Component B

Polyepoxide resin from bis-(4-hydroxyphenyl)-1,1-isobutane (melting point 30° C., epoxy value 0.35)	85
Toluene	15

Components A and B were mixed in the ratio by volume of 1 to 2 and also in the ratio of 1 to 1 and sprayed onto a clean steel pipe section at 20° to 30° C. The coating cured into a hard, tough, high gloss, enamel-like film in 16 to 24 hours.

Example VII

As in Example I, the following two component product was made without filler.

Component A

Acetone	9.7
Diethylene triamine	8.3
Refined coal tar	67.0
Toluene	15.0

Component B

Polyepoxide resin from Bis-phenol A and epichlorohydrin (melting point 25° C., epoxy value 0.35)	85.0
Toluene	15.0

Components A and B were mixed in the ratio of 1 to 2 by volume just before application and the resulting mixture was sprayed onto a clean steel surface at ambient temperature of 20–30° C. A hard tough, high gloss enamel-like film was obtained.

A second mixture was made mixing 1 part by volume of component A with 1 part by volume of component B and the resulting mixture sprayed onto clean steel surface at ambient temperature of 20 to 30° C. A hard high gloss enamel-like film was obtained in 16 to 24 hours.

Example VIII

As in Example V, the following two component was made with filler.

Component A

Acetophenone	8.4
Diethylene triamine.....	3.6
Refined coal tar.....	52.0
Toluene	15.0
Filler	21.0

Component B

Polyepoxide resin from Bis-phenol A and epichlorohydrin (melting point 25° C., epoxy value of 0.35)	85.0
Toluene	15.0

Components A and B were mixed in the ratio of 1 to 2 by volume just before application and the resulting mixture sprayed onto a clean steel surface at ambient temperature of 20–30° C. A hard tough high gloss enamel-like film was obtained in 16 to 24 hours.

A second mixture was made mixing 1 part by volume of component A with 1 part by volume of component B. The resulting mixture was sprayed onto a clean steel surface at an ambient temperature of 20–30° C. A hard high gloss enamel-like film was obtained in 16 to 24 hours.

The preceding examples illustrate some of the modifications of the invention that may be made in the parts or percentages of the curing agent compositions of the invention without in any way departing from the spirit of the invention or the scope of the appended claims.

I claim:

1. A process of making a curing agent containing a plurality of tertiary amino groups for glycidyl polyethers of polyhydric phenols and polyhydric alcohols, which comprises heating one mol of a polyfunctional aliphatic amine containing two primary amino groups and at least one secondary amino group with two mols of a ketone to 60° to 70° C. and maintaining this temperature until the reaction is complete, then mixing one part by weight of the resulting product with 5 to 6 parts by weight of a liquid refined coal tar obtained by the removal of water, ammonia and light oil from crude coal tar and containing compounds having hydroxyl groups capable of reacting chemically with amino groups and heating to 60° to 70° C. and maintaining this temperature until the reaction of the secondary amino groups with the hydroxyl groups present in the refined coal tar is complete.

2. A process of making a curing agent containing a plurality of tertiary amino groups for glycidyl polyethers of polyhydric phenols and polyhydric alcohols, which comprises heating one mol of a polyfunctional aliphatic amine containing two primary and at least one secondary amino groups with two mols of an aliphatic ketone to 60° to 70° C. and maintaining this temperature until the reaction is complete, then mixing one part by weight of the resulting product with 5 to 6 parts by weight of a liquid refined coal tar obtained by the removal of water, ammonia and light oil from crude coal tar and containing compounds having hydroxyl groups capable of reacting chemically with amino groups and heating to 60° to 70° C. and maintaining this temperature until the reaction of the secondary amino groups with the hydroxyl groups present in the refined coal tar is complete.

3. A process of making curing agent containing a plurality of tertiary amino groups for glycidyl polyethers of polyhydric phenols and polyhydric alcohols, which comprises heating one mol of a polyfunctional aliphatic amine containing two primary and at least one secondary amino groups with two mols of an aromatic ketone to 60° to 70° C. and maintaining this temperature until the reaction is complete, then mixing one part by weight of the resulting product with 5 to 6 parts by weight of a liquid refined coal tar obtained by the removal of water, ammonia and light oil from crude coal tar and contain-

ing compounds having hydroxyl groups capable of reacting chemically with amino groups and heating to 60° to 70° C. and maintaining this temperature until the reaction of the secondary amino groups with the hydroxyl groups present in the refined coal tar is complete.

4. A process as in claim 1 wherein the ketone is methyl isobutyl ketone.

5. A process as in claim 1 wherein the ketone is methyl isopropyl ketone.

6. A process as in claim 1 wherein the ketone is acetophenone.

7. A process as in claim 1 wherein the ketone is benzyl ethyl ketone.

8. A process of making a curing agent containing a plurality of tertiary amino groups for polyepoxides containing at least two epoxy groups in their molecules, which comprises heating one mol of a polyfunctional aliphatic amine containing two primary amino groups and at least one secondary amino group with two mols of a ketone to 60° to 70° C. and maintaining this temperature until the reaction is complete, then mixing one part by weight of the resulting product with 5 to 6 parts by weight of a liquid refined coal tar obtained by the removal of water, ammonia and light oil from crude coal tar and containing compounds having hydroxyl groups capable of reacting chemically with amino groups and heating to 60° to 70° C. and maintaining this temperature until the reaction of the secondary amino groups with the hydroxyl groups present in the refined coal tar is complete.

9. A process of making a curing agent containing a plurality of tertiary amino groups for glycidyl ethers of novolac resins, which comprises heating one mol of a polyfunctional aliphatic amine containing two primary amino groups and at least one secondary amino group with two mols of a ketone to 60° to 70° C. and maintaining this temperature until the reaction is complete, then mixing one part by weight of the resulting product with 5 to 6 parts by weight of a liquid refined coal tar obtained by the removal of water, ammonia and light oil from crude coal tar and containing compounds having hydroxyl groups capable of reacting chemically with amino groups and heating to 60° to 70° C. and maintaining this temperature until the reaction of the secondary amino groups with the hydroxyl groups present in the refined coal tar is complete.

10. A process of making a curing agent containing a plurality of tertiary amino groups for polyepoxides of glycidyl polyethers of dihydric phenols obtained by reacting epichlorohydrin with polyhydric phenols in an alkaline medium, which comprises heating one mol of a polyfunctional aliphatic amine containing two primary amino groups and at least one secondary amino group with two mols of a ketone to 60° to 70° C. and maintaining this temperature until the reaction is complete, then mixing one part by weight of the resulting product with 5 to 6 parts by weight of a liquid refined coal tar obtained by the removal of water, ammonia and light oil from crude coal tar and containing compounds having hydroxyl groups capable of reacting chemically with amino groups and heating to 60° to 70° C. and maintaining this temperature until the reaction of the secondary amino groups with the hydroxy groups present in the refined coal tar is complete.

11. A process of making a curing agent containing a plurality of tertiary amino groups for halogen containing polyether polyepoxides, which comprises heating one mol of a polyfunctional aliphatic amine containing two primary amino groups and at least one secondary amino group with two mols of a ketone to 60° to 70° C. and maintaining this temperature until the reaction is complete, then mixing one part by weight of the resulting product with 5 to 6 parts by weight of a liquid refined coal tar obtained by the removal of water, ammonia and light oil from crude coal tar and containing com-

2,980,601

13

pounds having hydroxyl groups capable of reacting chemically with amino groups and heating to 60° to 70° C. and maintaining this temperature until the reaction of the secondary amino groups with the hydroxyl groups present in the refined coal tar is complete.

5

2,528,417
2,658,026
2,765,288

14

References Cited in the file of this patent

UNITED STATES PATENTS

Bradley Oct. 31, 1950
MacLaren et al. Nov. 3, 1953
Whittier et al. Oct. 2, 1956