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(54) Title: SELF-DISPERSING EPOXY RESINS AND COATINGS THEREFROM

(57) Abstract

Self-dispersing curable epoxy resin dispersions prepared by a process comprising reducing the particle size of a mixture comprised of a self-dispersing curable epoxy resin based on a polyoxyalkyleneamine, water and an organic cosolvent and removing at least a major amount of said organic cosolvent from said mixture after said reducing, are provided. The self-dispersing curable epoxy resin is based on a polyoxyalkyleneamine. Thus, a polyoxyalkyleneamine was present as a chemical precursor of the epoxy resin or a starting material therefor. The self-dispersing curable epoxy resin of the invention is in the form of an aqueous dispersion. When cured, films of the self-dispersing curable epoxy resin dispersion are useful as a coating composition.

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"SELF-DISPERSING EPOXY RESINS AND COATINGS THEREFROM"

Cross-Reference to Related Applications

This application is a continuation-in-part of U.S. Serial No. 08/299,783, filed September 1, 1994, the disclosure of which is incorporated herein by reference.

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Field Of The Invention

The present invention relates to a method of making aqueous epoxy resin dispersions. The dispersions are useful in preparing coating compositions comprising the same.

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Background of the Invention

Epoxy resins have come into widespread use as components in coating compositions. Coatings which comprise cured epoxy resins are valued for their durability, chemical resistance, and excellent adhesion to a broad range of substrates. Particularly desirable from an environmental point of view are epoxy resins which may be applied to a substrate with either minimal or no release of volatile organic components. Toward this

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end, there has been much research directed to the development of aqueous dispersions and emulsions of epoxy resins.

One class of aqueous epoxy dispersions employs one or more additives, also known as dispersants or emulsifiers or surfactants, which are necessary to stabilize the epoxy resin in the dispersion or emulsion form. Representative examples include an aqueous epoxy dispersion as described in U.S. Patent No. 3,301,804 (employing the reaction product of a boric acid ester derived from boric acid with both an alkylene glycol and a beta-dialkyl-substituted aminoalkanol as an emulsifier), U.S. Patent No. 3,634,348 (employing a phosphate ester as an emulsifying agent), U.S. Patent No. 3,249,412 (employing in combination a cationic emulsifying agent selected from the group consisting of imidazolines and amides and a non-ionic emulsifying agent), and Specialty Chemicals Bulletin SC-021 titled "Water-Reducible Coatings via Epoxy Resin Modification with Jeffamine (Reg. TM) ED-2001 and Jeffamine (Reg. TM) M-1000" available from Texaco Chemical Company, Bellaire, Texas. Another example comes from the technical literature of Synthron Inc., Morgantown, North Carolina, which discloses the use of PROX-E-141, a diglycidyl ether of Pluronic (Reg. TM) F88 diol (an ethylene oxide - propylene oxide - ethylene oxide block copolymer available from BASF Performance Chemicals, Parsippany, New Jersey) as a reactive dispersant for epoxy resins. PROX-E-141 can act as a dispersant for epoxy resin in water, but then will react along with the epoxy resin when exposed to an amine functional curing agent.

The use of an additive to provide stability to an aqueous epoxy dispersion is preferably avoided as such additives add additional cost, formulation complexity, and may potentially interfere with the performance of a coating derived from the aqueous epoxy dispersion.

It is known to prepare aqueous epoxy dispersions from self-emulsifying epoxy resins. For example, U.S. Patent No. 4,315,044 describes a stable epoxy dispersion composition comprising (1) an aqueous medium; and (2) between about 50-70 weight percent of self-

emulsifying epoxy resin which is the addition product of reactants comprising (a) 40-90 parts by weight of diglycidyl ether of dihydric phenol, (b) 5-35 parts by weight of dihydric phenol, and (c) 2-15 parts by weight of diglycidyl ether of polyoxyalkylene glycol, wherein the molecular weight of the epoxy resin is in the range between about 500-20,000. The dispersion can also contain 1-25 weight percent based on resin solids of a water-immiscible C₈-C₂₀ aliphatic monoepoxide reactive diluent.

U.S. Patent No. 4,608,406 describes stable aqueous epoxy resin dispersions comprised of (1) an aqueous medium; and (2) between about 50 to about 70 weight percent of self-emulsifying epoxy resin which is the addition reaction product of (a) 40-90 parts by weight of a diglycidyl ether of a dihydric phenol; (b) 5-35 parts of a dihydric phenol; (c) 2-15 parts by weight of a diglycidyl ether of a polyoxyalkylene glycol; and (d) 2 to 15 parts by weight of an alkyl phenol-formaldehyde novolac resin wherein the molecular weight of the epoxy resin is in the range of about 1000 to about 20,000. The stable dispersions can be modified by the addition of about 1 to about 25 weight percent of an aliphatic monoepoxide reactive diluent.

In an attempt to improve freeze-thaw stability, the stable aqueous epoxy resin dispersions can be modified by the addition of about 5-20 weight percent, based on resin solids weight, of a water-miscible solvent which, preferably, is a 2 to 8 carbon glycol or glycol ether.

There remains a need for further improvements in terms of the freeze-thaw resistance of aqueous epoxy resin dispersions, and in terms of the corrosion resistance and chemical resistance of coatings derived from aqueous epoxy resin dispersions which are adapted for application as industrial maintenance coating systems.

Accordingly, it is a primary object of this invention to provide a self-dispersing curable epoxy resin which may be dispersed in water without the necessity for an additive to stabilize the epoxy dispersion.

Another object of this invention is to provide aqueous dispersions of self-dispersing curable epoxy resins which exhibit long term stability under ambient storage conditions.

Yet another object of this invention is to provide coating compositions incorporating a self-dispersing curable epoxy resin, where the coating composition exhibits excellent properties when cured.

Other objects and advantages of the present invention shall become apparent from the accompanying description and examples.

Summary of the Invention

It has been found that a self-dispersing curable epoxy resin dispersion can be prepared by a process comprising:

reducing the particle size of a mixture comprised of a self-dispersing curable epoxy resin based on a polyoxyalkyleneamine, water and an organic cosolvent and

removing at least a major amount of said organic cosolvent from said mixture after said reducing.

The self-dispersing curable epoxy resin is based on a polyoxyalkyleneamine. Thus, a polyoxyalkyleneamine was present as a chemical precursor of the epoxy resin or a starting material therefor.

The self-dispersing curable epoxy resin of the invention is in the form of an aqueous dispersion. When cured, films of the self-dispersing curable epoxy resin dispersion are useful as a coating composition.

Detailed Description of the Invention

The self-dispersing curable epoxy resin used as a starting material herein can be any one of several self-dispersing curable epoxy resins that are based upon a polyoxyalkyleneamine.

In certain embodiments, the self-dispersing curable epoxy resin based on a polyoxyalkyleneamine is prepared by reacting (a) 1.0 reactive equivalents of an epoxy resin, (b) from about 0.01 to 1.0 reactive equivalents (e.g. from about 0.4 to about 0.6 reactive equivalents or from about 0.65 to about 0.95 reactive equivalents) of a polyhydric phenol, and (c) from about 0.005 to 0.5 reactive equivalents of an amine-epoxy adduct, wherein the amine-epoxy adduct is formed upon contacting 1.0 equivalents of an aliphatic polyepoxide and from about 0.3 to about 0.9 reactive equivalents of a polyoxyalkyleneamine. Such self-dispersing curable epoxy resins are described in detail in U.S. Serial No. 08/255,732, filed June 14, 1994 (which is a continuation-in-part of U.S. Serial No. 08/086,288, filed June 30, 1993) and U.S. Serial No. 08/296,282, filed August 25, 1994, by J. Papalos et al., entitled "Self-Dispersing Curable Epoxy Resins, Dispersions Made Therewith, and Coating Compositions Made Therefrom" (which is a continuation-in-part of U.S. Serial No. 08/203,543, filed March 1, 1994), the disclosures of which are incorporated herein by reference.

In other embodiments, the epoxy resin is prepared by reacting an epoxy resin with a polyoxyalkyleneamine having a molecular weight of from about 3,000 to about 15,000 in a ratio of about 0.001 to 0.060 reactive equivalents of polyoxyalkyleneamine to about 1.0 reactive equivalents of epoxy resin. Such self-dispersing curable epoxy resins are described in detail in U.S. Serial No. 08/296,283, filed August 25, 1994, by J. Papalos et al., entitled "Self-Dispersing Curable Epoxy Resins, Dispersions Made Therewith, and Coating Compositions Made Therefrom" (which is a continuation-in-part of U.S. Serial No. 08/173,455, filed December 27, 1993), the disclosures of which are incorporated herein by reference.

In yet other embodiments, the epoxy resin composition is prepared by reacting (a) 1.0 reactive equivalents of an epoxy resin, (b) from about 0.005 to 0.5 reactive equivalents of an amine-epoxy adduct, and optionally (c) from about 0.01 to 1.0 reactive equivalents of a polyhydric

phenol, wherein the amine-epoxy adduct is formed upon contacting 1.0 equivalents of an aliphatic polyepoxide with from greater than about 1.0 equivalents (preferably from about 1.01 to about 2.5) reactive equivalents of a polyoxyalkyleneamine. Such self-dispersing curable epoxy resins are described in detail in U.S. Serial No. 08/296,281, filed August 25, 1994, by J. Papalos et al., entitled "Self-Dispersing Curable Epoxy Resins, Dispersions Made Therewith, and Coating Compositions Made Therefrom" (which is a continuation-in-part of U.S. Serial No. 08/173,847, filed December 27, 1993), the disclosures of which are incorporated herein by reference.

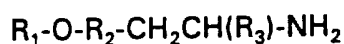
Other self-dispersing resins which can be employed herein are described in U.S. Serial No. 08/366,190, U.S. Serial No. 08/366,189, and U.S. Serial No. 08/366,343, all filed December 29, 1994, by K. S. Arora et al., the disclosures of which are incorporated herein by reference.

The Polyoxyalkyleneamine

The polyoxyalkyleneamine reactant comprises one or more amino-compounds where the amino-compound comprises both an amine group and a substantially water-soluble polyether chain. The polyoxyalkyleneamine reactant is soluble or at least partially soluble in water. Techniques to prepare suitable polyoxyalkyleneamine reactants are known in the art, and include reacting a hydroxyl group containing initiator with ethylene oxide and/or propylene oxide, followed by conversion of the resulting terminal hydroxyl group(s) to amine(s).

Illustrative of the polyoxyalkyleneamine reactants employed in the invention are the Jeffamine (Reg. TM) brand of polyoxyalkyleneamines available from Texaco Chemical Company, Bellaire, Texas.

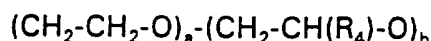
Polyoxyalkyleneamines of this invention have the structural formula



wherein

R_1 designates a monovalent organic radical selected from the group consisting of C_1 to C_{12} aliphatic, alicyclic or aromatic hydrocarbons, and

R_2 represents a polyoxyalkylene chain having the structural formula:



wherein

R_4 is a monovalent organic radical selected from the group
5 consisting of C_1 to C_4 aliphatic hydrocarbons,

'a' designates a number of ethoxy groups ($\text{CH}_2\text{-CH}_2\text{-O}$),

'b' designates a number of monosubstituted ethoxy groups ($\text{CH}_2\text{-CH(R}_4\text{)-O}$) where the substitution of one monosubstituted ethoxy group is independent from the substitution of any other monosubstituted ethoxy group in the polyoxyalkylene chain, the sum of 'a' and 'b' is equal to or greater than 10 but less than or equal to 200, and where the sequence of ethoxy and monosubstituted ethoxy groups within a polyoxyalkylene chain may be completely random and/or there may be blocks of ethoxy and/or monosubstituted ethoxy groups, and

15 R_3 designates H or a monovalent organic radical selected from the group consisting of C_1 to C_4 aliphatic hydrocarbons.

In certain embodiments, the polyoxyalkyleneamine is adducted with an aliphatic polyepoxide and the adduct is reacted with an epoxy resin.

20 In these embodiments, the preferred polyoxyalkyleneamines have R_1 , R_3 and R_4 each equal to methyl, and either (i) a ratio of 'a' and 'b' of about 4:1, wherein the ethoxy and iso-propoxy groups are arranged in random blocks and the molecular weight of the polyoxyalkyleneamine is less than about 4,000, or (ii) a block of 5 ethoxy groups joined to a random sequence of ethoxy and iso-propoxy groups wherein the ratio of 'a' and 'b' in the random sequence is about 7:3 and the molecular weight of the polyoxyalkyleneamine is less than about 4,000, or (iii) a ratio of 'a' and 'b' of about 95:5, wherein the ethoxy and iso-propoxy groups are arranged substantially in two blocks and the molecular weight of the polyoxyalkyleneamine is less than about 6,000, or (iv) a ratio of 'a' and 'b' of about 7:3, wherein the ethoxy and iso-propoxy groups are present in random sequence and the molecular weight of the polyoxyalkyleneamine is less than about 4,000, or (v) a ratio of 'a' and

'b' of about 4:1, wherein the ethoxy and iso-propoxy groups are present in random sequence and the molecular weight of the polyoxyalkyleneamine is less than about 4,000.

5 The most preferred polyoxyalkyleneamine is Jeffamine (Reg. TM) M-2070 from Texaco Chemical Company, Bellaire Texas. According to Texaco, this polyoxyalkyleneamine is prepared by reacting methanol with ethylene oxide and propylene oxide followed by conversion of the resulting terminal hydroxyl group to an amine. The most preferred polyoxyalkyleneamine has an approximate molecular weight of 2,000 and
10 a mole ratio of propylene oxide to ethylene oxide of 10/32.

In certain embodiments, the polyoxyalkyleneamine is directly reacted with an epoxy resin. In these embodiments, the polyoxyalkyleneamine will have a molecular weight of from about 3,000 to about 15,000 and will be directly reacted with the epoxy resin in a ratio of about 0.001 to 0.060
15 reactive equivalents of polyoxyalkyleneamine to about 1.0 reactive equivalents of epoxy resin. Preferred polyoxyalkyleneamines have R₁, R₃ and R₄ each equal to methyl, and either (i) a ratio of 'a' to 'b' of about 19:1 (e.g. a weight ratio of about 95% by weight ethoxy to about 5% by weight iso-propoxy), wherein the ethoxy and iso-propoxy groups are arranged in
20 substantially in two blocks and the molecular weight of the polyoxyalkyleneamine is from about 3,000 to about 4,000, or (ii) a random sequence of ethoxy and iso-propoxy groups wherein the ratio of 'a' and 'b' in the random sequence is about 7:3 (e.g. a weight ratio of about 70% by weight ethoxy to about 30% by weight iso-propoxy) and the molecular
25 weight of the polyoxyalkyleneamine is from about 3,000 to about 4,000, or (iii) a ratio of 'a' to 'b' of about 9:1 (e.g. a weight ratio of about 90% by weight ethoxy to about 10% by weight iso-propoxy), wherein the ethoxy and iso-propoxy groups are arranged substantially in two blocks and the molecular weight of the polyoxyalkyleneamine is from about 5,000 to about
30 6,000, or (iv) a ratio of 'a' to 'b' of about 7:3 (e.g. a weight ratio of about 70% by weight ethoxy to about 30% by weight iso-propoxy), wherein the ethoxy and iso-propoxy groups are present in random sequence and the

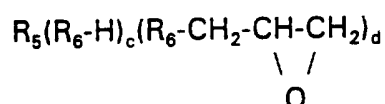
5 molecular weight of the polyoxyalkyleneamine is from about 5,000 to about 6,000, or (v) a ratio of 'a' to 'b' of about 9:1 (e.g. a weight ratio of about 90% by weight ethoxy to about 10% by weight iso-propoxy), wherein the ethoxy and iso-propoxy groups are arranged substantially in two blocks and the molecular weight of the polyoxyalkyleneamine is from about 9,000 to about 10,000 or (vi) a ratio of 'a' to 'b' of about 7:3 (e.g. a weight ratio of about 70% by weight ethoxy to about 30% by weight iso-propoxy), wherein the ethoxy and iso-propoxy groups are present in random sequence and the molecular weight of the polyoxyalkyleneamine is from about 9,000 to about 10,000.

10 The most preferred polyoxyalkyleneamines are the Jeffamine (Reg. TM) polyoxyalkyleneamines from Texaco Chemical Company, Bellaire Texas. According to Texaco, these polyoxyalkyleneamine are prepared by reacting methanol with ethylene oxide and propylene oxide followed by conversion of the resulting terminal hydroxyl group to an amine. The most preferred polyoxyalkyleneamine has an approximate molecular weight of 3,000 and a weight ratio of ethylene oxide to propylene oxide of about 19:1.

20 The Aliphatic Polyepoxide

25 The aliphatic polyepoxide reactant comprises one or more compounds each having a plurality of epoxide functional groups. The aliphatic polyepoxide reactant has at least 2 epoxide groups present in the molecule, and may have as many as 6 epoxide groups present in the molecule. Techniques to prepare suitable polyepoxide compounds are known in the art, and include reacting compounds having a plurality of hydroxyl groups with epichlorohydrin in the presence of a suitable catalyst. Suitable aliphatic polyepoxide compounds are commercially available from Henkel Corporation, Ambler Pennsylvania under the trademarks "Capcures Reg. TM" or "Photomers Reg. TM"

30 One representative class of aliphatic polyepoxide reactant according to the invention has the structural formula:

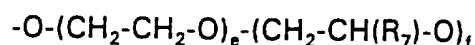


5 wherein

10 R_5 designates a linear, branched or cyclic aliphatic or alicyclic organic radical having a valency equal to the sum of 'c' and 'd', where the sum of 'c' and 'd' is equal to or greater than 2 but no more than or equal to 6 and where 'd' is equal to or greater than 2 but less than or equal to 6. When the sum of 'c' and 'd' equals two (2), R_5 designates a linear, branched or cyclic aliphatic or alicyclic divalent organic radical having from 2 to 14 carbon atoms, and specifically includes the hydrocarbon portions of the dihydric alcohols ethylene glycol, butylene glycol, hexylene glycol, decanediol and dodecanediol which remain after the hydroxyl groups have been removed, and when the sum of 'c' and 'd' equals three (3), R_5 designates a linear, branched or cyclic aliphatic or alicyclic trivalent organic radical having from 3 to 14 carbon atoms, and specifically includes the hydrocarbon portions of the trihydric alcohols glycerol, 1,1,1-tris(hydroxymethyl)ethane, and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol which remain after the hydroxyl groups have been removed, and when the sum of 'c' and 'd' equals four (4), R_5 designates a linear, branched or cyclic aliphatic or alicyclic tetravalent organic radical having from 5 to 30 carbon atoms, and specifically includes the hydrocarbon portion of the tetrahydric alcohol pentaerythritol which remains after the hydroxyl groups have been removed, and when the sum of 'c' and 'd' equals five (5), R_5 designates a linear, branched or cyclic aliphatic or alicyclic pentavalent organic radical having from 6 to 30 carbon

atoms, and when the sum of 'c' and 'd' equals six (6), R₅ designates a linear, branched or cyclic aliphatic or alicyclic hexavalent organic radical having from 8 to 30 carbon atoms, and specifically includes the hydrocarbon portion of the hexahydric alcohol dipentaerythritol which remains after the hydroxyl groups have been removed, and

R₆ represents a divalent polyoxyalkylene chain having the structural formula:



wherein

R₇ is a monovalent organic radical selected from the group consisting of C₁ to C₄ aliphatic hydrocarbons,

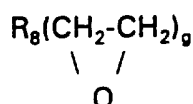
'e' designates a number of ethoxy groups (CH₂-CH₂-O),

'f' designates a number of monosubstituted ethoxy groups (CH₂-CH(R₇)-O) where the substitution of one monosubstituted ethoxy group is independent from the substitution of any other monosubstituted ethoxy group in the polyoxyalkylene chain, the sum of 'e' and 'f' is equal to or greater than 0 but less than or equal to 10, and where the sequence of ethoxy and monosubstituted ethoxy groups within a polyoxyalkylene chain may be completely random and/or there may be blocks of ethoxy and/or monosubstituted ethoxy groups.

The most preferred aliphatic polyepoxide compound is the reaction product of pentaerythritol, propylene oxide and epichlorohydrin, having an epoxide equivalent weight (EEW) of about 230.

The Epoxy Resin

The epoxy resin used in the practice of this invention comprises one or more polyglycidyl ethers of polyhydric phenols having two (2) or more epoxide groups and one (1) or more six-carbon aromatized rings present in the molecule, as represented by the structural formula:



wherein

R_g represents a 'g' valent C_6-C_{50} organic radical comprising at least one six-carbon aromatized ring (e.g. when g is 2, R_g can be $-CH_2 - O - \text{Ø} - C(CH_3)_2 - \text{Ø} - O - CH_2 -$ or R_g can be $-CH_2 - O - \text{Ø} - CH_2 - \text{Ø} - O - CH_2 -$ wherein Ø represents a phenyl group), and 'g' is equal to or greater than 2 but less than or equal to 6.

Techniques to prepare such epoxy resins are known in the art, and include reacting compounds having 2 or more hydroxyl groups with epichlorohydrin in the presence of a suitable catalyst. Suitable epoxy resins are commercially available from a variety of sources and include EPON (Reg. TM) epoxy resins from Shell Chemical Company, Houston, Texas, and DER (Reg. TM) or DEN (Reg. TM) epoxy resins from Dow Chemical Company, Midland, Michigan.

Examples of suitable epoxy resins are:

1) Polyglycidyl and poly(beta-methylglycidyl) esters obtainable by reacting a compound having at least two carboxy groups in the molecule with epichlorohydrin or beta-methyl-epichlorohydrin, respectively. The

reaction is advantageously carried out in the presence of bases. Examples of aromatic polycarboxylic acids which may be used include, for example, phthalic acid, isophthalic acid or terephthalic acid.

5 II) Polyglycidyl or poly(beta-methylglycidyl) ethers obtainable by reacting a compound having at least two free phenolic hydroxy groups with epichlorohydrin or beta-methyl-epichlorohydrin, respectively, under alkaline conditions, or in the presence of an acid catalyst and with subsequent alkali treatment.

10 The epoxy compounds of this type may be derived from mononuclear phenols, such as, for example, resorcinol or hydroquinone; or they are based on polynuclear phenols, such as, for example, bis(4-hydroxyphenyl)methane, 4,4'-dihydroxybiphenyl, bis(4-hydroxyphenyl)sulfone, 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane, 2,2-bis(4-hydroxyphenyl)propane, 2,2-bis(3,5-dibromo-4-hydroxyphenyl) propane, and from novolacs obtainable by
15 condensation of aldehydes, such as formaldehyde, acetaldehyde, chloral or furfuraldehyde, with phenols, such as phenol, or with phenols that are substituted in the nucleus by halide atoms or C₁-C₁₈ (preferably C₁-C₉) alkyl groups, such as, for example, 4-chlorophenol, 2-methylphenol or 4-tert-butylphenol, or by condensation with bisphenols, in the manner described
20 above.

There are preferably used epoxy resins that have an epoxy content of from 2 to 10 equivalents/mole and that are glycidyl ethers or glycidyl esters of aromatic or alkylaromatic compounds. Especially preferred epoxy resins are polyglycidyl ethers of bisphenols, such as, for example, of 2,2-bis(4-

hydroxyphenyl)propane (bisphenol A) or bis(4-hydroxyphenyl)methane (bisphenol F), or novolacs formed by reacting formaldehyde with a phenol. For reasons of cost and availability, the most preferred epoxy resins are polyglycidyl ethers based on bisphenol A.

Preferred epoxy resins have an epoxide equivalent weight of less than about 400 grams/equivalent, e.g. from about 100 grams/equivalent to about 350 grams/equivalent, more preferably from about 150 grams/equivalent to about 225 grams/equivalent, e.g. DER 331 available from Dow Chemical at about 182 grams/equivalent.

The Polyhydric Phenol

The polyhydric phenol reactant comprises one or more compounds each having a plurality of hydroxyl groups covalently bonded to one or more six-carbon aromatized rings. The polyhydric phenol reactant may contain substituents such as alkyl, aryl, sulfido, sulfonyl, halo, and the like. The polyhydric phenol is represented by the structural formula:



wherein

R_g represents an 'h' valent C_6-C_{50} organic radical comprising at least one six-carbon aromatized ring, and 'h' represents a number of phenolic hydroxyl groups where 'h' is equal to or greater than 2 but less than or equal to 6.

Techniques to prepare suitable polyhydric phenol compounds are known in the art. Suitable polyhydric phenol compounds are commercially

available from Dow Chemical Company, Midland, Michigan, and Shell Chemical Company, Houston, Texas.

Illustrative of suitable polyhydric phenols are

2,2-bis(4-hydroxyphenyl)propane, 2,2-bis(3-bromo-4-hydroxyphenyl)-
propane, 2,2-bis(3,5-dichloro-4-hydroxyphenyl)propane, 2,2-bis(3-chloro-4-
hydroxyphenyl)propane, bis(4-hydroxyphenyl)-methane, bis(4-
hydroxyphenyl)sulfone, bis(4-hydroxyphenyl)sulfide, resorcinol,
hydroquinone, phenol-formaldehyde novolac resins, and the like. The most
preferred dihydric phenols are 2,2-bis(4-hydroxyphenyl)propane (bisphenol
A) and bis(4-hydroxyphenyl)methane (bisphenol F) for reasons of cost and
availability.

The Amine-Epoxy Adduct

The preparation of certain of the self-dispersing curable epoxy resins of the invention proceeds through an amine-epoxy adduct, where the amine-epoxy adduct is subsequently reacted with an epoxy resin and, optionally, a polyhydric phenol. The structure of the amine-epoxy adduct is dependant on the structures of the polyoxyalkyleneamine and the aliphatic polyepoxide used in the preparation of the amine-epoxy adduct, as well as the relative ratio of the reactants. An adduct formed by reacting 1.0 equivalents of an aliphatic polyepoxide and from about 0.3 to 0.9 reactive equivalents, preferably from about 0.6 and 0.8 reactive equivalents of a polyoxyalkyleneamine will produce compounds having the structural formula:

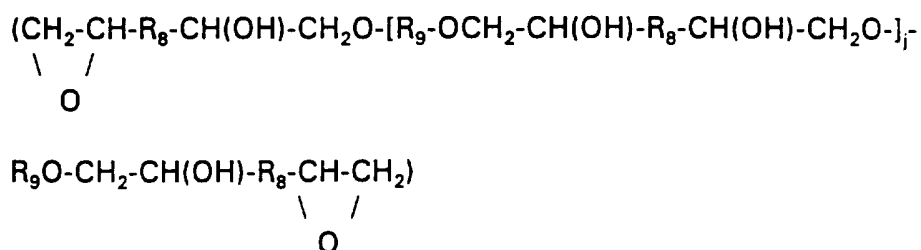
wherein 'i' indicates a number of repetitive units where 'i' is equal to or greater than zero (0) but less than or equal to about fifty, typically from about 10 to about 20.

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The Self-Dispersing Curable Epoxy Resin

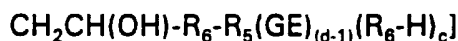
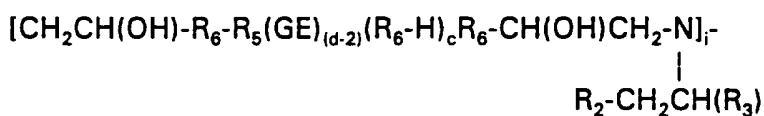
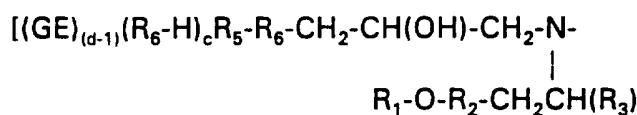
Certain of the self-dispersing curable epoxy resins of the invention can be prepared by reacting an amine-epoxy adduct with a polyhydric phenol and an epoxy resin. The structure and composition of the self-dispersing curable epoxy resin will depend on the identity of the amine-epoxy adduct, the identity of the epoxy resin, the identity of the polyhydric phenol and the relative ratio of the reactants. In certain embodiments, the amine-epoxy adduct is the reaction product of (a) 1.0 reactive equivalents of an epoxy resin, (b) from about 0.01 to 1.0 reactive equivalents, preferably from about 0.4 to 0.6 reactive equivalents of a polyhydric phenol, and (c) from about 0.005 to 0.5 reactive equivalents (typically from about 0.005 to 0.05 reactive equivalents, more typically from about 0.005 to 0.025 reactive equivalents, and preferably from about 0.005 to 0.015 reactive equivalents).

The products of the above reaction are envisioned to be an extremely complex mixture of polymeric materials comprising two distinct groups. A simplified structure for each group of reaction products can be shown if it is assumed that the phenolic component is dihydric and the epoxy component is a diepoxide.

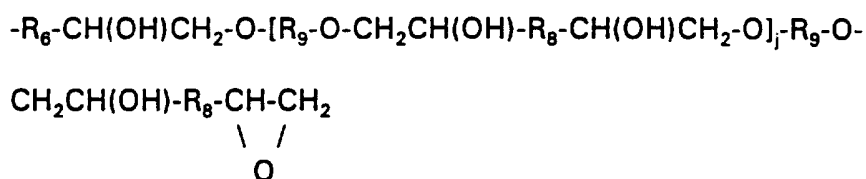
Structure [I]

wherein

'j' indicates a number of repeating units, and is equal to or greater than zero (0) but less than or equal to twenty (20).

Structure [II]

wherein 'GE' is defined as



and all other variables are as defined above.

Organic Cosolvents

The self-dispersing curable epoxy resin of the present invention may be combined with a non-reactive, organic cosolvent. The cosolvent serves to reduce the viscosity of the self-dispersible curable epoxy resin before its dispersion in water as well as that of the aqueous pre-emulsion of the epoxy resin and the aqueous emulsion that is formed by reduction of the particle size of the resin in the pre-emulsion. Another function that the organic cosolvent may perform is the prevention of agglomeration of dispersed resin particles which stabilizes the dispersion of the resin. A variety of organic cosolvents are considered suitable for use in this invention. Suitable cosolvents consist of non-solvents as well as solvents for the self-dispersible epoxy resins. The cosolvent may be miscible, partly miscible or immiscible with water. Mixtures of two or more organic cosolvents can also be employed in this invention. Examples of organic cosolvents include the lower fatty acid esters or alkyl ethers of monohydric and dihydric alcohols (or polyethers thereof), wherein the alkyl group comprises C₁-C₈ linear or branched aliphatic or alicyclic chains and lower alkyl ketones, e.g. ketones having a total of from 3 to 6 carbon atoms, preferably methyl lower-alkyl ketones, wherein said lower alkyl group has from 1 to 3 carbon atoms. The choice of cosolvent can affect the pot-life of the self-dispersing curable epoxy resin. For example, for a given resin it may be possible to increase the pot-life by substituting for a cosolvent such as Ektasolve EP (Eastman Chemicals) with one of the following cosolvents (the greater increase being

obtained in order): 1-methoxy-2-propyl acetate, methyl n-amyl ketone, or dipropylene glycol n-butyl ether.

Reactive Diluents

5 The preferred stable aqueous epoxy resin dispersions of the present invention are those which contain a water-immiscible C_8 - C_{20} aliphatic monoepoxide reactive diluent. The said monoepoxide component can contain alicyclic and aromatic structures, as well as halogen, sulfur, phosphorus, and other such heteroatoms. Suitable reactive diluents are
10 available from CVC Specialty Chemicals, Inc., Cherry Hill, New Jersey.

 Illustrative of monoepoxide reactive diluents are epoxidized unsaturated hydrocarbons such as decene and cyclohexene; glycidyl ethers of monohydric alcohols such as 2-ethylhexanol, dodecanol and eicosanol; glycidyl esters of monocarboxylic acids such as hexanoic acid; acetals of
15 glycidaldehyde; and the like. The preferred reactive diluent is glycidyl ether of monohydric C_8 - C_{10} aliphatic alcohols.

 The presence of a water-immiscible C_8 - C_{20} aliphatic monoepoxide reactive diluent in an aqueous epoxy resin dispersion has significant beneficial effects in addition to modifying the viscosity of the dispersion. For
20 example, the said water-immiscible reactive diluent appears to coat the particles of epoxy resin solids and thereby provide the aqueous dispersion with improved shear, freeze-thaw resistance, shelf viscosity stability, and paint gloss.

Also, since the reactive diluent is epoxy functional, it becomes chemically bonded into the film which is formed during the subsequent room temperature curing of the aqueous dispersion composition after it has been blended with a curing agent and coated on a surface. The total quantity of reactive diluent contributes to the calculated proportion of non-volatiles in the dispersion composition.

Preparation of the Self-Dispersing Curable Epoxy Resin

In preparing certain of the self-dispersing curable epoxy resins of this invention, an amine-epoxy adduct is first prepared by combining the polyoxyalkyleneamine reactant and the aliphatic polyepoxide reactant, heating the mixture slowly to about 130°C, holding the mixture at temperature for about 2.5 hours, and then discharging the amine-epoxy adduct from the reactor. The respective self-dispersing epoxy resin is prepared by combining the amine-epoxy adduct, the polyhydric phenol and the epoxy resin, and heating the mixture in the presence of a catalyst, e.g., potassium hydroxide, triphenyl phosphine, benzyl dimethylamine and the like, to a temperature of about 150°C with stirring. An exothermic reaction will then occur, and cooling is applied to maintain the reaction temperature at about 150-160°C. The mixture is maintained at about 160°C for about one hour subsequent to the conclusion of the exothermic reaction. If the reaction has not proceeded to the desired degree of completion (as determined by the epoxide equivalent weight of the resin), the mixture is then heated to 190°C. The mixture is then maintained at 190°C for about

15 minutes in order to drive the reaction to the desired degree of completion, then cooled to about 160°C whereupon a small amount of a water-soluble organic solvent is added prior to cooling and discharging the self-dispersing curable epoxy resin from the reactor.

5 In certain embodiments, the polyoxyalkyleneamine is reacted directly with the epoxy resin to prepare a self-dispersing curable epoxy resin. The conditions employed for such a reaction may be the similar to the conditions under which the amine-epoxy adduct is formed.

10 Preparation of an Aqueous Dispersion of the Self-Dispersing Curable Epoxy Resin

 The aqueous epoxy dispersion of the invention can be prepared by charging the self-dispersing curable epoxy resin, as a mixture with an organic cosolvent, to a reaction vessel, then heating the resin to about 50-
15 100°C with stirring. Water is then mixed with the mixture of organic cosolvent and self-dispersing curable epoxy resin to form an aqueous pre-emulsion which will typically be a disperse oil phase having a larger particle size. The relative amounts of the resin, water and organic cosolvent can vary broadly, but will typically be roughly equal, e.g. the amounts of each
20 of resin, water and organic cosolvent will range between about 20% to about 50% each, more typically from about 35% to about 45% resin, and about 25% to about 35% each of water and organic cosolvent. One or more reactive diluents can be mixed into the pre-emulsion prior to reduction

of particle size or they can be added to the aqueous dispersion after the reduction of the particle size.

5 The particle size of the oil phase in the aqueous dispersion can be modified by physical techniques to reduce the particle size. The particle size reduction is preferably accomplished by subjecting the aqueous dispersion to high shear, e.g. in a homogenizer such as that disclosed in U.S. Patent No. 4,533,254 (Cook et al.), the disclosure of which is incorporated herein by reference, and commercially available as MICROFLUIDIZER™ from Microfluidics Corporation, Newton, Massachusetts. Homogenizers are
10 discussed in W. C. Griffin, "Emulsions", Encyclopedia of Chemical Technology, Vol. 8, pp. 900-930 Mark-Othmer, eds., John Wiley & Sons, Inc., New York, New York, 3d ed., 1979), the disclosure of which is incorporated herein by reference. The reduction of particle size should be effective to reduce the mean (weight average) particle size of the oil phase
15 in the aqueous dispersion to less than about 5 microns, preferably less than about 3 microns and typically less than 1 micron. e.g. typically from about 0.1 to about 3 microns.

20 After reduction of the particle size, at least a portion of the organic cosolvent is removed. The organic cosolvent is removed by volatilizing the same from the mixture. This is an evaporative process that may be considered a distillation. Sufficient organic cosolvent should be removed so that the aqueous dispersion will be low in volatile organic compounds, and preferably essentially free of such compounds. Typically, less than 1%,

more typically less than 0.1% by weight of organic cosolvent remains in the aqueous dispersion.

The removal of the organic cosolvent will be facilitated by subjecting an agitated dispersion to elevated temperatures and/or reduced pressures, e.g. a vacuum distillation. The precise temperature and pressure employed to effect removal of the organic cosolvent will, of course, depend upon the volatility of the organic cosolvent chosen, but temperatures that will cause degradation or polymerization of the resin should be avoided. Distillation is discussed in E. Hafslund, "Distillation", Encyclopedia of Chemical Technology, vol. 7, pp. 849-891 (Kirk-Othmer, eds. John Wiley & Sons, N.Y., 3d ed. 1979) and evaporation is discussed in F. Standiford, "Evaporation", Encyclopedia of Chemical Technology, vol. 9, pp. 472-493 (Kirk-Othmer, eds. John Wiley & Sons, N.Y., 3d ed. 1980), the disclosures of which are incorporated by reference.

The aqueous dispersion of self-dispersing resin will typically exhibit excellent chemical and physical stability over an extended shelf-life, e.g. of from five to six months. As an example of the chemical stability, the epoxide equivalent weight (EEW) of the aqueous dispersion of self-dispersing resin should remain essentially constant, e.g. should show no trend of increasing molecular weight, over a period of at least one month from the preparation of the aqueous dispersion.

Epoxide equivalent weight can be determined by differential titration with perchloric acid using crystal violet as an indicator (e.g. a first sample is titrated with 0.1 N perchloric acid to an endpoint that shows the first sight

of green color from the crystal violet indicator, the amine equivalent weight of the dispersion is calculated from this titration, a second sample is mixed with excess tetraethylammonium bromide and titrated with 0.1 N perchloric acid to a green endpoint that persists for at least 30 seconds, total epoxide and amine equivalents are calculated from this titration, and the epoxide equivalent weight is calculated as the difference).

As an example of physical stability, the resin should not display layer formation for a period of at least one month from the preparation of the aqueous dispersion, i.e. there should be no formation of a macro-observable water phase as a layer separate from the dispersed resin phase.

Coating Compositions Comprising an Aqueous Dispersion of the Self-Dispersing Curable Epoxy Resin

The coating composition of the invention is prepared by combining the aqueous epoxy dispersion with a suitable hardening agent. The coatings are tack free after 45 minutes and have excellent film properties. An aqueous epoxy resin paint composition of the present invention may further contain additives conventionally employed in coating technology, such as organic pigments, inorganic pigments, surfactants, thickeners, and the like.

A room temperature curable water-borne coating composition is prepared by admixing a stable epoxy dispersion composition as described above with an epoxy-interacting curing vehicle, such as a polyamine curing agent. The ratio of active amino hydrogens to epoxy groups in the admixture is in the range of from 0.5:1 to 2:1 and, preferably, is in the range

between about 0.8:1 to 1.5:1. For purposes of industrial maintenance paint compositions, the amino hydrogens must be sufficiently reactive to effect crosslinking interaction with the epoxy groups at ambient temperatures.

5 Suitable polyamine curing agents are those which are soluble or dispersible in water and which contain more than 2 active hydrogen atoms per molecule. Examples of such curing agents are alkylene polyamines represented by the formula:



10 wherein 'T' is an alkylene radical containing 2 to 6 carbon atoms and 'u' is equal to or greater than zero (0) but less than or equal to five (5). Such alkylene polyamines include ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, propylene diamine, dibutylene triamine, hexamethylene diamine, and the like.

15 Other polyamine curing agents that can be employed in the practice of this invention are the polyamido amines, which are reaction products of alkylene polyamines and fatty acids. Such polyamidoamines are well known in the art and are described in U.S. Pat. Nos. 2,705,223, 2,811,495 and 2,899,397, which patents are hereby incorporated by reference. Other polyamine curing agents are the adducts of polyamines and epoxy
20 compounds such as those described in U.S. Pat. Nos. 2,651,589, 2,864,775 and 4,116,900, which patents are hereby incorporated by reference.

 Examples of useful curing agents also include those disclosed in U.S. patent application Serial No. 08/085,861, filed June 30, 1993, entitled

"Curing Agents for Aqueous Epoxy Resins", by Jason Chou et al., the disclosure of which is incorporated herein by reference. These epoxy curing agents comprise the reaction product of reactants consisting essentially of an alkylene polyamine having less than about 12 carbon atoms, an aromatic mono-glycidyl ether having less than about 18 carbon atoms, and a diglycidyl ether of an aromatic diol having an average degree of oligomerization of less than about 3.5, wherein the ratio of primary amine equivalents of said alkylene polyamine to the total epoxide equivalents of said aromatic glycidyl ether and said diglycidyl ether of an aromatic diol is not essentially less than one, and the ratio of epoxide equivalents of said aromatic mono-glycidyl ether to epoxide equivalents of said diglycidyl ether of an aromatic diol is greater than one. Another useful curing agent is described in U.S. Serial No. 08/279,587, filed July 25, 1994, the disclosure of which is incorporated herein by reference. These epoxy curing agents comprise the reaction product of reactants consisting essentially of: (a) an amine component consisting essentially of a mono-alkylene polyamine having less than about 12 carbon atoms (preferably a member selected from the group consisting of lower alkylene diamines, said member having from 2 to 8 carbon atoms and, more preferably, only straight-chain alkylene groups) and an alicyclic polyamine, said alicyclic polyamine being present in an amount of greater than about 10% of the amine equivalents of said amine component; (b) an aromatic mono-glycidyl ether having less than about 18 carbon atoms (preferably selected from the group consisting of mono-alkylphenyl glycidyl ethers and di-alkyl phenyl glycidyl ethers having from 9 to 13 carbon atoms); and (c) a diglycidyl ether of an

aromatic diol having an average degree of oligomerization of less than about 3.5 (preferably less than about 1.5, and preferably derived from an alkyl bis-phenol, e.g. bisphenol A), wherein (i) the ratio of primary amine equivalents of said alkylene polyamine to the total epoxide equivalents of said aromatic glycidyl ether and said diglycidyl ether of an aromatic diol are greater than essentially one (i.e. the molar equivalents of primary amine groups of said polyalkylene polyamine are in excess of the molar equivalents of glycidyl groups, e.g. a ratio of from about 1.5:1 to 2.5:1, preferably from about 1.75:1 to about 2.25:1), and (ii) the ratio of epoxide equivalents of said aromatic mono-glycidyl ether to epoxide equivalents of said diglycidyl ether of an aromatic diol is greater than one (preferably greater than 1.5, more preferably from about 2:1 to about 6:1, and most preferably from about 3:1 to 5:1).

In addition to the amine curing agent, a curing accelerator can be included in the coating composition. Such an accelerator will serve to reduce the time for the coating to become tack-free. Useful accelerators for amine curing agents include tertiary amines, e.g. N,N'-bis(dimethyl-amino-propyl) urea.

Other curing agents can be used in the composition of this invention, particularly when the coatings made from the compositions are heated to effect a cure. Examples of such additional curing agents are the aminoplast and phenoplast resins. Suitable aminoplast resins are the reaction products of ureas and melamines with aldehydes further etherified in some cases with an alcohol. Examples of aminoplast resin components are urea, ethylene urea, thiourea, melamine, benzoguanamine and acetoguanamine. Aldehydes

include formaldehyde, acetaldehyde and propionaldehyde. The aminoplast resins can be used in the alkylol form but, preferably, are utilized in the ether form wherein the etherifying agent is a monohydric alcohol containing from 1 to 8 carbon atoms. Examples of suitable aminoplast resins are methylol urea, dimethoxymethylol urea, butylated polymeric urea-formaldehyde resins, hexamethoxymethyl melamine, methylated polymeric melamine-formaldehyde resins and butylated polymeric melamine-formaldehyde resins.

Phenoplast resins are the reaction products of phenols and aldehydes which contain reactive methylol groups. These compositions can be monomeric or polymeric in nature depending on the molar ratio of phenol to aldehyde used in the initial condensation reaction. Examples of suitable phenols are phenol, o, m or p-cresol, 2,4-xyleneol, 3,4-xyleneol, 2,5-xyleneol, cardanol, p-tert-butyl phenol, and the like. Useful aldehydes are formaldehyde, acetaldehyde and propionaldehyde. Particularly useful phenoplast resins are polymethylol phenols wherein the phenolic group is etherified with an alkyl, e.g., methyl or ethyl, group. Other epoxy resin curing agents may also be useful, e.g. catalytic curing agents: Lewis bases (such as tertiary amines), Lewis acids (such as boron trifluoride), cationic curing agents (such as aryldiazonium salts, diaryliodonium salts, onium salts of Group VIa elements, especially sulfur) and reactive curing agents: mercaptans, isocyanates, carboxylic acids, and acid anhydrides. Curing agents for epoxy resins in general are discussed in the Encyclopedia of Polymer Science and Engineering, vol. 6, pp. 340-361 (John Wiley & Sons, Inc., N.Y., N.Y., 1986), the disclosure of which is incorporated by reference.

The following examples are further illustrative of the present invention. The reactants and other specific ingredients are presented as being typical, and various modifications can be derived in view of the foregoing disclosure within the scope of the invention.

EXAMPLES

Example 1

Preparation of Amine-epoxide Adduct (66% Capped)

5 Into a one liter reaction flask equipped with a stirrer, heating mantle,
nitrogen line, cooling condenser, and thermometer is charged 485 grams
10 (0.4 equivalents) Jeffamine 2000 (Texaco Chemical Company, Houston,
Texas) and 142.2 grams (0.61 equivalents) of polyepoxide of propoxylated
(5PO) pentaerythritol (Henkel Corporation, Ambler, PA). The reaction mixture
is heated slowly to 125°-130°C with stirring and held at this temperature
for about 2.5 hours. The reaction mixture is then cooled to 70°C and
analyzed for epoxide and amine content. The product amine polyepoxide
adduct has 0.4 meq./gm of total amine and 0.33 meq./gm of epoxide which
15 indicates that about 66% of the initial free epoxide groups have been
reacted with the amine.

Example 1A

Amine-epoxide adduct (50% capped)

20 Example 1 was repeated except 75.0 gm (0.063 equivalent) of
polyethoxy amine* and 35.5 gm (0.126 equivalent) polyepoxide of
propoxylated (5PO) pentaerythritol were reacted. The resulting adduct
yielded a product containing 0.34 me*/gm of total amine and 0.54 me/gm
of epoxide which represents 50% of the original epoxide moiety capped with
the amine.

- * TEXACO's Jeffamine M-2070
- * me (milliequivalent)

5

Example 1BAmine-epoxide adduct (75% capped)

Example 1 was repeated except 75 gm (0.063 equivalent) of polyethoxy amine* and 23.6 gm (0.083 equivalent) polyepoxide of propoxylated (5PO) pentaerythritol were reacted. The resulting adduct yielded a product containing 0.4 me/gm of total amine and 0.26 me/gm of epoxide which represents about 75% of the initial epoxide capped with the amine.

10

- * TEXACO's Jeffamine M-2070

15

Example 1CAmine-epoxide adduct (66% capped)

Example 1 was repeated except 50.0 gm polyethoxy amine* (0.0831 equivalent) and 35.0 gm (0.1245 equivalent) polyepoxide of propoxylated (5PO) pentaerythritol were reacted. The resulting adduct contained 0.61 me/gm of total amine and 0.37 me/gm of epoxide which represents about 66% of the initial epoxide capped with the amine.

20

- * TEXACO's Jeffamine M-1000

Example 1D

Example 1 was repeated except 150.0 gm (0.102 equivalent) of polyethoxy amine* and 41.6 gm (0.153 equivalent) polyepoxide of propoxylated (5PO) pentaerythritol were reacted. The resulting adduct contained 0.32 me/gm of total amine and 0.31 me/gm of epoxide which represents about 66% of the initial epoxide capped with the amine.

* TEXACO's Experimental amine No. 6940-29 (MW 3,000)

Example 2Preparation of Self-Dispersing Resin.

Into a 250 ml reaction flask equipped with heating mantle, nitrogen line, cooling condenser, thermometer and stirring means is charged 66.4 grams (0.348 equivalents) of the diglycidyl ether of bis-phenol A, and 19.6 grams (0.172 equivalents) of bis-phenol A. The reactants are heated to 95°C and then 12.0 grams (0.004 equivalents) of the amine-epoxide adduct prepared above (Example 1) is added with 0.15 grams triphenyl phosphine. The reaction mixture is heated slowly to 150°C with stirring whereupon an exothermic reaction is observed. Cooling is immediately applied to maintain the reaction temperature between 150°C and 160°C. After the exothermic reaction subsides, the reaction mixture is maintained at 160°C for an additional hour followed by a 15 minute period at 190°C. The reaction mixture is then cooled to 160°C and 14 grams of propyl cellosolve is added which immediately begins refluxing. The reaction mixture is cooled to 100°C and analyzed. The resultant self-dispersing resin, present at 87.5%

solids in propyl cellosolve, has 0.07 meq./gm total amine and an epoxide equivalent weight of 552 based on resin solids.

5

Example 2A

Example of a Larger Scale Preparation of Self-Dispersing Resin.

Into a 5 l. reaction flask equipped with heating mantle, nitrogen line, cooling condenser, thermometer and stirrer, is charged 1716 grams (8.99 equivalents) of the diglycidyl ether of bis-phenol A, and 506.4 grams (4.44 equivalents) of bis-phenol A. The reactants were heated to 95°C and then 10 413.4 grams (0.138 equivalents) of the amine-epoxide adduct prepared according to Example 1 along with 2.1 grams of triphenyl phosphene is added. The reaction mixture is heated carefully to about 150°C with stirring whereupon an exothermic reaction is noted. Cooling is immediately applied 15 to maintain the temperature between 150°C and 160°C. After the exotherm subsides, the reaction mixture is maintained at 160°C for an additional hour followed by a 15 minute period at 190°C. The reaction mixture is then cooled to about 160°C and 362.1 grams of propyl cellosolve is added. Cooling is continued to about 100°C when it is sampled and 20 analyzed for epoxide equivalent weight. The resulting self-dispersing resin has an epoxide equivalent weight of 550 based on resin solids.

Example 3

Preparation of Self-Dispersing Resin.

5 Into a reaction flask equipped with heating mantle, nitrogen line, cooling condenser, thermometer and stirring means is charged 215.0 grams (1.15 equivalents) of the diglycidyl ether of bis-phenol A, 105.6 grams (0.926 equivalents) of bis-phenol A, 61.1 grams of the amine epoxide adduct prepared above (Example 1), and 0.60 grams triphenyl phosphine. The reactants are heated to 95°C with stirring under an atmosphere of nitrogen. After 0.5 hours, the reaction mixture is heated to 165°C. The mixture is held at 165°C for 50 minutes at which time the epoxy equivalent weight of the formed resin should be 1670 grams/equivalent (by perchloric acid, thymol blue indicator). After 1.5 hours of heating at 165°C, propoxyethanol is added with simultaneous cooling of the mixture to 100°C. Addition of propoxyethanol solvent (101.6 grams total) is completed in 0.5 hours and the temperature was allowed to increase to 120°C. After mixing for 0.5 hours at 120°C, the mixture is allowed to cool.

Examples 3A - 3F

20 A series of resins were prepared by means substantially similar to the procedure of Example 3 and in accordance with the parameters set forth in Table 1. (In Example 3A, the reactant charge included an aliphatic glycidyl ether which is the glycidylation reaction product of mixed seven carbon aliphatic alcohols and is available from CVC Specialty Chemicals, Cherry Hill, New Jersey, as GE-7.)

TABLE I
EPOXY RESINS OF EXAMPLES 3 A - 3F

PROPERTIES OF RESIN	3A	3B	3C	3D	3E	3F
BPA/DER 331 RATIO (MOLE)	0.83	0.83	0.80	0.80	0.80	0.80
WT. % AMINE-EPOXY ADDUCT	20	16	16	16	16	16
WT. % PROPYL CELLOSOLVE	18	21	21	21	21	21
EPOXY EQUIVALENT WEIGHT (SOLIDS)	2,041	1,919	1,647	1,732	1,703	1,720
% COMPOSITION						
DER-331	27.90	28.02	28.38	28.38	28.38	28.38
BPA	13.95	14.01	13.64	13.64	13.64	13.64
AMINE EPOXY ADDUCT	10.43	8.02	7.98	7.98	7.98	7.98
PROPYL CELLOSOLVE	11.92	13.29	13.29	13.29	13.29	13.29
CAT (RESIDUE)	0.08	0.08	0.08	0.08	0.08	0.08
GE-7	2.61	---	---	---	---	---

Example 4APreparation of Amine-Epoxy Adduct

(zero epoxide and 50% excess hydrogen equivalent of amine)

5 Into a 250 ml reaction flask equipped with a stirrer, heating mantle,
nitrogen line, cooling condenser, and thermometer is charged 74.9 grams
(0.063 equivalent) Jeffamine M-2070 (Texaco Chemical Company, Houston,
Texas) and 11.84 grams (0.042 equivalent) of polyepoxide of propoxylated
(5 moles of propylene oxide per mole of) pentaerythritol (Henkel Corporation,
Ambler, PA). The reaction mixture is heated at 125-130°C for two hours
10 and at 140°C for another two hours. It is then cooled to 70°C and the
reaction product is analyzed for epoxide and amine content. Analysis show
no epoxide moiety (zero), and total amine value of 0.48 meq/g.

Example 4BPreparation of Amine-Epoxy Adduct

15 (zero epoxide and 75% excess hydrogen equivalent of amine).

Example 4A above is repeated except 87.47 grams (0.0735
equivalent) of Jeffamine M-2070 and 11.84 grams (0.042 equivalent) of
polyepoxide of propoxylated (5 moles propylene oxide per mole of)
pentaerythritol is heated at 125-130°C for two hours and at 140°C for one
20 hour. The resulting product is cooled to 70°C and analyzed. Analysis
shows zero epoxide content and 0.42 meq/g of total amine value.

Example 5A

Preparation of Self-Dispersing Resin

Into a 250 ml reaction flask equipped with heating mantle, nitrogen line, cooling condenser, thermometer and stirring means is charged 66.4
5 grams (0.348 equivalents) of the diglycidyl ether of bis-phenol A, and 19.6 grams (0.172 equivalents) of bis-phenol A which are heated to melt at 95°C. Then 0.15 grams of triphenyl phosphine is added.

The reaction mixture is heated slowly to 150°C with stirring whereupon an exothermic reaction is observed. Cooling is immediately
10 applied to maintain the reaction temperature between 150°C and 160°C. After the exothermic reaction subsides, the reaction mixture is maintained at 160°C for an additional hour followed by a 15 minute period at 190°C. The reaction mixture is then cooled to 160°C and 14 grams of propyl cellosolve is added which immediately begins refluxing. The reaction
15 mixture is cooled to 125°C and 12.0 g of the Example 1A adduct is added. The reaction mixture is heated at 125-130°C for one hour. It is then cooled to 100°C and analyzed. The resulting resin is about 87.5% solids in propyl cellosolve has an equivalent weight (EEW) about 617 (based on solids) and 0.07 meq/g of total amine.

20

Example 5B

Preparation of Self-Dispersing Resin

Example 5A was repeated except 12.0 g of the amine/epoxide adduct from example 4B is used. The resulting self-dispersing resin is about 87.5% solids in propyl cellosolve with an EEW (epoxy equivalent weight) of 594.0.

Example 6APreparation of Self-Dispersing Resin (SDR)

Into a 250 ml reaction flask equipped with heating mantle, nitrogen
line, cooling condenser, thermometer and stirring means is charged 66.4
5 grams (0.348 equivalents) of the diglycidyl ether of bis-phenol A, and 19.6
grams (0.172 equivalents) of bis-phenol A which are heated to melt at
95°C. Then 0.15 grams of triphenyl phosphine is added.

The reaction mixture is heated slowly to 150°C with stirring
whereupon an exothermic reaction is observed. Cooling is immediately
10 applied to maintain the reaction temperature between 150°C and 160°C.
After the exothermic reaction subsides, the reaction mixture is maintained
at 160°C for an additional hour followed by a 15 minute period at 190°C.
The reaction mixture is then cooled to 160°C and 14 grams of propyl
cellosolve is added which immediately begins refluxing. The reaction
15 mixture is cooled to 125°C and 10.32 g of Jeffamine 6940-20
(experimental amine from Texaco) is added. The reaction mixture is heated
at 125-130°C for one hour. It is then cooled to 100°C and analyzed. The
resulting SDR should be about 88% solids in propyl cellosolve and should
have an equivalent weight (EEW) about 617 (solid) and 0.07 meq/g total
20 amine.

Example 6B

Preparation of Self-dispersion Resin (SDR) Example 6A is repeated except 6.0 of Jeffamine 6940-29 (experimental amine from Texaco, having an EO/PO ratio of 95/5 and molecular weight of 3,000) is used. The resulting SDR should be about 87% solids in propyl cellosolve and should have an EEW of 546 (based on solids).

Example 6CPreparation Self-dispersing Resin (SDR)

Into a similar reactor as described in Example 6A, is charged 8.8 g propyl cellosolve which is heated to 90°C. Then 53.0 g epoxy resin DER-662 (Dow Chemical) is charged and dissolved. When a clear solution is obtained 3.7 g of Jeffamine 6940-20 is added and reaction mixture is heated at 125-130°C for one hour. It is then cooled to 100°C and the product is analyzed. The product should be 87% solids in propyl cellosolve and should have an EEW of 759.0.

Examples 7A - 7NPreparation of Water-Borne Dispersion.

A solution of the self-dispersing resins prepared as in Example 2 is prepared by mixing 84 parts by weight of the self-dispersing resin with 49 parts by weight of methyl ethyl ketone. The mixture is stirred and warmed to effect a homogenous mixture. This mixture is then poured into 56 parts by weight of deionized water with vigorous stirring with a high speed mixer.

The resulting pre-emulsion is then twice passed through a Microfluidizer, Model 110T, at 85 psi. The resulting dispersion is then subjected to rotary evaporation to reduce the level of methyl ethyl ketone to less than 0.5% by weight as measured by gas chromatography.

5

Example 7B

The procedure, of Example 7A is repeated, except the self-dispersing resin is prepared as in Example 2A.

Example 7C

10 The procedure, of Example 7A is repeated, except the self-dispersing resin is prepared as in Example 3.

Example 7D

The procedure, of Example 7A is repeated, except the self-dispersing resin is prepared as in Example 3A.

Example 7E

15 The procedure, of Example 7A is repeated, except the self-dispersing resin is prepared as in Example 3B.

Example 7F

The procedure, of Example 7A is repeated, except the self-dispersing resin is prepared as in Example 3C.

Example 7G

The procedure, of Example 7A is repeated, except the self-dispersing resin is prepared as in Example 3D.

Example 7H

- 5 The procedure, of Example 7A is repeated, except the self-dispersing resin is prepared as in Example 3E.

Example 7I

The procedure, of Example 7A is repeated, except the self-dispersing resin is prepared as in Example 3F.

10

Example 7J

The procedure, of Example 7A is repeated, except the self-dispersing resin is prepared as in Example 5A.

Example 7K

- 15 The procedure, of Example 7A is repeated, except the self-dispersing resin is prepared as in Example 5B.

Example 7L

The procedure, of Example 7A is repeated, except the self-dispersing resin is prepared as in Example 6A.

Example 7M

The procedure, of Example 7A is repeated, except the self-dispersing resin is prepared as in Example 6B.

Example 7N

5 The procedure, of Example 7A is repeated, except the self-dispersing resin is prepared as in Example 6C.

Example 8Preparation of Coating Composition.

10 Into a 25 ml plastic cup is charged the water-borne dispersion prepared according to Example 7A followed by an equal equivalent amount of epoxy curing agent available as 8290 by HiTech (a modified diethylene triamine with a hydrogen equivalent weight of 163). Sufficient water is then added to bring the mixture to a spreadable consistency. The epoxy dispersion/curing agent blend is aged for 10 minutes then a film casting is
15 produced by drawing the blend down on pre-sanded TRU COLD cold rolled steel panel (3 x 6 x 0.32 inches) using a #34 wire wound steel rod. This example can be repeated but with substitution of the self-dispersing resin prepared according to each of Examples 7B - 7N in each case for the self-dispersing resin prepared according to each of Example 7A.

20 The principles, preferred embodiments and modes of operation of the present invention have been described in the foregoing specification. The invention which is intended to be protected herein, however, is not to be

construed as limited to the particular forms disclosed, since these are to be regarded as illustrative rather than restrictive. Variations and changes may be made by those skilled in the art without departing from the spirit of the invention.

What is claimed is:

1. A process for preparing a self-dispersing curable epoxy resin dispersion, said process comprising:

reducing the particle size of a mixture comprised of a self-dispersing curable epoxy resin based on a polyoxyalkyleneamine, water and an organic cosolvent and

removing at least a major amount of said organic cosolvent from said mixture after said reducing.

2. A process as claimed in claim 1 further comprising preparing said self-dispersing curable epoxy resin composition by reacting (a) 1.0 reactive equivalents of an epoxy resin, (b) from about 0.01 to 1.0 reactive equivalents of a polyhydric phenol, and (c) from about 0.005 to 0.5 reactive equivalents of an amine-epoxy adduct prepared by reacting a polyoxyalkyleneamine and an aliphatic polyepoxide, wherein the ratio of the reactive equivalents of the polyoxyalkyleneamine and the aliphatic polyepoxide is in the range from about 0.3:1 to 0.9:1.

3. A process as claimed in claim 2 wherein said reactive equivalents of said polyhydric phenol are from about 0.4 to about 0.6 reactive equivalents.

4. A process as claimed in claim 2 wherein said reactive equivalents of said polyhydric phenol are from about 0.65 to about 0.95 reactive equivalents.
5. A process as claimed in claim 1 further comprising preparing said self-dispersing curable epoxy resin composition by reacting an epoxy resin with a polyoxyalkyleneamine having a molecular weight of from about 3,000 to about 15,000 in a ratio of about 0.001 to 0.060 reactive equivalents of polyoxyalkyleneamine to about 1.0 reactive equivalents of epoxy resin.
6. A process as claimed in claim 1 further comprising preparing said self-dispersing curable epoxy resin composition by reacting (a) 1.0 reactive equivalents of an epoxy resin, (b) from about 0.005 to 0.5 reactive equivalents of an amine-epoxy adduct, and optionally (c) from about 0.01 to 1.0 reactive equivalents of a polyhydric phenol, wherein the amine-epoxy adduct is formed upon contacting 1.0 equivalents of an aliphatic polyepoxide with from greater than about 1.0 equivalents reactive equivalents of a polyoxyalkyleneamine.
7. A process as claimed in claim 6 wherein said reactive equivalents of a polyoxyalkyleneamine are from about 1.01 to about 2.5 reactive equivalents.
8. A process as claimed in claim 1 wherein said organic cosolvent is selected from the group consisting of lower fatty acid esters or alkyl ethers

of monohydric and dihydric alcohols, and polyethers thereof, wherein the alkyl group comprises C₁-C₈ linear or branched aliphatic or alicyclic chains and ketones having a total of from 3 to 6 carbon atoms.

9. A process as claimed in claim 8 wherein said organic cosolvent is a methyl lower-alkyl ketones, wherein said lower alkyl group has from 1 to 3 carbon atoms.
10. A process as claimed in claim 1 wherein the amounts of said resin, water and organic cosolvent will range between about 20% to about 50% each by weight of said mixture.
11. A process as claimed in claim 1 wherein the amount of said resin in said mixture is from about 35% to about 45% by weight of said mixture and the amounts of water and organic cosolvent each range from about 25% to about 35% of said mixtures.
12. A process as claimed in claim 1 wherein said removing is by vacuum distillation.
13. A process as claimed in claim 1 wherein said removing is effective to reduce the amount of organic cosolvent in said mixture to less than 1% by weight of said mixture.

14. A process as claimed in claim 1 wherein said removing is effective to reduce the amount of organic cosolvent in said mixture to less than 0.1% by weight of said mixture.

15. A process as claimed in claim 1 wherein said reducing is effective to reduce the mean particle size of the oil phase in said mixture to less than about 3 microns.

16. A process as claimed in claim 1 wherein said reducing is effective to reduce the mean particle size of the oil phase in said mixture to a particle size in the range from about 0.1 microns to about 3 microns.

17. An aqueous dispersion comprising a self-dispersing epoxy resin prepared by the steps comprising:

(a) preparing a self-dispersing curable epoxy resin based on a polyoxyalkyleneamine,

(b) reducing the particle size of a mixture comprised of said self-dispersing curable epoxy resin, water and an organic cosolvent, and

(c) removing at least a major amount of said organic cosolvent from said mixture after said reducing.

18. An aqueous dispersion as claimed in claim 17 wherein said preparing comprises first preparing an amine-epoxy adduct by contacting a polyoxyalkyleneamine and a polyepoxide, where the ratio of the reactive

equivalents of the polyoxyalkyleneamine and the polyepoxide is in the range from about 0.3:1 to 0.9:1, and then contacting said amine-epoxy adduct with a polyhydric phenol and an epoxy resin, where the ratio of the reactive equivalents of the polyhydric phenol and the polyglycidyl ether of a polyhydric phenol is in the range from about 0.01:1 to about 1.0:1, and where the ratio of the reactive equivalents of the amine-epoxy adduct and the polyglycidyl ether of the polyhydric phenol is in the range from about 0.005:1 to about 0.5:1 to produce a self-dispersing curable epoxy resin

INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C08G 59/50, 65/26; C08K 3/20; C08L 63/02

US CL : 523/404; 528/111

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 523/404; 528/111

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

NONE

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

NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,415,682 (BECKER) 15 November 1983, see abstract and column 7, lines 5-65	1-18
Y	US, A, 4,421,906 (WADDILL ET AL.) 20 December 1983, see column 2, lines 10-16 and 43-46.	1-18
Y	US, A, 4,423,170 (WADDILL) 27 December 1983, see abstract and column 1, lines 51-56.	2-4, 6, 7 and 18
Y	US, A, 5,221,700 (GILBERT ET AL.) 22 June 1993, see abstract.	2-4, 6, 7, and 18
Y	GB, A, 2,127,829 (MOBAY CHEMICAL CORPORATION) 18 April 1984, see entire document.	1-18

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	* & * document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

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17 OCT 1995

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