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(54) **Title:** Waterborne curing agent composition for epoxy coatings

(57) **Abstract:** The present invention discloses a waterborne curing agent composition for epoxy coatings, a coating formulation comprising said curing agent composition and a coating comprising the cured coating formulation. The curing agent composition comprises an adduct of a polyaminoamide and an epoxide; a polyoxyalkyleneamine; a cycloaliphatic amine; and water.

Waterborne curing agent composition for epoxy coatings

Technical field

The invention relates to waterborne curing agents for epoxy coatings, and particularly to a waterborne curing agent composition for epoxy coatings comprising an adduct of a polyaminoamide and an epoxide.

Background art

Epoxy coating with excellent corrosion resistance, good adhesion on diverse substrate, and good mechanical properties can be used in tank lining, pipe lining, machinery, transportation and steel structure sub-market, etc. Due to more stringent environmental regulations in some regions, waterborne epoxy coating becomes a good candidate technology with low VOC emission and balanced overall coating properties. However, deficiencies of waterborne coating limits its wide application.

For example, it is difficult to develop stable emulsions with water which have high solids content and low viscosity, and therefore good flowability. In this regard, US 6245835 B1 proposes an amino-epoxy adduct curing agent prepared by reacting a polyoxyalkylenediamine with a polyepoxide and polyoxyalkylene glycol diglycidyl ether and emulsifying the reaction product in water.

Some commercial waterborne curing agents have high amine hydrogen equivalent weight (AHEW). The use of excessive amine monomers has been restricted due to the safety management of field workers. US 9550912 B2 discloses a waterborne curing agent prepared by reacting a diglycidyl ether of a bisphenol with a first polyamine, then distilling free basic amine, and then blending a second polyamine, which results in low amine hydrogen equivalent weight with high solid.

Despite the improvements made to date on waterborne curing agents, problems especially like poor early water immersion and water spot resistance in metal

coatings as thin and thick films, causing bubbles, flash rusty, declining corrosion resistance and loss of adhesion in zinc-rich primer and non-zinc content primer still need to be better addressed.

Summary of the invention

One objective of the present invention is to provide a waterborne curing agent, which generate excellent early film performance, like early water immersion and early water spot resistance.

This objective of the present invention is achieved by a waterborne curing agent composition comprising

a) an adduct of a polyaminoamide and an epoxide;

b) a polyoxyalkyleneamine;

c) a cycloaliphatic amine; and

d) water.

Such waterborne curing agent composition can be used in all water-based systems while maintaining the same performance as solvent-borne epoxy resin coatings and demonstrates reduced toxicity.

Thus, another objective of the present invention is to provide a coating formulation comprising the waterborne curing agent composition as defined above and an epoxy resin.

Yet another objective of the present invention is to provide a coating comprising the cured coating formulation as mentioned above.

The coating can demonstrate good overall mechanical properties, and good early water spot and water immersion resistance at an early stage.

Other advantages of the present invention would be apparent for a person skilled in the art upon reading the specification.

Brief summary of the drawings

Fig. 1 shows the results of an early water immersion resistance test for samples 1-4; and

Fig. 2 shows the results of an early water spot resistance test for samples 5-8.

Detailed description of the invention

Waterborne curing agent composition

The waterborne curing agent composition may be prepared by mixing polyoxyalkyleneamines and cycloaliphatic amines with the adduct of a polyaminoamide and an epoxide, then adding water while stirring at the temperature of 60-80°C.

a) Adduct of a polyaminoamide and an epoxide

The adduct of a polyaminoamide and an epoxide can provide the curing agent composition with good corrosion resistance.

The amount of the adduct of a polyaminoamide and an epoxide in the waterborne curing agent composition is 20-70 wt.%, preferably 30-60 wt.%.

The adduct of a polyaminoamide and an epoxide may be prepared by the adduction reaction of a polyaminoamide and an epoxide.

The epoxide-polyaminoamide adduction reaction can be conducted under conventional conditions, preferably conducted over a temperature range from 20°C to 150°C, preferably 40°C to 120°C, more preferably 80°C to 100°C. The reaction

can be conducted in the presence of a suitable solvent. The most preferred solvent is propylene glycol monomethyl ether.

Polyaminoamide

The polyaminoamides useful in preparing the adduct of a polyaminoamide and an epoxide are particularly based on the condensation products of one or more carboxylic acids having 20-60 carbon atoms and at least two carboxyl groups and/or the corresponding ester(s) with one or more polyalkyleneamines. The condensation product may be prepared via a condensation reaction of the carboxylic acid and/or the corresponding ester with the polyalkyleneamine.

Carboxylic acid:

Preferably, the carboxylic acid is a dimerized fatty acid. However, it should be understood that higher orders of oligomerized fatty acids, such as, trimers, tetramers, may be adopted as the carboxylic acid. Also, other multi-carboxylic acids may be employed.

In addition, or alternatively, one or more esters derived from a carboxylic acid having 20-60 carbon atoms and at least two carboxyl groups can be used. C1 to C4 alkyl esters are preferred.

The term dimerized fatty acid, or dimer fatty acid, is well known in the art and refers to the dimerization product of mono- or polyunsaturated fatty acids and/or esters thereof. Preferred dimer fatty acids are dimers of fatty acids with C10 to C30, more preferably C12 to C24, particularly C14 to C22, and especially C16 to C20 alkyl chains. Particularly preferred dimer fatty acids include dimerization products of palmitoleic acid (C16), stearic acid (C18), oleic acid (C18), linoleic acid (C18), linolenic acid (C18), elaidic acid (C18), gondoic acid (C20), or any mixtures thereof. The dimerization products of the unsaturated fatty acid mixtures obtained in the hydrolysis of natural fats and oils, e.g. sunflower oil, soybean oil, olive oil, rapeseed oil, cottonseed oil, jujuba oil, and tall oil, may also be used. After dimerization, the

mixture may be hydrogenated (partially or fully), to generate saturated dicarboxylic acid, tricarboxylic acid, etc.

The above mentioned dimerized fatty acids are commercially available from chemical manufacturers. For example, Pripol® 1006, 1009, 1013, 1017, 1022, 1025, and 1029 dimer acids (Croda Coatings & Polymers), Empol®1018 and 1019 (Cognis Corp.), Haridimer™ 250S (Harima M.I.D., Inc.), and Unidyme® 18 and SYLVADYME™ T18 (Arizona Chemical Co.).

In some embodiments, monocarboxylic acids can be used in addition to the dimerized fatty acid as chain stopper. Preferred monocarboxylic acids are tall oil fatty acids (TOFA).

Polyalkyleneamine:

Polyalkyleneamine compounds that are useful in producing the polyaminoamide of the present invention include, but are not limited to, polyethyleneamines, polypropyleneamines, aminopropylated ethylenediamines, aminopropylated propylenediamines and combinations thereof. Non-limiting examples of polyethyleneamines include ethylenediamine, diethylenetriamine, triethylenetetramine, teraethylenepentamine, pentaethylenehexamine, and other higher polyethyleneamines. Suitable polypropyleneamines include, but are not limited to, propylenediamine, dipropylenetriamine, tripropylenetetramine, and other higher polypropyleneamines. Aminopropylated ethylenediamines and aminopropylated propylenediamines include, but are not limited to, N-3-aminopropyl ethylenediamine (N3), N,N'-bis(3-aminopropyl)ethylenediamine (N4), N,N,N'-tris(3-aminopropyl)ethylenediamine (N5), N-3-aminopropyl diethylenetriamine (N4), N-3-aminopropyl-[N'-3-[N-3-aminopropyl]aminopropyl]diethylenetriamine (N6), N,N'-bis(3-aminopropyl)diethylenetriamine (N5), N,N-bis(3-aminopropyl)diethylenetriamine (N5), N,N,N'-tris(3-aminopropyl)diethylenetriamine (N6), N,N',N''-tris(3-aminopropyl)diethylenetriamine (N6), N,N,N',N'-tetrakis(3-

aminopropyl)diethylenetriamine (N7), N,N-bis(3-aminopropyl)-[N'-3-[N-3-aminopropyl]aminopropyl]-[N'-3-aminopropyl]diethylenetriamine (N8), N-3-aminopropyl-[N'-3-[N-3-aminopropyl]aminopropyl]-[N'-3-aminopropyl]diethylenetriamine (N7), N-3-aminopropyl-1,3-diaminopropane, N,N'-bis(3-aminopropyl) -1,3-diaminopropane, and N,N,N'-tris(3-aminopropyl)-1,3-diaminopropane, and the like.

Mixtures of polyalkyleneamine compounds can be employed in the present invention.

In one example of the present invention, the polyalkyleneamine is triethylenetetramine (TETA).

In another example of the present invention, the polyalkyleneamine is tetraethylenepentamine (TEPA).

In yet another example, the polyalkyleneamine is a mixture of TETA and TEPA.

The polyalkyleneamines are preferably used in a large molar excess of the carboxylic acid to yield the amino-terminated polyaminoamide. Generally, the unreacted polyalkyleneamine represent 5-15 wt.% with respect to the total reactant amount of the polyalkyleneamine.

The condensation reaction occurs under conventional dehydration condensation reaction conditions, preferably by heating to a temperature of 120 °C to 280 °C, more preferably to a temperature of 180°C to 280°C. The elevated temperature ensures that water, as co-product of the condensation, can be removed from the mixture. The heating condition endures for 0.5 to 10 hours, preferably 1 to 5 hours. Preferably, the heating condition is accompanied by rigorous stirring, for example, under 100 rpm to 200 rpm stirring.

To prevent side reactions such as oxidation, a non-oxidative atmosphere can preferably be applied during the condensation. The non-oxidative atmosphere can be formed preferably by charging nitrogen gas, or any other inert or reductive gas, e.g., argon.

Epoxide

The epoxide useful in preparing the adduct of a polyaminoamide and an epoxide preferably includes at least one monofunctional or multifunctional epoxide.

The at least one monofunctional epoxide includes one or more epoxides or epoxy resins having one epoxide group per molecule. The at least one multifunctional epoxide includes, but is not limited to, epoxides having two, three, four, or at least five epoxide groups per molecule.

Useful compounds are a multitude of those known for this purpose that contain more than one epoxide group, preferably two epoxide groups, per molecule. These epoxide compounds are preferably either saturated or unsaturated. They are preferably aliphatic, cycloaliphatic, aromatic or heterocyclic, and have hydroxyl groups. They preferably contain such substituents that do not cause any side reactions under the mixing or reaction conditions, for example alkyl or aryl substituents, ether moieties and the like. They are preferably glycidyl ethers which derive from polyhydric phenols, especially bisphenols and novolac, and which have molar masses based on the number of epoxide groups (EEW, “epoxide equivalent weights”, “EV value”) between 100 and 1500 g/eq.

Examples of polyhydric phenols include: resorcinol, hydroquinone, 2,2-bis(4-hydroxyphenyl)propane (bisphenol A), bis(4-glycidyloxyphenyl)methane (bisphenol E), isomer mixtures of dihydroxydiphenylmethane (bisphenol F), 4,4'-dihydroxydiphenylcyclohexane, 4,4'-dihydroxy-3,3'-dimethyldiphenylpropane, 4,4'-dihydroxydiphenyl, 4,4'-dihydroxybenzophenone, bis(4-hydroxyphenyl)-1,1-ethane, bis(4-hydroxyphenyl)-1,1-isobutane, 2,2-bis(4-hydroxy-tert-butylphenyl)propane,

bis(2-hydroxynaphthyl)methane, 1,5-dihydroxynaphthalene, tris(4-hydroxyphenyl)methane, bis(4-hydroxyphenyl) ether, bis(4-hydroxyphenyl) sulphone inter alia, and the chlorination and bromination products of the aforementioned compounds, for example tetrabromobisphenol A. Very particular preference is given to using liquid diglycidyl ethers based on bisphenol A and bisphenol F having an epoxide equivalent weight of 160 to 1000 g/eq, preferably 170-600 g/eq, and more preferably 190-500 g/eq. It is also possible to use polyglycidyl ethers of polyols, for example ethane-1,2-diol diglycidyl ether, propane-1,2-diol diglycidyl ether, propane-1,3-diol diglycidyl ether, butanediol diglycidyl ether, pentanediol diglycidyl ether (including neopentyl glycol diglycidyl ether), hexanediol diglycidyl ether, diethylene glycol diglycidyl ether, dipropylene glycol diglycidyl ether, higher polyoxyalkylene glycol diglycidyl ethers, for example higher polyoxyethylene glycol diglycidyl ethers and polyoxypropylene glycol diglycidyl ethers, co-polyoxyethylene-propylene glycol diglycidyl ethers, polyoxytetramethylene glycol diglycidyl ethers, polyglycidyl ethers of glycerol, of hexane-1,2,6-triol, of trimethylolpropane, of trimethylolethane, of pentaerythritol or of sorbitol, polyglycidyl ethers of oxyalkylated polyols (for example of glycerol, trimethylolpropane, pentaerythritol, inter alia), diglycidyl ethers of cyclohexanedimethanol, of bis(4-hydroxycyclohexyl)methane and of 2,2-bis(4-hydroxycyclohexyl)propane, polyglycidyl ethers of castor oil, triglycidyl tris(2-hydroxyethyl)isocyanurate.

Further useful components include: poly(N-glycidyl) compounds obtainable by dehydrohalogenation of the reaction products of epichlorohydrin and amines such as aniline, n-butylamine, bis(4-aminophenyl)methane, m-xylylenediamine or bis(4-methylaminophenyl)methane. The poly(N-glycidyl) compounds also include triglycidyl isocyanurate, triglycidylurazole and oligomers thereof, N,N'-diglycidyl derivatives of cycloalkyleneureas and diglycidyl derivatives of hydantoins inter alia.

The monofunctional epoxide includes, but is not limited to, an epoxidized unsaturated hydrocarbon such as ethylene, propylene, butylene, cyclohexene, and

styrene oxides, and the like; halogen-containing epoxides such as epichlorohydrin; epoxy-ethers of monohydric alcohols such as methyl, ethyl, butyl, 2-ethylhexyl, dodecyl alcohol, and the like; epoxy-ethers of monohydric phenols such as phenol, cresol, and other phenols substituted in the ortho or para positions; glycidyl esters of saturated or unsaturated carboxylic acids; epoxidized esters of unsaturated alcohols or unsaturated carboxylic acids; acetals of glycidaldehyde; or combination thereof. Preferably, the monofunctional glycidyl ether includes o-cresyl glycidyl ether, phenyl glycidyl ether, p-tert-butylphenyl glycidyl ether, n-butyl glycidyl ether, 2-ethyl hexyl glycidyl ether, any alkyl C_8 to C_{14} glycidyl ether, or any combination thereof.

The multifunctional epoxide includes, but is not limited to a bisphenol A diglycidyl ether, bisphenol E diglycidyl ether, bisphenol F diglycidyl ether, 1,4-butanediol diglycidyl ether, cyclohexane dimethylol diglycidyl ether, resorcinol diglycidyl ether, glycerol triglycidyl ether, trimethylol propane triglycidyl ether, novolac epoxy resin, any other aliphatic diglycidyl or triglycidyl ether, any other cycloaliphatic diglycidyl or triglycidyl ether, or any combination thereof. Preferably, the multifunctional epoxide is a bisphenol A epoxy resin, a bisphenol F epoxy resin, 1,4-butanediol diglycidyl ether, cyclohexane dimethylol diglycidyl ether, resorcinol diglycidyl ether, glycerol triglycidyl ether, trimethylol propane triglycidyl ether, or novolac epoxy resin, or a combination thereof.

The epoxide is added in amount of 1-25 wt.%, such as 3-20 wt.%, for example, 5-15 wt.%, based upon the amount of the polyaminoamide added in the epoxide-polyaminoamide adduction reaction.

b) Polyoxyalkyleneamine

The curing agent composition according to the present invention further comprises a polyoxyalkyleneamine.

Polyoxyalkyleneamine, sometimes termed “polyetheramine” or “poly(alkyleneoxy) amine”, is a group of organic amines with one or more amino groups attached to polyether backbone. Amino groups include primary amino group (-NH_2), secondary amino groups (-NHR, wherein R is an organic radical other than H atom), and tertiary amino groups (-NR_1R_2, wherein R_1 and R_2 are independently organic radicals other than H atom).

The polyether backbone in polyoxyalkyleneamines used herein contains at least two oxyalkylene moieties (OC_nH_{2n}, n being an integer of 2 to 10). In some preferable embodiments, the number of oxyalkylene moiety is larger than 2, for example, 3, 4, or 5. The oxyalkylene moiety may preferably be selected from oxyethylene (-OCH_2CH_2-), oxypropylene (-$OCH(CH_3)CH_2$-, or -$OCH_2CH_2CH_2$-), oxybutylene (-$OCH(CH_3)CH(CH_3)$-, -$OCH(CH_2CH_3)CH_2$-, and -$OC(CH_3)_2CH_2$-), or any other similar group having the chemical formula (OC_nH_{2n}, n being an integer of 2 to 10). The oxyalkylene moieties may be identical or different, for example, a mixture of oxyethylene and oxypropylene.

The polyoxyalkyleneamine used in the present disclosure has at least two primary amino groups, for example, Jeffamine® D series polyetheramines. In some preferable embodiments, the polyoxyalkyleneamine has three or more primary amino groups, for instance, Jeffamine® T series polyetheramines may be used.

Preferably, the polyoxyalkyleneamine includes at least one amino-terminated polyoxyethylene, amino-terminated polyoxypropylene, or amino-terminated polyoxybutylene.

Preferably, the polyoxyalkyleneamine includes an amino-terminated polyoxypropylene.

In some preferable embodiments, the polyoxyalkyleneamine includes a polyoxyethyleneamine, having the following formula (II):

$$H_2NCH_2CH_2[OCH_2CH_2]_xNH_2 \quad (II)$$

wherein x is an integer ranging from 2 to 70. Specific examples are Jeffamine® EDR series diamines from Huntsman Corporation.

In some preferable embodiments, the polyoxyalkyleneamine includes a polyoxypropyleneamine, having the following formula (III):

$$H_2NCH(CH_3)CH_2[OCH_2CH(CH_3)]_xNH_2 \quad (III)$$

wherein x is an integer ranging from 2 to 70. Specific examples are Jeffamine® D series diamines from Huntsman Corporation.

In some preferable embodiments, the polyoxyalkyleneamine includes a polyoxybutyleneamine, having the following formula (IV):

$$H_2NCH(CH_2CH_3)CH_2[OCH_2CH(CH_2CH_3)]_xNH_2 \quad (IV)$$

wherein x is an integer ranging from 2 to 70.

In some preferable embodiments, the polyoxyalkyleneamine includes a polyoxybutyleneamine, having the following formula (V):

$$H_2NCH(CH_3)CH(CH_3)[OCH(CH_3)CH(CH_3)]_xNH_2 \quad (V)$$

wherein x is an integer ranging from 2 to 70.

In some preferable embodiments, the polyoxyalkyleneamine includes a poly(oxypropylene-co-oxyethylene) amine, having the following formula (VI):

$$H_2NCH_2CH_2[OCH_2CH_2]_x[OCH_2CH(CH_3)]_yNH_2 \quad (VI)$$

wherein x and y are integers independently ranging from 2 to 70.

In some preferable embodiments, the polyoxyalkyleneamine includes a poly(oxypropylene-co-oxyethylene) amine, having the following formula (VII):

$$H_2NCH_2CH_2[OCH_2CH_2]_x[OCH_2CH(CH_3)]_y[OCH_2CH_2]_zNH_2 \quad (VII)$$

wherein x, y and z are integers independently ranging from 2 to 70.

In some preferable embodiments, the polyoxyalkyleneamine includes a poly(oxypropylene-co-oxyethylene) amine, having the following formula (VIII):

$$H_2NCH(CH_3)CH_2[OCH_2CH(CH_3)]_x[OCH_2CH_2]_y[OCH_2CH_2]_zNH_2 \quad (VIII)$$

wherein x, y and z are integers independently ranging from 2 to 70. Specific examples are Jeffamine® HK511 diamine (prepared by aminating a diethylene glycol grafted with propylene oxide, with an average molar mass of 220.) or Jeffamine® ED series diamines from Huntsman Corporation.

In some preferable embodiments, the polyoxyalkyleneamine is based on a poly(tetramethylene ether) glycol and polypropylene glycol copolymer, for example, having the following formula (IX):

$$H_2NCH(CH_3)CH_2[O(CH_2)_4]_xOCH(CH_3)CH_2NH_2 \quad (IX)$$

wherein x is an integer ranging from 1 to 70. Specific examples are Jeffamine® THF series diamines from Huntsman Corporation.

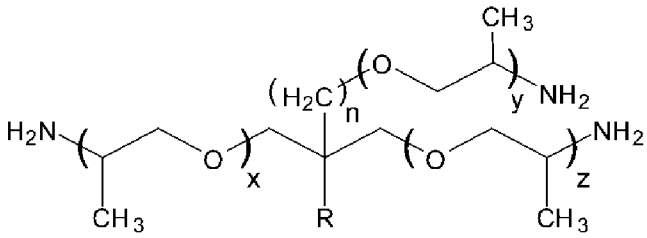
In some preferable embodiments, the polyoxyalkyleneamine includes a

poly(oxypropylene-co-oxyethylene) amine, having the following formula (X):

$$H_2N(CH_2)_3[OCH_2CH_2]_xO(CH_2)_3NH_2 \quad (X)$$

wherein x is an integer ranging from 1 to 70. Specific examples are 1,13-diamino-4,7,10-trioxatridecane (Ancamine® 1922A from Evonik Resource Efficiency GmbH) or 4,7-dioxadecane-1,10-diamine.

In some preferable embodiments, the polyoxyalkyleneamine includes a polyoxypropyleneamine, having the following formula (XI):



(XI)

wherein, R is a radical selected from H, CH_3, CH_2CH_3, $CH_2CH_2CH_3$, or $CH(CH_3)_2$; n is 0 or 1; x, y, and z are integers independently ranging from 1 to 30; and the sum of x, y, and z is ranging from 3 to 90. Specific examples are Jeffamine® T series triamines from Huntsman Corporation.

It will be appreciated that polyoxyalkyleneamines used in the present disclosure may be a mixture of polymers or oligomers having varying degrees of polymerization. For example, when polyoxypropyleneamine is used, the repeating number x as in $H_2NCH(CH_3)CH_2[OCH_2CH(CH_3)]_xNH_2$ may be within a distribution, for example, a distribution ranging from 2 to 30, rather than a specific integer.

In some preferable embodiments, a diamine, triamine, or tetraamine that has a primary amino-terminated polyoxyalkylene backbone may be employed. Specific examples include Jeffamine® RFD270 amine from Huntsman Corporation, which

contains both rigid cycloaliphatic and flexible polyetheramine segments in the same molecule. Other reference may be made to Jeffamine® XTJ616 from Huntsman Corporation, which comprises a polyetheramine based on pentaerythritol and propylene oxide with an average molecular weight of about 660.

The above mentioned polyoxyalkyleneamines are commercially available from various chemical manufacturers. For example, Jeffamine® D230, Jeffamine® D400, Jeffamine® D2000, Jeffamine® D4000, Jeffamine® ED600, Jeffamine® ED900, Jeffamine® ED2003, Jeffamine® EDR104, Jeffamine® EDR148, Jeffamine® EDR176, Jeffamine® EDR192, Jeffamine® THF100, Jeffamine® THF140, Jeffamine® THF170, Jeffamine® T403, Jeffamine® T3000, Jeffamine® T5000, Jeffamine® RFD270, Jeffamine® XTJ616 from Huntsman Corporation; Baxxodur® EC 301, Baxxodur® EC 310, Baxxodur® EC 302, Baxxodur® EC 303, Baxxodur® EC 311 from BASF SE; or Ancamine® 1922A from Evonik Operations GmbH.

The amount of polyoxyalkyleneamines in the curing agent composition is preferably 3-20 wt. %, more preferably 5-15 wt. %, even more preferably 5 wt. % to 10 wt. %. By incorporating polyoxyalkyleneamine into the curing agent composition, the flexibility and water solubility are improved.

c) Cycloaliphatic amines

Cycloaliphatic amines provide curing agent compositions with better early water resistance and mechanical properties. Weight percentage of cycloaliphatic amines in the curing agent composition is preferably 3-30 wt. %, more preferably 5-25 wt. %, even more preferably 8 wt. % to 20 wt. %.

The most preferred cycloaliphatic amine includes one or more selected from the group consisting of 4,4'-diaminodicyclohexylmethane (PACM), isophorone diamine, methylcyclohexyldiamine, cyclohexyldiamine, 4,4'-methylenebis(cyclohexylamine), isomers of xylylenediamines, 1,2-bis aminomethylcyclohexane, 1,3-bis

aminomethylcyclohexane, 1,4-bis aminomethylcyclohexane, or hydrogenated copolymer of formaldehyde-aniline. It is thought that hydrogenated copolymer of formaldehyde-aniline additionally introduces good chemical resistance to the curing agent composition.

d) Water

Water can be added to the mixture of the epoxide-polyaminoamide adduct, the polyoxyalkyleneamine and the cycloaliphatic amine to yield the curing agent composition of the invention. The amount of water can preferably range from 5 to 50 wt.%, more preferably 10 to 45 wt.%, still more preferably 15 to 40 wt.% by weight of the curing agent composition.

Coating formulation

The present disclosure further provides a coating formulation comprising the waterborne curing agent composition as described above and at least one epoxy resin. The epoxy resin may be those already known in the art. The coating formulation may be prepared by mixing the waterborne curing agent composition of the present invention and an epoxy resin.

Other components in coating formulation

To bring in more functionality or features to satisfy industrial requirements, the coating formulation preferably includes additives. Additives are understood to mean substances which are added to alter the properties of the coating formulation in the desired direction, for example to match viscosity, wetting characteristics, stability, reaction rate, blister formation, storability or adhesion, and use properties, to the end application. Several additives are described, for example, in WO 99/55772.

Preferred additives are selected from the group consisting of fillers, reinforcing

agents, coupling agents, toughening agents, defoamers, dispersants, lubricants, colorants, marking materials, dyes, pigments, IR absorbers, UV absorbers, antistats, anti-blocking agents, nucleating agents, crystallization accelerators, crystallization delayers, conductivity additives, carbon black, graphite, carbon nanotubes, graphene, desiccants, de-molding agents, levelling auxiliaries, flame retardants, separating agents, optical lighteners, rheology additives, photochromic additives, softeners, adhesion promoters, anti-dripping agents, metallic pigments, stabilizers, metal glitters, metal coated particles, porosity inducers, glass fibers, nanoparticles, flow assistants, or combinations thereof.

The coating formulation may be used to prepare coatings, adhesives, mortars, and fiber reinforced composites.

The present invention further provides a coating comprising the inventive coating formulation which has been cured. The inventive coating is a coating comprising the cured coating formulation as mentioned above. Such cured coating formulation is typically a layer formed by curing the inventive coating formulation.

The present invention further provides a coated article comprising a substrate and the inventive coating coated on the substrate.

The present disclosure also is directed to articles of manufacture comprising the compositions disclosed herein. For example, an article can comprise a cured coating formulation which coating formulation comprises the waterborne curing agent composition and an epoxy resin. Articles of manufacture produced from coating formulations disclosed herein include, but are not limited to, adhesives, coatings, primers, sealants, curing compounds, construction products, flooring products, and composite products. Further, such coatings, primers, sealants, or curing compounds can be applied to metal or cementitious substrates. Coating formulations can be solvent-free or can contain diluents, such as water or organic solvents, as needed for the particular application. Coating formulations can contain

various types and levels of pigments for use in paint and primer applications. Cured coating formulations comprise a layer having a thickness ranging from 40 to 400 μm (micrometer), preferably 80 to 300 μm, more preferably 100 to 250 μm, for use in a protective coating applied on to metal substrates. In addition, for use in a flooring product or a construction product, coating compositions comprise a layer having a thickness ranging from 50 to 10,000 μm, depending on the type of product and the required end-properties. A coating that delivers limited mechanical and chemical resistances comprises a layer having a thickness ranging from 50 to 500 μm, preferably 100 to 300 μm; whereas a coating such as, for example, a self-levelling floor that delivers high mechanical and chemical resistances comprises a layer having a thickness ranging from 1,000 to 10,000 μm, preferably 1,500 to 5,000 μm.

Numerous substrates are suitable for the application of coatings of the present disclosure with proper surface preparation, as is well known to one of ordinary skill in the art. Such substrates include, but are not limited to, concrete and various types of metals and alloys, such as steel and aluminum. Coatings of the present disclosure are suitable for the painting or coating of large metal objects or cementitious substrates including ships, bridges, industrial plants and equipment, and floors.

Coatings of the present disclosure can be applied by any number of techniques including spray, brush, roller, paint mitt, and the like. In order to apply very high solids content or 100% solids coatings of the present disclosure, plural component spray application equipment can be used, in which the amine and epoxide components are mixed in the lines leading to the spray gun, in the spray gun itself, or by mixing the two components together as they leave the spray gun. Using this technique can alleviate limitations regarding the pot life of the formulation, which typically decreases as both the amine reactivity and the solids content increases. Heated plural component equipment can be employed to reduce the viscosity of the components, thereby improving ease of application.

Construction and flooring applications include compositions comprising the coating compositions of the present disclosure in combination with concrete or other materials commonly used in the construction industry. Applications of compositions of the present disclosure include, but are not limited to the composition's use as a primer, a deep penetrating primer, a coating, a curing compound, and/or a sealant for new or old concrete, such as referenced in ASTM C309-97, which is incorporated herein by reference. As a primer or a sealant, the coating formulations of the present disclosure can be applied to surfaces to improve adhesive bonding prior to the application of a coating. As it pertains to concrete and cementitious application, a coating is an agent used for application on a surface to create a protective or decorative layer or a coat. Crack injection and crack filling products also can be prepared from the formulations disclosed herein. Coating formulations of the present disclosure can be mixed with cementitious materials such as concrete mix to form polymer or modified cements, tile grouts, and the like.

The following is a list of preferred items of the invention:

Item 1. A waterborne curing agent composition for epoxy coatings comprising:

a) an adduct of a polyaminoamide and an epoxide;

b) a polyoxyalkyleneamine;

c) a cycloaliphatic amine; and

d) water.

Item 2. The curing agent composition of item 1, wherein the polyaminoamide is based on the reaction product of a carboxylic acid having 20-60 carbon atoms and at least two carboxyl groups and/or an ester derived from a carboxylic acid having 20-60 carbon atoms and at least two carboxyl groups with a polyalkyleneamine.

Item 3. The curing agent composition of item 2, wherein the polyalkyleneamine is selected from polyethyleneamines, polypropyleneamines, aminopropylated

ethylenediamines, aminopropylated propylenediamines and any combinations thereof.

Item 4. The curing agent composition of item 2 or 3, wherein the polyalkyleneamine is TETA, TEPA, or a mixture of TETA and TEPA.

Item 5. The curing agent composition of any of items 2-4, wherein the carboxylic acid is a dimerized fatty acid.

Item 6. The curing agent composition of item 5, wherein monocarboxylic acids is used in addition to the dimerized fatty acid.

Item 7. The curing agent composition of any of the preceding items, wherein the epoxide is selected from glycidyl ethers which derive from polyhydric phenols having an epoxide equivalent weight between 100 and 1500 g/eq.

Item 8. The curing agent composition of any of the preceding items, wherein the epoxide is a diglycidyl ether of bisphenol A and/or a diglycidyl ether of bisphenol F having an epoxide equivalent weight of 160 to 1000 g/eq, preferably 170-600 g/eq, more preferably 190-500 g/eq.

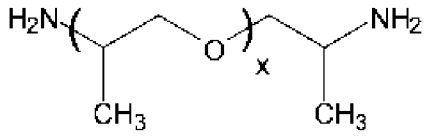
Item 9. The curing agent composition of any of the preceding items, wherein the amount of the epoxide is 1-25 wt.%, such as 3-20 wt.%, for example, 5-15 wt.%, based upon the amount of the polyaminoamide in preparation of the adduct of a polyaminoamide and an epoxide.

Item 10. The curing agent composition of any of the preceding items, the amount of adduct of a polyaminoamide and an epoxide is 20-70 wt.%, preferably 30-60 wt.%, based on the total amount of the waterborne curing agent composition.

Item 11. The curing agent composition of any of the preceding items, wherein the polyoxyalkyleneamine is selected from at least one amino-terminated polyoxyethylene, amino-terminated polyoxypropylene, or amino-terminated polyoxybutylene.

Item 12. The curing agent composition of any of the preceding items, wherein the polyoxyalkyleneamine includes an amino-terminated polyoxypropylene.

Item 13. The curing agent composition of any of the preceding items, wherein the polyoxyalkyleneamine includes



wherein x is an integer ranging from 2 to 70.

Item 14. The curing agent composition of any of the preceding items, wherein the polyoxyalkyleneamine has a weight percentage of 3-20 wt.%, preferably 5-15 wt.%, more preferably 5-10 wt.%, in the curing agent composition.

Item 15. The curing agent composition of any of the preceding items, wherein the cycloaliphatic amine includes one or more selected from the group consisting of isophorone diamine, methylcyclohexyldiamine, cyclohexyldiamine, 4,4'-methylenebis(cyclohexylamine), isomers of xylylenediamine, 1,2-bis aminomethylcyclohexane, 1,3-bis aminomethylcyclohexane, 1,4-bis aminomethylcyclohexane or hydrogenated copolymer of formaldehyde-aniline.

Item 16. The curing agent composition of any of the preceding items, wherein the cycloaliphatic amine has a weight percentage of 3-30 wt.%, preferably 5-25 wt.%, more preferably 8-20 wt.%, in the curing agent composition.

Item 17. A coating formulation comprising the curing agent composition of any one of the preceding items and an epoxy resin.

Item 18. A coating comprising the cured coating formulation of item 17.

Item 19. A coated article comprising a substrate and the coating of item 18 coated on the substrate.

The invention is now described in detail by the following examples. The scope of the invention should not be limited to the embodiments of the examples.

Examples

The following materials were employed in the examples.

NPEL-128 from Nanya Plastics Corporation is a diglycidyl ether of bisphenol A.
Dimer acid from Wilmar International is a dimerized fatty acid (C18-Unsatd. fatty acids dimers) Cas 61788-89-4.
TOFA from Li Shan Jiujiang is a tall oil fatty acid.
Tego Foamax 810 from Evonik Specialty Chemicals (Shanghai) Co., Ltd. is a polyether siloxane.
Zetasperse 3800 from Evonik Specialty Chemicals (Shanghai) Co., Ltd. is polyvinyl copolymer mixtures.
Dowanol PM from the Dow Chemical Company is 1-Methoxy-2-propanol.
Dowanol PPh from the Dow Chemical Company is 1-Phenoxy-2-propanol.

Some parameters in the examples were calculated or measured as follow.

a) Amine hydrogen equivalent weight in g/mol, or AHEW, is calculated as molecular weight of the amine divided by the number of amine hydrogen atoms per molecule.

b) Gardner color was measured according to Standard test method: ASTM D 1544-80.

c) Viscosity was measured according to ASTM D445-83 by a Brookfield DV-II+Pro Viscometer at 25 °C.

Example 1

Preparation of the curing agent composition according to the present invention

The synthesis of the curing agent was carried out in the following 4 steps.

Step 1: A 500 mL four neck round bottom flask with a dropping funnel, a nitrogen outlet and a stir bar was charged with Dimer acid 260g and TOFA 40g and heated to 80 °C under stirring. Tetraethylenepentamine (TEPA) 130g and triethylenetetramine (TETA) 30g were added to the flask over a 1 hour period and maintained at 230 °C for 2 hours to remove water and complete reaction to yield Intermediate (1).

Step 2: Intermediate (1) was cooled down to 90°C, and Bisphenol A epoxy resin NPEL 128 (EEW~184-190), 40g was charged into the flask by the dropping funnel over a period of 1 h to react with intermediate (1), and maintained under 90°C for 2 hours to yield Mixture (2).

Step 3: Mixture (2) was maintained at 90°C, and 20g 4,4'-diaminodicyclohexylmethane (PACM) and 10g Jeffamine® D230 were added into Mixture (2) by the dropping funnel during a period of 1 hour step by step to obtain Mixture (3).

Step 4: Mixture (3) was maintained at 70°C and 126 g water was added to obtain the curing agent, which was a clear amber liquid with a solid content of 80%, amine hydrogen equivalent weight (AHEW) of about ~150 and a Gardner color of 6-8 and viscosity of 15000 cps @ 25°C.

Comparative Example 1

Preparation of a curing agent composition, absent the polyoxyalkyleneamine

The synthesis of the curing agent of comparative example 1 was carried out in the following 4 steps.

Step 1: A 500 mL four neck round bottom flask with a dropping funnel, a nitrogen outlet and a stir bar was charged with Dimer acid 300g and heated to 80°C under stirring. Triethylenetetramine (TETA) 150g was added to the flask over a 1 hour period and maintained at 230°C for 2 hours to remove water and complete reaction to yield Intermediate (1).

Step 2: Intermediate (1) was cooled down to 90°C, and Bisphenol A epoxy resin 671x75PM (EEW~600-800; commercially available from Olin), 75% solid content in propylene glycol monomethyl ether (PM) 100g was charged into the flask by the dropping funnel over a period of 1 h to react with Intermediate (1), then PM was removed by distillation under 110°C for 2 hours to yield Mixture (2).

Step 3: Mixture (2) was maintained at 90°C, and 25g 3-aminomethyl-3,5,5-trimethlycyclohexylamine (IPDA) was added into Mixture (2) by the dropping funnel during a period of 1 hour to obtain Mixture (3).

Step 4: Mixture (3) was maintained at 70°C and 352 g water was added to obtain the curing agent, which was a clear amber liquid with a solid content of 60%, amine hydrogen equivalent weight (AHEW) of about ~195 and a Gardner color of 6-8 and viscosity of 33000 cps @ 25°C.

Comparative Example 2

Preparation of a curing agent composition, absent the polyoxyalkyleneamine

The synthesis of the curing agent of comparative example 2 was carried out in the following 4 steps.

Step 1: A 500 mL four neck round bottom flask with a dropping funnel, a nitrogen outlet and a stir bar was charged with Dimer acid 260g and TOFA 40g and heated to 80°C under stirring. Tetraethylenepentamine (TEPA) 130g and triethylenetetramine (TETA) 30g were added to the flask over a 1 hour period and maintained at 230°C for 2 hours to remove water and complete reaction to yield Intermediate (1).

Step 2: Intermediate (1) was cooled down to 90°C, and Bisphenol A epoxy resin NPEL 128 (EEW~184-190), 40g was charged into the flask by the dropping funnel over a period of 1 h to react with Intermediate (1), and under 90°C for 2 hours to yield Mixture (2).

Step 3: Mixture (2) was maintained at 90°C, and 30g 4,4'-diaminodicyclohexylmethane (PACM) was added into Mixture (2) by the dropping funnel during a period of 1 hour step by step to obtain Mixture (3).

Step 4: Mixture (3) was maintained at 70°C and 126 g water was added to obtain the curing agent, which was a hazy liquid with a solid content of 80%, amine hydrogen equivalent weight (AHEW) of about ~138 and a Gardner color of 6-8 and viscosity of 17500 cps @ 25°C.

Comparative Example 3

Preparation of a curing agent composition, absent the epoxide-polyaminoamide adduct

The synthesis of the curing agent of comparative example 3 was carried out in the following 3 steps.

Step 1: A 500 mL four neck round bottom flask with a dropping funnel, a nitrogen outlet and a stir bar was charged with Dimer acid 260g and TOFA 40g and heated to 80°C under stirring. Tetraethylenepentamine (TEPA) 130g and triethylenetetramine (TETA) 30g were added to the flask over a 1 hour period and

maintained at 230°C for 2 hours to remove water and complete reaction to yield Intermediate (1).

Step 2: Intermediate (1) was maintained at 90°C, and 20g 4,4'-diaminodicyclohexylmethane (PACM) and Jeffamine®D230 10g were added into Intermediate (1) by the dropping funnel during a period of 1 hour step by step to obtain Mixture (2).

Step 3: Mixture (2) was maintained at 70°C and 199 g water was added to obtain the curing agent, which was a turbid liquid with a solid content of 70%, amine hydrogen equivalent weight (AHEW) of about ~150 and a Gardner color of 6-8 and viscosity of 3500 cps @ 25°C.

Coating performance test

Waterborne coating used for container application (correlative standards of water based coating for freight container HJ/T E06-2015) requires fully curing at elevated temperature, 60°C-80°C for 30 mins, resulting in finished coating film, which can generate good adhesion, corrosion resistance with quite low VOC emission. For example for internal top coat, external mid-coat and external top coat, VOC was seriously limited < 100g/L. Whereas, other coating sub-markets, like steel structure, machinery application usually cured under ambient temperature with diverse conditions, not only focused on good corrosion resistance and mechanical properties, but also required epoxy coating to show robust properties at thin dry film thickness, 30-45μm, like early film water immersion resistance, and early film water spot resistance. In this regard, following special test methods were conducted:

Water immersion resistance test process: once spray coating on Q-panel, leave for 24 hours at ambient temperature (20-27°C), then dip the bottom halves of the panels into water.

Water spot resistance test process: once spray coating on Q-panel, leave for 24 hours at ambient temperature, then drop water on panel surface then cover water by watch glass.

In order to determine the properties of the inventive curing agent in pigment formulation, a coating formulation was prepared by mixing Epoxy resin part A based on solid epoxy resin dispersion (Ancarez AR555, Evonik) with waterborne curing agent part B. The formulations for part A and part B are shown below in Table 1 and Table 2, respectively. The film properties are summarized in Table 3.

Surprisingly, it was found that only the inventive formulation using the inventive curing agent gave excellent early film properties as cured only 24h at 23°C as shown in Table 3. The inventive formulation also showed balanced mechanical properties, like adhesion and impact resistance, due to good compatibility of the polyamide adduct backbone structure with polyoxyalkyleneamine structure. In contrast, Comparative formulations 1-2 without polyoxyalkyleneamine and Comparative formulation 3 without the adduct of a polyaminoamide and an epoxide all showed bubbles and rust, and significantly lower salt spray resistance.

Table 1 Lab starting coating formulation-Epoxy resin part A

Materials		Amount(wt.%)
Distilled water	-	8
Tego Foam 810	Defoamer	0.3
Zetasperse 3800	Dispersant	1.2
Dowanol PM	Co-solvent	4.8
Dowanol PPh	Co-solvent	1.5
Talc (1250 mesh)	Filler	16.5
Zinc phosphonic	Anti-corrosive pigment	8.8
Red iron oxide	Pigment	7.5
Mica (500 mesh)	Filler	8
Dispersion condition: disperse at 3000rpm for 30-60min with a ø4.5cm dentate stirrer		
AR555 (53-55%) EEW = 1300	WB epoxy resin	43.4
Dispersion condition: 1500rpm disperse 15min with ø4.5cm dentate stirrer. Rest over night		
Total amount of Part A		100
PVC = 37.8%, NVM= 65.2%, NVV= 50.4%, Density=1.45g/ml		

Note:

PVC: Pigment volume concentration

NVM: non-volatile matter

NVV: non-volatile matter by volume

Density: Standard test method: ASTM D1475

Table 2 Lab starting coating formulation-waterborne curing agent part B

Part B / Materials		Part B-Comparative formulation 1	Part B-Inventive formulation	Part B-Comparative formulation 2	Part B-Comparative formulation 3
Comparative Example 1	Curing agent	100g			
Example 1	Curing agent		100g		
Comparative Example 2	Curing agent			100g	
Comparative Example 3	Curing agent				100
Water	Curing agent	115g	115g	115g	115g
PM	Co-solvent	60g	60g	60g	60g
DPnB	Co-solvent	15g	15g	15g	15g
Total		290g	290g	290g	290g
AHEW		551	435	402	435

Note:

DPnB: 2-(2-butoxyethoxy)ethanol

Table 3 Overall coating film performance evaluation in pigment formulation

	Sample 1	Sample 2	Sample 3	Sample 4
Part A lab formulation	100 g	100 g	100 g	100 g
Part B- Comparative formulation 1	18.4 g			
Part B- Inventive formulation		14.5 g		
Part B- Comparative formulation 2			13.4g	
Part B- Comparative formulation 3				14.5 g
Dry speed[1]/mins	15	15	25	15
DFT[2]/μ	36	37	41	40
Water immersion resistance/cure 24h	Small bubbles and rusty	Good and no surface defects	Lots of Bubbles and rusty	Lots of Bubbles and rusty
Water spot resistance/cure 24h	Bubbles	Good and no surface defects	Some bubbles	bubbles
Salt spray resistance[3] (hour)	<150	>300	<150	<100
Adhesion[4]	5	5	4	3
Impact resistance/cm.kg	50	70	45	30

[1], determined according to ASTM D5895

[2], determined according to ASTM D7091-13; DFT: Dry film thickness

[3], determined according to ASTM D714-2009, JTT 810-2011

[4], determined according to ASTM D3359-93,

Note:

curing condition: 7days at 23°C with 75% RH,

adhesion rating: 5B-No film loss, excellent, 0B-complete failure, poor

stoichiometry of epoxide/amine =1/1

impact resistance: Standard test method: ASTM D2794-93

Figure 1 clearly demonstrates the superior early water immersion resistance of the sample using the curing agent according to the present invention. The superior coating performance can be attributed to hydrophobic barrier properties provided by polyamide adduct and cycloaliphatic structure and good compatibility benefits from polyoxyalkyleneamine.

The overall performance of the inventive curing agent used in a zinc-rich primer was tested.

A zinc-rich primer coating formulation was prepared by mixing the formulation of Epoxy resin part A as shown in Table 4 with the formulation of waterborne curing agent part B as shown in Table 2. Coating performance like water immersion resistance, water spot resistance and salt spray resistance are shown in Table 5.

As shown in Table 5, Comparative formulations 1-3 all showed whitish surface due to water penetrating into coating film and destroyed film as only cured 24h at 23°C with 75% RH. Whereas Sample 6 using the inventive curing agent gave good early film properties as cured at the same condition. Based on the salt spray test data as shown in Table 5, the inventive curing agent also showed balanced corrosion resistance even with quite thin film thickness ~40μm which benefits from combined contribution of polyamide adduct, cycloaliphatic barrier structure and good compatibility of polyoxyalkyleneamine with resin part of the polyamide adduct. Figure 2 clearly demonstrates the superior early water spot resistance of the sample using the curing agent according to the present invention.

Table 4 Lab zinc-rich primer starting coating formulation-Epoxy resin part A

Part A components	Raw materials		Weight %
1	Epoxy Resin	RE600	28.0
2	Reactive Diluent	Epodil 742	3.0
3	Pigment	Metallic Zinc	64.2
4	Plasticizer	Benzyl alcohol	2.0
5	Solvent	PM	2.0
6	Additive-rheological agent	Bentone SD2	0.5
7	Additive-defoamer	Surfynol DF62	0.1
8	Additive-defoamer	Surfynol 420	0.1
9	Additive-wetting agent	Surfynol CT 111	0.1
Total			100.0

Note:

RE600: one commodity modified epoxy resin used for Waterborne coating, commercially available from Shanghai Huayi Holding Group Co., Ltd.

Epodil 742: available from Evonik

Table 5 Overall coating film performance evaluation in zinc-rich primer formulation

	Sample 5	Sample 6	Sample 7	Sample 8
Part A-lab formulation	100	100	100	100
Part B-Comparative formulation 1	33.5			
Part B-Inventive formulation		26.5		
Part B-Comparative formulation 2			24.5	
Part B-Comparative formulation 3				26.5
DFT[1]/μ	39	40	39	42
Water immersion resistance/Cured 24h	A little whitish	Good and no surface defects	Bubbles and whitish	Bubbles and whitish
Water spot resistance/cured 24h	A little whitish	Good and no surface defects	Bubbles and whitish	Whitish
Salt spray resistance[2] (hour)	<400	>600	<400	<100

[1] determined according to ASTM D7091-13

[2] determined according to ASTM D714-2009, JTT 810-2011,

Note:

curing condition: 7days at 23°C with 75% RH,

stoichiometry epoxide/amine =1/1

As used herein, terms such as “comprise(s)” and the like as used herein are open terms meaning 'including at least' unless otherwise specifically noted.

All references, tests, standards, documents, publications, etc. mentioned herein are incorporated herein by reference. Where a numerical limit or range is stated, the endpoints are included. Also, all values and subranges within a numerical limit or range are specifically included as if explicitly written out.

The above description is presented to enable a person skilled in the art to make and use the invention, and is provided in the context of a particular application and its requirements. Various modifications to the preferred embodiments will be readily apparent to those skilled in the art, and the generic principles defined herein may be applied to other embodiments and applications without departing from the spirit and scope of the invention. Thus, this invention is not intended to be limited to the embodiments shown, but is to be accorded the widest scope consistent with the principles and features disclosed herein. In this regard, certain embodiments within the invention may not show every benefit of the invention, considered broadly.

Claims

1. A waterborne curing agent composition for epoxy coatings comprising:
a) an adduct of a polyaminoamide and an epoxide;
b) a polyoxyalkyleneamine;
c) a cycloaliphatic amine; and
d) water.

2. The curing agent composition of claim 1, wherein the polyaminoamide is based on the reaction product of a carboxylic acid having 20-60 carbon atoms and at least two carboxyl groups and/or an ester derived from a carboxylic acid having 20-60 carbon atoms and at least two carboxyl groups with a polyalkyleneamine.

3. The curing agent composition of claim 2, wherein the polyalkyleneamine is selected from polyethyleneamines, polypropyleneamines, aminopropylated ethylenediamines, aminopropylated propylenediamines and any combinations thereof.

4. The curing agent composition of claim 2 or 3, wherein the polyalkyleneamine is TETA, TEPA, or a mixture of TETA and TEPA.

5. The curing agent composition of any of claims 2-4, wherein the carboxylic acid is a dimerized fatty acid.

6. The curing agent composition of claim 5, wherein monocarboxylic acids is used in addition to the dimerized fatty acid.

7. The curing agent composition of any of the preceding claims, wherein the epoxide is selected from glycidyl ethers which derive from polyhydric phenols having an epoxide equivalent weight between 100 and 1500 g/eq.

8. The curing agent composition of any of the preceding claims, wherein the epoxide is a diglycidyl ether of bisphenol A and/or a diglycidyl ether of bisphenol F having an epoxide equivalent weight of 160 to 1000 g/eq, preferably 170-600 g/eq, more preferably 190-500 g/eq.

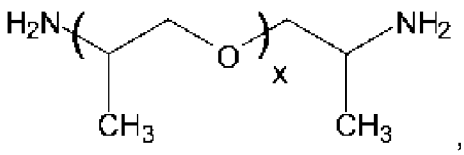
9. The curing agent composition of any of the preceding claims, wherein the amount of the epoxide is 1-25 wt.%, such as 3-20 wt.%, for example, 5-15 wt.%, based upon the amount of the polyaminoamide in preparation of the adduct of a polyaminoamide and an epoxide.

10. The curing agent composition of any of the preceding claims, the amount of adduct of a polyaminoamide and an epoxide is 20-70 wt.%, preferably 30-60 wt.%, based on the total amount of the waterborne curing agent composition.

11. The curing agent composition of any of the preceding claims, wherein the polyoxyalkyleneamine is selected from at least one amino-terminated polyoxyethylene, amino-terminated polyoxypropylene, or amino-terminated polyoxybutylene.

12. The curing agent composition of any of the preceding claims, wherein the polyoxyalkyleneamine includes an amino-terminated polyoxypropylene.

13. The curing agent composition of any of the preceding claims, wherein the polyoxyalkyleneamine includes



wherein x is an integer ranging from 2 to 70.

14. The curing agent composition of any of the preceding claims, wherein the polyoxyalkyleneamine has a weight percentage of 3-20 wt.%, preferably 5-15 wt.%, more preferably 5-10 wt.%, in the curing agent composition.

15. The curing agent composition of any of the preceding claims, wherein the cycloaliphatic amine includes one or more selected from the group consisting of isophorone diamine, methylcyclohexyldiamine, cyclohexyldiamine, 4,4'-methylenebis(cyclohexylamine), isomers of xylylenediamine, 1,2-bis aminomethylcyclohexane, 1,3-bis aminomethylcyclohexane, 1,4-bis aminomethylcyclohexane or hydrogenated copolymer of formaldehyde-aniline.

16. The curing agent composition of any of the preceding claims, wherein the cycloaliphatic amine has a weight percentage of 3-30 wt.%, preferably 5-25 wt.%, more preferably 8-20 wt.%, in the curing agent composition.

17. A coating formulation comprising the curing agent composition of any one of the preceding claims and an epoxy resin.

18. A coating comprising the cured coating formulation of claim 17.

19. A coated article comprising a substrate and the coating of claim 18 coated on the substrate.



Sample 1 Sample 2 Sample 3 Sample 4

Fig. 1



Sample 5 Sample 6 Sample 7 Sample 8

Fig. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/CN2023/106960

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08G59/50 C08G59/54 C09D163/00 C08G59/18
ADD.

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)
C08G C09J C09D

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 99/45053 A1 (SHELL INT RESEARCH [NL]) 10 September 1999 (1999-09-10) claims 1-16 Examples; table 1	1-19
A	US 2013/072597 A1 (ELMORE JIM [US] ET AL) 21 March 2013 (2013-03-21) claims 1-13	1-19
A	WO 2022/165729 A1 (EVONIK OPERATIONS GMBH [DE]; YAN ZHENLONG [CN]) 11 August 2022 (2022-08-11) Examples claims 1-21	1-19

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

☒ See patent family annex.

* Special categories of cited documents :

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

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

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
30 November 2023	19/12/2023

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Pouilley, Delphine

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/CN2023/106960

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9945053 A1	10-09-1999	AT E241658 T1	15-06-2003
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		CN 1292008 A	18-04-2001
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