Abstract: An epoxy modified cement composition having (A) epoxy resin comprising at least one epoxy resin, (B) a curing agent comprising water and at least one amine compound selected from the group consisting of polyamine, polyamide, a polyamidoamine polyamine-polyepoxide adduct, polyamide-polyepoxide adduct, and a mixture of at least two of these compounds, and (C) a solid component comprising at least one hydraulic inorganic binder. The curing agent is at least one amine compound selected from the group consisting of polyamine, polyamide, a polyamidoamine polyamine-polyepoxide adduct, polyamide-polyepoxide adduct or a mixture of at least two of these compounds. The amine compound contains compounds sufficiently contact reactive to epoxy resin and the solid component to form a solid article having a compressive strength greater than about 70 MPa.
EPOXY MODIFIED CEMENT COMPOSITION

BACKGROUND OF THE INVENTION

[0001] The present disclosure relates to water-based curing agents and epoxy modified cement systems exhibiting a beneficial combination of properties including excellent compressive strength.

[0002] Epoxies are known for their excellent adhesion, chemical and heat resistance, good-to-excellent mechanical properties, and good electrical insulating properties. Cured epoxy resin systems have found extensive applications ranging from coatings, adhesives, and composites. Specific examples include epoxy composites using carbon fiber and fiberglass reinforcements, protective coatings for metal surfaces, and construction products for concrete, cementitious or ceramic substrates, often referred to as civil engineering applications, such as formulations for concrete flooring.

[0003] Cured epoxy resin systems consist of two components that may chemically react with each other to form a cured epoxy, which is a hard, duroplastic material. The first component is an epoxy resin and the second component is a curing agent, often referred to as a hardener. Epoxy resins are substances or mixtures which contain epoxide groups. The curing agents include compounds which are reactive to the epoxide groups of the epoxy resins, such as amines, carboxylic acid, and mercaptanes (H. Lee and K. Neville "Handbook of Epoxy Resins" McGraw Hill, New York, 1967, pages 5-1 to 5-24). The epoxy resins may be cross-linked or cured by curing agents. The curing process is the chemical reaction of the epoxide groups in the epoxy resins and the reactive groups in the curing agents. The curing converts the epoxy resins, which have a relatively low molecular weight, into relatively high molecular weight materials by chemical addition of the curing agents to the epoxy resins. Additionally, the curing agent may contribute to many of the properties of the cured epoxy.

[0004] For flooring systems, there are diverse requirements. Desired properties may be, for example, aesthetic appearance, mechanical strengths and chemical resistance, adhesion strength. There are other requirements, for example, good handling properties, solvent free and good smoothness. Current flooring materials include flooring materials that are organic or organic hybrid systems.

[0005] It is difficult to combine the desired properties, some of which are contradictory in terms of their physical requirements, within a flooring coating system. When using solvent free epoxy resin coatings, for example, a freshly prepared concrete surface can generally not be coated, for example, until after 28 days, since the residue moisture
content of concrete must not exceed 5%. In these known systems, if the time is not permitted to elapse, there is a risk of blistering in epoxy coating. In systems that utilize a solvent-free flooring coating typically results in a low impact resistance. Typical requirements for such flooring coating system are compressive strength of at least 40MPa, flexural strength of at least 10MPa, impact resistance of at least 50kg cm, bonding strength of at least 1.5MPa. The compressive strength is very important property of flooring materials. The flooring coatings with high compressive strength usually serve heavy duty traffic and longer durability. The mechanical properties, such as compressive strength and chemical stability, of conventional two component waterborne epoxy coating is relatively low.

[0006] U.S. Patent Publication No. 201 1166259A discloses a compound particularly suitable as curing agent for epoxy resin, which can be used in the form of aqueous curing agent and form stable aqueous emulsion in particular. This facilitates the formulation of epoxy modified cement compounds for use primarily as coating. In an embodiment, ECC compositions with invented curing agent have good processability, have very good mechanical properties and hardener with impeccable surface appearance. U.S. Patent Publication No. 201 1166259A lacks desired compressive strength for flooring coatings. The curing agents disclosed in U.S. Patent Publication No. 201 1166259A have relatively high viscosity (Example 13 of U.S. Patent Publication No. 201 1166259A, for example, has 16 Pa.s at 50% solid), high viscosity of curing agent when formulated into ECC composition may cause inferior flowability and uneven finish and then may need more water demands to achieve smooth finish. U.S. Patent Publication No. 201 1166259A remains silent to the ability to emulsify liquid epoxy resin and may not be used with liquid epoxy resin in epoxy cement concrete (ECC) compositions.

[0007] AU201 40292167 discloses a multicomponent composition comprising A) a binder component (A) comprising at least one epoxy resin, B) an aqueous hardener component (B) comprising at least one amine compound as amine hardener and water and C) a solid component comprising at least one hydraulic inorganic binder, preferably cement, wherein the multicomponent composition, based on the total weight, comprises at least 8% by weight of organic binder, where the total amount of epoxy resin and amine hardener constitutes the organic binder. The organic binder content is at least 8 wt%. Binder content is an understood term for polymer content which comprises solid of epoxy resin and solid of curing agent in the composition. Binder content has significant impact on formulation cost and performance. Generally, high binder content gives better
strength and other performance but also higher cost, which limit its use because usually binder (i.e. epoxy polymer) is expensive. Binder contents at the required levels of AU201402921.67 are very expensive and not cost effective. AU201402921.67 discloses primarily thin coating end applications.

[0008] EP2851351A1 The invention relates to a multi-component composition, comprising A) a binder component (A) comprising at least one epoxy resin, B) a hardener component (B) comprising at least one amine compound as an amine hardener, and C) a solid component (C) comprising a hydraulic inorganic binder, wherein the hydraulic inorganic binder is a ternary binder composed of aluminous cement, calcium sulfate, and optionally Portland cement, wherein the solid component (C) contains 2 to 30 wt.% aluminous cement, 1 to 16 wt.% calcium sulfate, and 0 to 20 wt.% Portland cement. The multi-component composition is suitable in particular as a self-levelling floor-levelling compound for a floor covering or as a mortar. The organic binder content is no more than 4 wt%. EP2851351A1 discloses that the composition utilized is a cost effective composition by replacement for binder of polymer with inorganic binder. However, the disclosed compositional ranges permitting this cost effective composition result in undesirable strength and workability.

[0009] JP4794007B2 discloses a coating material composition as a water-base epoxy resin mortar composition comprising hydraulic cement, aggregate and a water-base epoxy resin, and in which the weight ratio between the hydraulic cement and water is 0.3 to 0.4, also, the resin solid content is 4 to 10% to the total solid content weight, the quantity of all pores in a hardened matter is 0.05 to 0.2 cc/g, its viscosity directly after mixing is 0.3 to 8 Pa s/23 °C, and also, T.I value is 1.0 to 1.5, and in which the hydraulic cement is white cement. JP4794007 fails to disclose desirable compressive strength values for flooring coatings and is limited to a non-emulsifying epoxy resin.

[0010] CN103951352 discloses an aqueous epoxy-modified cement mortar which comprises the following components in percentage by weight: 3-25% of an aqueous epoxy emulsion, 15-25% of cement, 30-70% of aggregates, 1-5% of an assistant and 2-6% of water. The aqueous epoxy emulsion consists of an epoxy emulsion and a Mannich type aqueous epoxy hardener, wherein the epoxy emulsion and the Mannich type aqueous epoxy hardener are prepared in a molar ratio of epoxy groups to amine hydrogen of (1:0.85)-(1:1.15). CN103951352 is limited to an epoxy-modified cement mortar and fails to disclose the combination of properties for use as self-levelling flooring coating.
[0011] JP2014181137A discloses a coating material composition that is an aqueous epoxy resin mortar composition including a hydraulic cement, an aggregate and an aqueous epoxy resin in which the weight ratio of the hydraulic cement and water is not less than 0.33 to not more than 0.37; the weight of resin solids is not less than 8% to not more than 9%; the total pore volume of the cured product is not more than 0.10 cc/g to not more than 0.15 cc/g; and the T.I value is not less than 1.1 to not more than 1.3. The aqueous epoxy resin comprises a non-emulsifying epoxy resin and a self-emulsifiable curing agent. The coating material composition has a viscosity of not less than 2 Pa s/23 °C to not more than 3 Pa s/23 °C, uses white cement as a hydraulic cement, and is coated in a thickness of 0.8-1.2 mm on a base concrete and cured. The floor construction method uses the coating material composition. The floor structure is formed by the method. JP2014181137A fails to disclose desirable compressive strength values for flooring coatings and is limited to a non-emulsifying epoxy resin.

[0012] The disclosure of the foregoing publications, including patents and patent applications, is hereby incorporated by reference.

[0013] There are numerous amine-based curing agents and amine-epoxy compositions that are employed in the amine-epoxy coating industry; however, known products fail to completely address the needs or solve the problems noted above. Accordingly, it is to this end that the present invention is directed. Specifically, it has not been possible to manufacture epoxy resin modified cementitious systems having high compressive strength more than 70MPa, while combined with other properties, such as good impact resistance, smooth finish and excellent adhesion on wet concrete. Methods for making epoxy curing agents and cured epoxy cement products having compressive strength more than 70MPa, desirable impact resistance, finish and excellent adhesion on wet concrete and not suffering from the above drawbacks would be desirable in the art.

**BRIEF SUMMARY OF THE INVENTION**

[0014] The present disclosure discloses an epoxy modified cement system exhibiting a beneficial combination of properties including excellent compressive strength of greater than about 70 MPa, high flexural strength and high impact resistance, good adhesion and smooth finish. The epoxy modified cement system, according to the present disclosure, is advantageously a water-based epoxy cement composition, comprising at least 3 components including epoxy resin, water-based curing agent and cement aggregates. The system is suitable for use in coatings, adhesives, mortars, grouts and
polymer modified concrete, especially suitable for high performance self-levelling flooring coatings.

[0015] In one embodiment, a water-based curing agent composition including water and an amine compound selected from the group consisting of polyamine, polyamide, a polyamidoamine polyamine-polyepoxide adduct, polyamide-polyepoxide adduct, and a mixture of at least two of these compounds. The amine compound contains compounds sufficiently contact reactive to epoxy resin and a solid component to form a solid article having a compressive strength greater than about 70 MPa.

[0016] In another exemplary embodiment, an epoxy modified cement composition having (A) epoxy resin comprising at least one epoxy resin, (B) a curing agent comprising water and at least one amine compound selected from the group consisting of polyamine, polyamide, a polyamidoamine polyamine-polyepoxide adduct, polyamide-polyepoxide adduct, and a mixture of at least two of these compounds, and (C) a solid component comprising at least one hydraulic inorganic binder. The curing agent is at least one amine compound selected from the group consisting of a polyamine, polyamide, a polyamidoamine polyamine-polyepoxide adduct, polyamide-polyepoxide adduct, or a mixture of at least two of these compounds. The amine compound contains compounds sufficiently contact reactive to epoxy resin and the solid component to form a solid article having a compressive strength greater than about 70 MPa.

[0017] In another exemplary embodiment, an epoxy system comprising the contact product of (A) epoxy resin comprising at least one epoxy resin, (B) a curing agent comprising water and at least one amine compound, and (C) a solid component comprising at least one hydraulic inorganic binder. The epoxy system forms an article having a compressive strength greater than about 70 MPa.

[0018] In another exemplary embodiment, an article comprising the contact product of (A) epoxy resin comprising at least one epoxy resin, (B) a water-based curing agent comprising at least one amine compound and water, and (C) a solid component comprising at least one hydraulic inorganic binder. The article has a compressive strength greater than about 70 MPa.

[0019] Other features and advantages of the present disclosure will be apparent from the following more detailed description of the preferred embodiment, taken in conjunction with the accompanying drawings which illustrate, by way of example, the principles of the invention.
DETAILED DESCRIPTION OF THE INVENTION

[0020] The coating, according to the epoxy modified cement composition, has excellent compressive strength, flexural strength, impact resistance and good adhesion to wet substrate. The epoxy modified cement composition may be used for coating, adhesive, sealer, grouting and mortar. Particularly, it is suitable for a mortar or coating, more particularly used for self-leveling floor coating.

[0021] The epoxy modified cement composition, according to the present disclosure, includes a combination of (A) epoxy resin comprising at least one epoxy resin, (B) a curing agent comprising water and at least one amine compound selected from the group consisting of polyamine, polyamide, a polyamidoamine polyamine-polyepoxide adduct, polyamide-polyepoxide adduct, and a mixture of at least two of these compounds, and (C) a solid component comprising at least one hydraulic inorganic binder. The curing agent is at least one amine compound selected from the group consisting of a polyamine, polyamide, a polyamidoamine polyamine-polyepoxide adduct, polyamide-polyepoxide adduct, or a mixture of at least two of these compounds.

[0022] The epoxy modified cement composition includes a curing agent having an amine compound in a sufficient concentration and in a ratio such that a cured epoxy modified cement article formed from the epoxy modified cement composition has a compressive strength greater than about 70 MPa or greater than about 75 MPa or greater than about 80 MPa or greater than 82 Mpa as measured by, for example, European standard BS EN196-1:2005. The compressive strength in one embodiment is measured at 7 days after application of the epoxy modified cement composition. In another embodiment, the compressive strength is measured 28 days after the application of the epoxy modified cement composition.

[0023] The terms "contact product" and "contact reactable" are used herein to describe compositions and the properties resulting as a result of the components being contacted together in any order, in any manner, and for any length of time. For example, the components may be contacted by blending or mixing. Further, contacting of any component may occur in the presence or absence of any other component of the compositions or formulations described herein. Still further, two or more of the components of the contact product may react to form other components composing the composition. Combining additional materials or components may be done by any method known to one of skill in the art.
[0024] The relative amount chosen for the epoxy composition, the curing agent composition and the solid component may vary depending upon, for example, the end-use article, its desired properties, and the fabrication method and conditions used to produce the end-use article. In the epoxy modified cement composition, water to hydraulic inorganic binder in the solid component (C) is in the range from 0.1 to 1, more preferably 0.3 to 0.5. In another embodiment, water may be added as a standalone component. In the epoxy modified cement composition, percentage of solid amount of epoxy resin and hardener, also known as binder content is in the range from 1.0% to 50%, preferably 2.0% to 20%, more preferably 3.0% to 8.0%. The epoxy modified cement composition, solid amount of epoxy resin and hardener ratio to hydraulic inorganic binder by weight, also known as polymer to cement ratio, is in the range of 0.05 to 1, preferably 0.1 to 0.5, more preferably 0.15 to 0.35. In the epoxy modified cement composition, the stoichiometric ratio of the curing agent functionality to the epoxy resin functionality is in the range from 0.7 to 1.3.

[0025] In a preferred embodiment, the component (A) contains water. The component (A) preferably is an aqueous epoxy resin dispersion, wherein it can be an epoxy resin emulsion, a so-called "emulsifiable epoxy resin", or an epoxy resin dispersion.

[0026] An epoxy resin dispersion preferably comprises additional water, at least one epoxy resin, at least an emulsifier, in particular a non-ionic emulsifier. Epoxy resin dispersions or emulsions may have, for example, a solids content in the range of 40-70 wt.%. Component (A) may contain one or more further additives.

[0027] Epoxy modified cement compositions of the present disclosure comprise the contact product of the curing agent composition, a solid component and an epoxy composition comprising at least one multifunctional epoxy resin. Multifunctional epoxy resin, as used herein, describes compounds containing 2 or more 1,2-epoxy groups per molecule.

[0028] The epoxy resin is selected from the group consisting of aromatic epoxy resin, alicyclic epoxy resin, aliphatic epoxy resin, glycidyl ester resin, thio glycidyl ether resin, N-glycidyl ether resin, and combinations thereof.

[0029] Aromatic epoxy resin suitable for use in the present disclosure comprises the glycidyl ethers of polyhydric phenols, including the glycidyl ethers of dihydric phenols. Illustrative examples include, but are not limited to, the glycidyl ethers of resorcinol, hydroquinone, bis-(4-hydroxy-3,5-difluorophenyl)-methane, 1,1-bis-(4-hydroxyphenyl)-ethane, 2,2-bis-(4-hydroxy-3-methylphenyl)-propane, 2,2-bis-(4-hydroxy-3,5-dichlorophenyl) propane, 2,2-bis-(4-hydroxyphenyl)-propane (commercially known as...
bisphenol A), bis-(4-hydroxyphenyl)-methane (commercially known as bisphenol F, and which may contain varying amounts of 2-hydroxyphenyl isomers), and the like, or any combination thereof. Additionally, advanced dihydric phenols of the following structure also are useful in the present disclosure:

\[
\text{O} - \left[ \text{O} - \text{R} - \text{O} - \text{OH} \right]_{p} \text{O} - \text{R} - \text{O} - \text{O} - \text{R}
\]

wherein R' is a divalent hydrocarbon radical of a dihydric phenol, such as those dihydric phenols listed above, and p is an average value between 0 and about 7. Materials according to this formula may be prepared by polymerizing mixtures of a dihydric phenol and epichlorohydrin, or by advancing a mixture of a diglycidyl ether of the dihydric phenol and the dihydric phenol. While in any given molecule the value of p is an integer, the materials are invariably mixtures which may be characterized by an average value of p which is not necessarily a whole number. Polymeric materials with an average value of p between 0 and about 7 may be used in one aspect of the present disclosure.

[0030] In one aspect of the present disclosure, the at least one multifunctional epoxy resin is a diglycidyl ether of bisphenol-A (DGEBA), an advanced or higher molecular weight version of DGEBA, a diglycidyl ether of bisphenol-F, a diglycidyl ether of novolac resin, or any combination thereof. Higher molecular weight versions or derivatives of DGEBA are prepared by the advancement process, where excess DGEBA is reacted with bisphenol-A to yield epoxy terminated products. The epoxy equivalent weights (EEW) for such products range from about 450 to about 3000 or more. Because these products are solid at room temperature, they are often referred to as solid epoxy resins.

[0031] In certain embodiments, the at least one multifunctional epoxy resin is the diglycidyl ether of bisphenol-F or bisphenol-A represented by the following structure:

\[
\text{R}'' = \text{H or CH}_3, \\
\text{DGEBA when } \text{R}'' = \text{CH}_3
\]

[0032] DGEBA or advanced DGEBA resins are often used in coating formulations due to a combination of their low cost and generally high performance properties. Commercial grades of DGEBA having an EEW ranging from about 174 to about 250, and more commonly from about 185 to about 195, are readily available. At these low molecular weights, the epoxy resins are liquids and are often referred to as liquid epoxy.
resins. It is understood by those skilled in the art that most grades of liquid epoxy resin are slightly polymeric, since pure DGEBA has an EEW of about 174. Resins with EEWs between about 250 and about 450, also generally prepared by the advancement process, are referred to as semi-solid epoxy resins because they are a mixture of solid and liquid at room temperature. Generally, multifunctional resins with EEWs based on solids of about 160 to about 750 are useful in the present disclosure. In another aspect, the multifunctional epoxy resin has an EEW in a range from about 170 to about 250.

[0033] Examples of alicyclic epoxy compounds include, but are not limited to, polyglycidyl ethers of polyols having at least one alicyclic ring, or compounds including cyclohexene oxide or cyclopentene oxide obtained by epoxidizing compounds including a cyclohexene ring or cyclopentene ring with an oxidizer. Some particular examples include, but are not limited to, hydrogenated bisphenol A diglycidyl ether; 3,4-epoxy cyclohexylmethyl-3,4-epoxycyclohexyl carboxylate; 3,4-epoxy-1-methylcyclohexyl-3,4-epoxy-1-methylhexane carboxylate; 6-methyl-3,4-epoxycyclohexylmethyl-6-methyl-3,4-epoxycyclohexane carboxylate; 3,4-epoxy-3-methylcyclohexylmethyl-3,4-epoxy-3-methylcyclohexane carboxylate; 3,4-epoxy-5-methylcyclohexylmethyl-3,4-epoxy-5-methylcyclohexane carboxylate; bis(3,4-epoxycyclohexylmethyl)adipate; methylene-bis(3,4-epoxycyclohexane); 2,2-bis(3,4-epoxycyclohexyl)propane; dicyclopentadiene diepoxide; ethylene-bis(3,4-epoxycyclohexane carboxylate); diocyl epoxyhexahydrophthalate; and di-2-ethylhexyl epoxyhexahydrophthalate.

[0034] Examples of aliphatic epoxy compounds include, but are not limited to, polyglycidyl ethers of aliphatic polyols or alkylene-oxide adducts thereof, polyglycidyl esters of aliphatic long-chain polybasic acids, homopolymers synthesized by vinyl-polymerizing glycidyl acrylate or glycidyl methacrylate, and copolymers synthesized by vinyl-polymerizing glycidyl acrylate or glycidyl methacrylate and other vinyl monomers. Some particular examples include, but are not limited to, glycidyl ethers of polyols, such as 1,4-butanediol diglycidyl ether; 1,6-hexanediol diglycidyl ether; a triglycidyl ether of glycerin; a triglycidyl ether of trimethylol propane; a tetraglycidyl ether of sorbitol; a hexaglycidyl ether of dipentaerythritol; a diglycidyl ether of polyethylene glycol; and a diglycidyl ether of polypropylene glycol; polyglycidyl ethers of polyether polyols obtained by adding one type, or two or more types, of alkylene oxide to aliphatic polyols, such as ethylene glycol, propylene glycol, trimethylol propane, and glycerin.

[0035] Glycidyl ester resins are obtained by reacting a polycarboxylic acid compound having at least two carboxyl acid groups in the molecule and epichlorohydrin. Examples of such polycarboxylic acids include aliphatic, cycloaliphatic, and aromatic polycarboxylic
acids. Examples of aliphatic polycarboxylic acids include oxalic acid, succinic acid,
glutaric acid, adipic acid, pimelic acid, sebacic acid, suberic acid, azelaic acid, or
dimerised or trimerised linoleic acid. Cycloaliphatic polycarboxylic acids include
tetrahydrophthalic acid, 4-methyltetrahydrophthalic acid, hexahydrophthalic acid or 4-
methylhexahydrophthalic acid. And aromatic polycarboxylic acids include phthalic acid,
isophthalic acid or terephthalic acid.

[0036] Thioglycidyl ether resins are derived from dithiols, for example, ethane-1,2-
dithiol or bis(4-mercaptomethylphenyl) ether.

[0037] N-glycidyl resins are obtained by dehydrochlorination of the reaction products of
epichlorohydrin with amines containing at least two amine hydrogen atoms. Such amines
are, for example, aniline, n-butylamine, bis(4-aminophenyl)methane, m-xylylenediamine
or bis(4-methylenaminophenyl)methane. The N-glycidyl resins also include, however,
triglycidyl isocyanurate, N,N'-diglycidyl derivatives of cycloalkylene ureas, e.g., ethylene
urea or 1,3-propylene urea, and diglycidyl derivatives of hydantoins, e.g., 5,5-
dimethylhydantoin.

[0038] For one or more of the embodiments, the epoxy resin component (A) further
includes a reactive diluent. One or more reactive diluents may be used. Suitable reactive
diluents include mono- or polyepoxides. The addition of a reactive diluent for epoxy resin
causes a reduction in viscosity. Reactive diluents are compounds that participate in a
chemical reaction with the hardener component during the curing process and become
incorporated into the cured composition, and are generally monofunctional epoxides.
Reactive diluents may also be used to vary the viscosity and/or cure properties of the
curable compositions for various applications. For some applications, reactive diluents
may impart a lower viscosity to influence flow properties, extend pot life and/or improve
adhesion properties of the curable compositions. For example, the viscosity may be
reduced to allow an increase in the level of pigment and filler in a formulation or
composition while still permitting easy application, or to allow the use of a higher
molecular weight epoxy resin. Thus, it is within the scope of the present disclosure for
the epoxy component, which comprises at least one multifunctional epoxy resin, to
further comprise a monofunctional epoxide. Examples of monoeoxides include, but are
not limited to, styrene oxide, cyclohexene oxide and the glycidyl ethers of phenol,
cresols, tert-butylphenol, other alkyl phenols, butanol, 2-ethylhexanol, C4 to C14
alcohols, and the like, or combinations thereof. The multifunctional epoxy resin may also
be present in a solution or emulsion, with the diluent being water, an organic solvent, or a
mixture thereof. The amount of multifunctional epoxy resin may range from about 50% to
100%, about 50% to about 90%, about 60% to about 90%, about 70% to 90%, and in some cases about 80% to about 90%, by weight, of the epoxy component (A). For one or more of the embodiments, the reactive diluent is less than 60 weight percent of a total weight of the resin component (A).

[0039] Particularly suitable multifunctional epoxy compounds are the diglycidyl ethers of bisphenol-A and bisphenol-F, the advanced diglycidyl ethers of bisphenol-A and bisphenol-F, and the epoxy novolac resins. The epoxy resin may be a single resin, or it may be a mixture of mutually compatible epoxy resins.

[0040] The epoxy modified cement composition includes a curing agent component (B) comprising at least one amine compound as amine hardener and water. The water-based curing agent component (B) is preferably a liquid component. In one embodiment, the curing agent is at least one amine compound, such as a polyamine, polyamide, a polyamidoamine polyamine-polyepoxide adduct, polyamide-polyepoxide adduct, or a mixture of at least two of these compounds. Particularly, a polyamine-polyepoxide adduct is preferred. The curing agent component contains amine compounds sufficiently contact reactable to epoxy resin and a solid component to form a solid article having a compressive strength greater than about 70 MPa or greater than about 75 MPa or greater than about 80 MPa or greater than 82 MPa.

[0041] A particularly suitable amine compound for use in the curing agent includes the water soluble polyamine adduct compounds disclosed in U.S. Patent No. 6,916,505, the disclosure of which is incorporated by reference in its entirety. The water soluble polyamine adduct compounds include a reaction product of: (a) an alkoxo group modified polyepoxide resin containing an average of at least 1.5 epoxide groups per molecule; and (b) a Mannich base polyamine. The Mannich base polyamine is a reaction product of a polyamine containing at least two amino groups with an N-Mannich condensate prepared from a reaction of a phenolic compound, an aldehyde, and a secondary amine wherein the secondary amine of the N-Mannich condensate is replaced by one of the at least two amino groups of the polyamine, and wherein the ratio of the Mannich base polyamine to the alkoxo group modified polyepoxide resin contains an excess of an active amine hydrogen relative to epoxide groups so that the water soluble polyamine adduct has an amine hydrogen equivalent weight of at most 1000 based on solids content. One suitable compound, according to the above water soluble polyamine adduct compound, is commercially available as ANQUAMINE 287 available from Air Products and Chemicals, Inc.
Another particularly suitable amine compound for use in the curing agent includes a water compatible polyamine-epoxy adduct compound disclosed in U.S. Patent No. 5,246,984, the disclosure of which is incorporated by reference in its entirety. The water compatible polyamine-epoxy adduct compounds include a water compatible polyamine-epoxy adduct formed by the reaction of a polyamine with a mixture of a monoepoxide and polyepoxides, the monoepoxide being added in an amount to react with about 10 to 50% of the primary amino groups in said polyamine and the polyepoxides being added in an amount to react with from about 35 to 65% of the remaining primary amino groups. One suitable compound, according to the above water compatible polyamine-epoxy adduct compound, is commercially available as ANQUAMINE 401 available from Air Products and Chemicals, Inc.

Another particularly suitable amine compound for use in the curing agent includes commercially available water compatible, polyamine-epoxy adduct compounds, polyamine-polyepoxide adduct compounds and/or polyepoxide modified polyamine compounds. Suitable compounds include, but are not limited to ANQUAMINE 287, ANQUAMINE 401, SUNMIDE WH900, SUNMIDE WH1000 and ANQUAMINE 701 and Anquawhite 100 from Air Products and Chemicals, Inc.

The curing agent component (B) may optionally comprise one or more other additives, such as defoamer, levelling agent, acid neutralizer, dispersing agent, superplasticizer, thixotropic agent, thickener, colorant.

Solid component (C) comprises a hydraulic inorganic or other mineral binder, which is preferably a cement. Suitable hydraulic inorganic binder is cement or calcium sulfate hemihydrate (plaster of Paris), preferably cement. Examples of suitable cements include Portland cement, alumina cement, pozzolanic cement, slag cement, magnesia cement and phosphate cement. A particularly suitable cement is Portland cement or white cement. The solid component (C) may further comprise one or more additives. Examples are calcium sulfate, calcium hydroxide, sand and admixture, such as plasticizer, setting accelerator, water reducers, defoamer. Other fillers that may suitably be included as additives in the solid component (C) include glass, such as crushed glass, quartz, silicon, barites, limestone, alumina and other like earthen materials, such as mica, talc and the like. Sand is a preferred water insoluble filler for use in the solid component (C).

The present disclosure also includes articles of manufacture comprising a contact product of the composition as described above. Such articles may include, but are not limited to, an adhesive, a coating, a primer, a sealant, a curing compound, a
construction product, a flooring product, a composite product, laminate, potting compounds, grouts, fillers, cementitious grouts, or self-leveling flooring.

[0047] Additional components or additives may be used together with the compositions of the present disclosure to produce articles of manufacture. Further, such coatings, primers, sealants, curing compounds or grouts may be applied to metal or cementitious substrates.

[0048] The curing reaction to form the contact product begins with the mixing of the epoxy modified cement compositional components. The epoxy group of the epoxy resin and optionally of the reactive diluent react with the reactive NH hydrogens to form the organic binder matrix, while the hydraulic inorganic binder with water, with hydration reactions, forms the inorganic binder matrix, as a result of which the composition ultimately cures.

[0049] The present disclosure includes a method for producing a flooring coating utilizing the epoxy modified cement composition, according to an exemplary embodiment. The method comprising the following steps:

(1) mixing component (A) and the water-based curing agent component (B);
(2) add the solid component (C) to mixture obtained in step (1) with stirring to give a coating composition;
(3) applying the coating to a substrate, which is preferably provided with a primer, preferably a cured mixture of component (A) and component (B);
(4) smoothing and deaerating the applied coating composition; and
(5) curing the applied coating composition to form a flooring coating.

[0050] Application of the coating composition and curing take place at a temperature in the range from 5 to 40 °C.

[0051] Compositions of the present disclosure may be used to produce various articles of manufacture. Depending on the requirements during the manufacturing of or for the end-use application of the article, various additives may be employed in the formulations and compositions to tailor specific properties. These additives include, but are not limited to, solvents (including water), accelerators, plasticizers, fillers, fibers, such as glass or carbon fibers, pigments, pigment dispersing agents, rheology modifiers, thixotropes, flow or leveling aids, surfactants, defoamers, biocides, or any combination thereof. It is understood that other mixtures or materials that are known in the art may be included in the compositions or formulations and are within the scope of the present disclosure.

[0052] Articles in accordance with the present disclosure include, but are not limited to, a coating, an adhesive, a construction product, a flooring product, or a composite
product. Coatings may contain various types and levels of pigments for use in paint and primer applications. Modified epoxy cement compositions 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 onto 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 product 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 product, such as, for example, a self-leveling 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.

[0053] Various substrates are suitable for the application of coatings of this invention 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.

[0054] Coatings of this invention may 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 this invention, plural component spray application equipment may be used, in which the amine and epoxy 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 may alleviate limitations with regard to the pot life of the formulation, which typically decreases as both the amine reactivity and the solids content increases. Heated plural component equipment may be employed to reduce the viscosity of the components, thereby improving ease of application.

[0055] Construction and flooring applications include compositions comprising the amine-epoxy 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, its 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 amine-epoxy compositions of the present
Disclosure may 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 may be prepared from the compositions disclosed herein. Amine-epoxy compositions of the present disclosure may be mixed with cementitious materials, such as concrete mix, to form polymer or modified cements, tile grouts, and the like.

EXAMPLES

[0056] The following Examples are provided to illustrate certain aspects or embodiments of the instant invention and shall not limit the scope of the claims appended hereto.
Table 1 shows examples of modified epoxy cement compositions, according to the present disclosure.

Component A of example 2 and example 3:
Epoxy resin component as an emulsion of approximately 50.4 wt.% of an epoxy resin from diglycidyl ether of bisphenol A, 11.1 wt.% mono epoxide reactive diluent, 2.5 wt.% surfactant and 36 wt% water.

Component A of example 1:
Low viscosity epoxy resin from diglycidyl ether of bisphenol A, mono epoxide reactive diluent, for example, a commercial product D.E.R. 324 from Dow Chemical.

Component B of example 1:
Mixture of 3.42g ANQUAMINE 287 and 0.05g SURFYNOL DF70. 10.1g water should be added after mixing 3.56g Part A of example 1 and 3.42g ANQUAMINE 287.

Component B of example 2:
Mixture of 3.34g ANQUAMINE 287 and 0.05g SURFYNOL DF70 and 8.1g water.

<table>
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<th>Raw material</th>
<th>Example 1</th>
<th>Example 2</th>
<th>Example 3</th>
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<tr>
<td>Part A</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Epoxy emulsion EM-1(EEW 325)</td>
<td>5.65</td>
<td>5.35</td>
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<tr>
<td>D.E.R. 324</td>
<td>3.56</td>
<td></td>
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<tr>
<td>Part B</td>
<td></td>
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</tr>
<tr>
<td>ANQUAMINE 287*</td>
<td>3.42</td>
<td>3.34</td>
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</tr>
<tr>
<td>ANQUAMINE 401**</td>
<td></td>
<td></td>
<td>2.63</td>
</tr>
<tr>
<td>SURFYNOL DF 70</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Water</td>
<td>10.1</td>
<td>8.1</td>
<td>9.05</td>
</tr>
<tr>
<td>Part C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silica sand 0.1~0.3mm</td>
<td>51.00</td>
<td>51.00</td>
<td>51.00</td>
</tr>
<tr>
<td>White Portland cement 52.5</td>
<td>31.00</td>
<td>31.00</td>
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</tr>
<tr>
<td>Additives***</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
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*waterborne polyepoxide modified polyamine solution
**waterborne polyepoxide modified polyamine solution
***Additives include plasticizer, defoamer, set accelerator, thickener, fiber, expansion agent, retarder.
Component B of example 3
Mixture of 2.63g ANQUAMINE 401 and 0.05g SURFYNOL DF70 and 9.05g water.

In the compositional examples shown in Table 1, component (A) and component (B) were mixed together. Then component (C) was added to obtain a homogeneous mixture. In example 1, component (A) was first mixed with ANQUAMINE 287 to get a homogeneous emulsion, then the additional water of example 1 was added to the emulsion. Then component (C) was added to obtain a homogeneous mixture. Working time, flowability, compressive strength, flexural strength, impact resistance, bonding strength and surface moisture content were tested. For this, coating was prepared on a concrete substrate and test specimen with the obtained mixtures.

**TABLE 2**

<table>
<thead>
<tr>
<th>Properties</th>
<th>Example 1</th>
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<tr>
<td>Working time, minutes</td>
<td>30min</td>
<td>35min</td>
<td>55min</td>
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<tr>
<td>Surface evaluation</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Flowability, 5min</td>
<td>145mm</td>
<td>141mm</td>
<td>150mm</td>
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<tr>
<td>Flowability, 30min</td>
<td>134mm</td>
<td>132mm</td>
<td>140mm</td>
</tr>
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<td>Hardness, 7days</td>
<td>78D</td>
<td>78D</td>
<td>83D</td>
</tr>
<tr>
<td>Compressive strength, 7days</td>
<td>74MPa</td>
<td>73MPa</td>
<td>75MPa</td>
</tr>
<tr>
<td>Compressive strength, 28days</td>
<td>86MPa</td>
<td>84MPa</td>
<td>82MPa</td>
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<tr>
<td>Flexural strength, 7days</td>
<td>16MPa</td>
<td>15MPa</td>
<td>12MPa</td>
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<td>Flexural strength, 28days</td>
<td>19MPa</td>
<td>20MPa</td>
<td>18MPa</td>
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<tr>
<td>Impact resistance, 28days</td>
<td>&gt;100kg.cm</td>
<td>&gt;100kg.cm</td>
<td>&gt;100kg.cm</td>
</tr>
<tr>
<td>Bonding strength to concrete(C30), 14days</td>
<td>3.5MPa</td>
<td>3.3MPa</td>
<td>3.8MPa</td>
</tr>
<tr>
<td>Surface moisture content after 24hours</td>
<td>4.10%</td>
<td>4.10%</td>
<td>3.90%</td>
</tr>
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</table>

This experiment was conducted under 21-25 ºC and 30-80% relative humidity. The working time is determined by the end time of the mixture losing self-levelling property.

The flowability was determined according to JC/T985. The mixture remained in the cup for 30 minutes and then was checked for flowability, so called flowability at 30 minutes. The surface was determined whether there are defects, such as pinholes, blisters, white stains, bleeding and cracks, as ranked by poor, sufficient, good. The compressive strength and flexural strength were determined according to BS EN196-1:2005 with 40X40X160mm prisms. Before measurement, the prisms were cured for a certain number of days. The impact resistance was determined by BS IS06272-2. The bonding strength was determined according to ASTM D4541 on a sandblasted concrete slab. Before measurement, the composition on the substrate was cured for 14 days.
surface moisture of an applied coating of the composition on the concrete substrate was determined using a moisture meter of Trarnex, wherein the moisture content is determined by means of an electronic impedance measurement. Before measurement, the composition was cured for 24 hours. The components, mixing ratios and results used are shown in Table 1 and Table 2.

[0066] The surface moisture is reduced to less than 5%, resulting in fast overcoatability.

[0067] The modified epoxy cement composition after cure can give good smooth surface appearance, excellent mechanical strengths and bonding strength and good moisture barrier properties.

[0068] While the invention has been described with reference to certain aspects or embodiments, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the invention. In addition, many modifications may be made to adapt the teachings of the invention without departing from the essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiment disclosed as the best mode contemplated for carrying out this invention, but that the invention will include all embodiments falling within the scope of the appended claims.
WHAT IS CLAIMED IS:

1. A water-based curing agent composition comprising:
   water; and
   an amine compound selected from the group consisting of polyamine,
   polyamide, a polyamidoamine polyamine-polyepoxide adduct, polyamide-
   polyepoxide adduct and a mixture of at least two of these compounds;
   wherein the amine compound contains compounds sufficiently contact
   reactable to epoxy resin and a solid component to form a solid article having
   a compressive strength greater than about 70 MPa.

2. The composition of claim 1, wherein the at least one amine compound
   comprises a polyamine-polyepoxide adduct.

3. The water-based composition of claim 1, wherein the at least one amine
   compound comprises a water soluble polyamine adduct, the water soluble
   polyamine adduct being a reaction product of: (a) an alkoxy group modified
   polyepoxide resin containing an average of at least 1.5 epoxide groups per
   molecule; and (b) a Mannich base polyamine. The Mannich base polyamine is a
   reaction product of a polyamine containing at least two amino groups with an N-
   Mannich condensate prepared from a reaction of a phenolic compound, an
   aldehyde, and a secondary amine wherein the secondary amine of the N-
   Mannich condensate is replaced by one of the at least two amino groups of the
   polyamine, and wherein the ratio of the Mannich base polyamine to the alkoxy
   group modified polyepoxide resin contains an excess of an active amine
   hydrogen relative to epoxide groups so that the water soluble polyamine adduct
   has an amine hydrogen equivalent weight of at most 1000 based on solids
   content.

4. The water-based composition of claim 1, wherein the at least one amine
   compound comprises a water compatible polyamine-epoxy adduct formed by the
   reaction of a polyamine with a mixture of a monoepoxide and polyepoxides, the
   monoepoxide being added in an amount to react with about 10 to 50% of the
   primary amino groups in said polyamine and the polyepoxides being added in an
   amount to react with from about 35 to 65% of the remaining primary amino
   groups.

5. The water-based composition of claim 1, wherein the at least one amine
   compound comprises one or more of water compatible, polyamine-epoxy adduct
compounds, polyamine-polyepoxide adduct compounds or polyepoxide modified polyamine compounds.

6. An epoxy modified cement composition comprising:
   (A) epoxy resin comprising at least one epoxy resin;
   (B) a curing agent comprising water and at least one amine compound selected from the group consisting of polyamine, polyamide, a polyamidoamine polyamine-polyepoxide adduct, polyamide-polyepoxide adduct, and a mixture of at least two of these compounds; and
   (C) a solid component comprising at least one hydraulic inorganic binder;

   wherein the curing agent is at least one amine compound selected from the group consisting of a polyamine, polyamide, a polyamidoamine polyamine-polyepoxide adduct, polyamide-polyepoxide adduct, or a mixture of at least two of these compounds;

   wherein the amine compound contains compounds sufficiently contact reactable to epoxy resin and the solid component to form a solid article having a compressive strength greater than about 70 MPa.

7. The water-based composition of claim 6, wherein the polymer to cement ratio is in the range of 0.05 to 1.

8. The water-based composition of claim 7, wherein the polymer to cement ratio is in the range of 0.1 to 0.5.

9. The water-based composition of claim 8, wherein the polymer to cement ratio is in the range of 0.15 to 0.35.

10. The water-based composition of claim 6 wherein the water to hydraulic inorganic binder is in the range from 0.1 to 1.

11. The water-based composition of claim 10, wherein the water to hydraulic inorganic binder is in the range from 0.3 to 0.5.

12. The water-based composition of claim 6 wherein the stoichiometric ratio of the curing agent functionality to the epoxy resin functionality is in the range of 0.7 to 1.3.

13. The composition of claim 6 wherein at least one hydraulic inorganic binder includes cement.

14. The composition of claim 13, wherein the cement is Portland cement or white

20
cement.

15. The composition of claim 6, wherein the curing agent is a polyamine-polyepoxide adduct.

16. The composition of claim 6, wherein the at least one amine compound comprises a water soluble polyamine adduct, the water soluble polyamine adduct being a reaction product of: (a) an alkoxy group modified polyepoxide resin containing an average of at least 1.5 epoxide groups per molecule; and (b) a Mannich base polyamine. The Mannich base polyamine is a reaction product of a polyamine containing at least two amino groups with an N-Mannich condensate prepared from a reaction of a phenolic compound, an aldehyde, and a secondary amine wherein the secondary amine of the N-Mannich condensate is replaced by one of the at least two amino groups of the polyamine, and wherein the ratio of the Mannich base polyamine to the alkoxy group modified polyepoxide resin contains an excess of an active amine hydrogen relative to epoxide groups so that the water soluble polyamine adduct has an amine hydrogen equivalent weight of at most 1000 based on solids content.

17. The composition of claim 6, wherein the at least one amine compound comprises a water compatible polyamine-epoxy adduct formed by the reaction of a polyamine with a mixture of a monoepoxide and polyepoxides, the monoepoxide being added in an amount to react with about 10 to 50% of the primary amino groups in said polyamine and the polyepoxides being added in an amount to react with from about 35 to 65% of the remaining primary amino groups.

18. An epoxy system comprising the contact product of:
   (A) a curing agent composition of claim 1;
   (B) epoxy resin comprising at least one epoxy resin;
   (C) a solid component comprising at least one hydraulic inorganic binder;
   wherein the epoxy system forms an article having a compressive strength greater than about 70 MPa.

19. An article comprising the contact product of:
   (A) epoxy resin comprising at least one epoxy resin;
   (B) a water-based curing agent comprising at least one amine compound and water; and
   (C) a solid component comprising at least one hydraulic inorganic binder;
wherein the article has a compressive strength greater than about 70 MPa.

20. The article of claim 19, wherein the article is selected from the group consisting of a coating, adhesive, sealer, grouting, mortar and polymer modified concrete.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
C08G 59/40(2006.01)i; C08L 63/00(2006.01)i; C04B 28/00(2006.01)i; C04B 24/28(2006.01)i

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)
C08L63/00-,C08G59/00-,C04B

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)
CNPAT,CNKI,WP,EPODOC epoxy, epoxide?, cur+, hard+, +amine?, mannich, adduct+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>US 5246984 A (AIR PROD &amp; CHEM) 21 September 1993 (1993-09-21) description, column 2, line 52 to column 6, line 62</td>
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Further documents are listed in the continuation of Box C.

Date of the actual completion of the international search

16 January 2017

Date of mailing of the international search report

23 January 2017

Name and mailing address of the ISA/CN

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TANG, Dongmei

Facsimile No. (86-10)62019451

Telephone No. (86-10)62084436
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