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(54) Title: COATING COMPOSITION

(57) Abstract: A curable composition including: (a) at least one epoxy resin; (b) at least one curing agent; and (c) at least one amphiphilic block copolymer toughening agent ; wherein the curable composition has a low volatile organic component (VOC) property of less than about 250 g/L as measured by ASTM D2369; and wherein the curable composition, when cured, provides an anti-corrosive cured coating product with improved properties such as flexibility, impact resistance, and corrosion resistance.



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COATING COMPOSITION

FIELD

The present invention is related to a coating composition and more specifically to a high solids coating composition; and a process for preparing the high solids
5 coating composition.

BACKGROUND

Epoxy based anti-corrosion coatings are widely used for the protection of metal and concrete substrates. In addition to anti-corrosion performance, it is very important for epoxy based coatings to exhibit other essential properties such as toughness as
10 well as low volatile organic compounds (VOC) which are required in certain coating applications. Heretofore, solid epoxy resins such as D.E.R. 671 have been widely used in anti-corrosion coatings to incorporate better toughness to the coatings. However, the known solid epoxy resins are not suitable for use as low VOC coatings because such epoxy resins exist in the solid state. A large amount (e.g., greater than 30 percent based on volume) of
15 solvent is required to dissolve the solid epoxy resins and dilute the resins sufficiently for use. This requirement hinders the solid epoxy resin from being used in low VOC, high solids applications.

Heretofore, liquid epoxy resins such as D.E.R.331 have also been used for coatings. The coatings based on liquid epoxy resin requires less solvent, however, such
20 coatings are very brittle.

In some instances, reactive diluents can be used to significantly reduce the viscosity of a coating formulation or system but such reactive diluents can compromise the reactivity or functionality of the resin, which will lead to long drying times for such resin or to poor chemical resistance of the coating.

25 Heretofore, aliphatic epoxy resins such as D.E.R. 736, D.E.R. 732, and D.E.R. 852 have also been used for coatings. Aliphatic epoxy resins can improve the flexibility of a coating but such aliphatic epoxy resins still compromise the reactivity of resin, which will lead to long drying times as well.

For example, U.S. Patent No. 8,021,586 discloses amphiphilic block
30 copolymer-toughened epoxy resins and powder coatings made therefrom. The above patent

discloses a curable solid resin composition which is useful for powder coating, wherein the composition includes an epoxy resin, an amphiphilic block copolymer containing an epoxy resin immiscible block segment and an epoxy resin miscible block segment; and optionally, a curing agent. In the above patent, anti-corrosion is not a property of a coating that is mentioned since the coating composition disclosed is used for preparing a powder coating, not a high solids coating. Also, the amphiphilic block copolymer disclosed in the above patent is not a carboxyl group terminated amphiphilic block copolymer or an epoxy group terminated amphiphilic block copolymer.

U.S. Patent Application Publication No. 2011/0319523A1 discloses a thermosettable composition containing a combination of an amphiphilic block copolymer and a polyol; and a thermoset product prepared from the thermosettable composition. The above publication discloses a thermosettable composition for preparing curable thermoset products. The thermosettable composition includes an amphiphilic block copolymer, a polyol, an epoxy resin having oxirane rings, and an anhydride hardener containing anhydride ring and catalyst. In the above publication, no carboxyl group terminated amphiphilic block copolymer or epoxy group terminated amphiphilic block copolymer is used as a toughener or toughening agent. The composition disclosed in the above publication is not used for coating applications; and anti-corrosion is not a property that is mentioned in the above publication.

WO2013/138994 discloses a modified epoxy resin composition used in high solids coatings. In WO2013/138994, the epoxy resin composition is useful in a low volatile organic compound high solids coating composition, which is useful for coating a substrate, such as metal, plastic, wood, stone, glass, fabric, concrete, primed surfaces, previously painted surfaces and cementitious substrates. However, the coating composition of WO2013/138994 does not disclose a carboxyl group terminated amphiphilic block copolymer or an epoxy group terminated amphiphilic block copolymer used as toughener or toughening agent.

PCT Patent Application No. PCT/CN13/084305, filed September 26, 2013, discloses an epoxy system for nano toughening and providing a transparent appearance to a coating. An amphiphilic block copolymer based on ethylene oxide/butylene oxide (EO/BO) for nano phase separation and transparent appearance is disclosed in the above PCT patent

application. Anti-corrosion properties for coating applications are not disclosed in the above PCT patent application.

U.S. Patent Application Publication No. 2011/0114257A1 discloses a reaction product based on amphiphilic block copolymers and the use of such copolymers as impact modifiers for coatings. Amphiphilic block copolymers based on EO/BO as impact modifiers are disclosed in the above publication, but no anti-corrosion properties for coating applications are disclosed.

U.S. Patent Application Publication No. discloses a method of toughening epoxy resins and toughened epoxy resin composites prepared from the resins. The above publication discloses a novel toughener selected from the group of polyurea, polyurethane and poly(urea-urethane) using a facile synthesis method. The toughener forms thick-interface particles and creates an effective toughness improvement for epoxy resins. In the above publication, neither a carboxyl group terminated amphiphilic block copolymer nor an epoxy group terminated amphiphilic block copolymer is disclosed as toughener for epoxy resins. In addition, the above publication does not disclose anti-corrosion performance for high solids coatings.

There is a need in the industry for a high solids coating formulation or composition that uses a carboxyl group terminated amphiphilic block copolymer or an epoxy group terminated amphiphilic block copolymer and that provides a high solids coating with anti-corrosion performance and other essential properties to the coating such as toughness and low volatile organic compounds.

SUMMARY

The present invention is directed to a high solids curable coating formulation, system, or composition. One embodiment of the curable coating composition of the present invention includes, for example: (a) at least one epoxy resin (such as D.E.R. 331 or Oudraflex LC.301), (b) at least one curing agent, and (c) at least one amphiphilic block copolymer toughener such as a carboxyl group terminated amphiphilic block copolymer (such as FORTEGRA 202) or an epoxy group terminated amphiphilic block copolymer (such as FORTEGRA 202 adduct).

In one preferred embodiment, an epoxy terminated amphiphilic block copolymer is used such as FORTEGRA 202 adduct. FORTEGRA 202 adduct is a reaction

product of FORTEGRA 202 with an epoxy resin such as D.E.R. 331 wherein the final FORTEGRA 202 adduct product is terminated by epoxy groups. The amphiphilic block copolymers, such as FORTEGRA 202 and FORTEGRA 202 adduct are used as a toughener or toughening agent in the coating composition. The coating composition of the present invention offers at least two benefits: (1) better impact resistance and flexibility, and (2) better anti-corrosion performance.

Another embodiment of the present invention is directed to a process for preparing the above curable coating composition suitable for preparing a coating.

Still another embodiment of the present invention is directed to a cured product prepared by curing the above curable coating composition on a substrate.

Yet another embodiment of the present invention is directed to a process for producing the above cured coating product.

The present invention realizes the benefit of excellent impact resistance and flexibility and excellent anti-corrosion performance in a high solids coating.

DETAILED DESCRIPTION

“High solids” and “high solids content” herein, with reference to a composition, means a solid content of greater than 70 percent (%) based on volume. For example, the solid content of the composition generally is more than 70 % based on volume in one embodiment, more than 75 % based on volume in another embodiment, and more than 80 % based on volume in still another embodiment.

“Low volatile organic compounds (VOC)” herein, with reference to a coating composition, means a solvent content of less than 250 g/L.

“Epoxy resin immiscible block segment” herein, with reference to a composition, means an oxide segment, such as an ethylene oxide (EO) segment, that is not miscible with an epoxide resin.

“Epoxy resin miscible block segment” herein, with reference to a composition, means an oxide segment, such as a butylene oxide (BO) segment, that is miscible with an epoxide resin.

One broad embodiment of the present invention is directed to a curable coating formulation or composition which is useful for coating substrates or parts and forming an anti-corrosion coating on the substrates or parts, particularly parts used in the marine, steel structure, maintenance, and transportation industries. The curable composition useful as a coating composition in general contains (a) at least one epoxy resin, (b) at least one amphiphilic block copolymer toughening agent such as for example at least one carboxyl group terminated amphiphilic block copolymer or at least one epoxy group terminated amphiphilic block copolymer, and (c) at least one curing agent. Optionally, the coating composition may include reactive diluents, pigments, fillers, solvents, and other additives. In a preferred embodiment of the present invention, the curable composition is first prepared and then the curable composition is cured to form a cured coating material, particularly for forming an anti-corrosion coating on a substrate.

The epoxy resin compound, component (a), useful in preparing the present invention curable epoxy resin coating composition can be any conventional epoxy resin compound. The epoxy resin can be a single epoxy resin compound used alone or a mixture of two or more epoxy compounds used in combination, i.e., component (a) of the curable epoxy resin coating composition which is cured to form the coating material of the present invention includes at least one epoxy resin.

The epoxy resin (a) includes, but is not limited to, aliphatic epoxy resins, cycloaliphatic epoxy resins, bisphenol A epoxy resins, bisphenol F epoxy resins, phenol novolac epoxy resins, cresol-novolac epoxy resins, biphenyl epoxy resins, polyfunctional epoxy resins, naphthalene epoxy resins, divinylbenzene dioxide, 2-glycidylphenylglycidyl ether, dicyclopentadiene-type epoxy resins, phosphorous containing epoxy resin, multi-aromatic resin type epoxy resins, and mixture therefore.

A few non-limiting embodiments of epoxy resins useful in the present invention include, for example, trimethylpropane epoxide; cyclohexanedimethanol diglycidyl ether; diglycidyl-1,2-cyclohexane dicarboxylate; diglycidyl ether of bisphenol A; diglycidyl ether of bisphenol F; resorcinol diglycidyl ether; triglycidyl ethers of para-aminophenols; halogen (for example, chlorine or bromine)-containing epoxy resins such as diglycidyl ether of tetrabromobisphenol A; epoxidized phenol novolac; epoxidized bisphenol A novolac; an oxazolidone-modified epoxy resin; an epoxy-terminated polyoxazolidone; and mixtures thereof.

Suitable commercially available epoxy resin compounds utilized in the composition of the present invention may be for example the D.E.R.TM 300 series, the D.E.N.TM 400 series, the D.E.R.TM 500 series, the D.E.R.TM 600 series and the D.E.R.TM 700 series of epoxy resins commercially available from The Dow Chemical Company. For example, epoxy resins useful in the present invention can include LERs, such as D.E.R. 331 (a bisphenol A diglycidyl ether), D.E.R. 354 (a bisphenol F diglycidyl ether), D.E.R. 324 (a diluent modified epoxy resin), D.E.R. 353 (a low viscosity epoxy resin blend) and other well known epoxy resins and blends of the above known epoxy resins. D.E.R. 324, D.E.R. 330, D.E.R. 331, D.E.R. 332, D.E.R. 354, and D.E.R. 353 are commercially available epoxy resins from The Dow Chemical Company.

Other commercially available epoxy resin compounds useful in the present invention include for example Oudraflex LC301, a modified bisphenol A diglycidyl ether.

As an illustration, a preferred embodiment of the epoxy resin compound useful in the present invention may include a liquid epoxy resin, such as D.E.R. 331 a diglycidylether of bisphenol A (DGEBCA) having an epoxide equivalent weight of from about 182 to about 192, a viscosity of from about 11 Pa·s to about 14 Pa·s and a density of about 1.16 g/cc.

An extensive enumeration of epoxy resins useful in the present invention can be found in Lee, H. and Neville, K., "Handbook of Epoxy Resins," McGraw-Hill Book Company, New York, 1967, Chapter 2, pages 257-307; incorporated herein by reference. The preparation of epoxy compounds useful in the present invention is described for example in Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd Ed., Vol. 9, pp 267-289, incorporated herein by reference. Other suitable epoxy resins useful as component (a) in the present invention are disclosed in, for example, U.S. Patent Nos. 3,018,262; 7,163,973; 6,887,574; 6,632,893; 6,242,083; 7,037,958; 6,572,971; 6,153,719; 5,137,990; 6,451,898; and 5,405,688; PCT Publication WO 2006/052727; and U.S. Patent Application Publication Nos. 20060293172 and 20050171237, all of which are incorporated herein by reference.

In general, the concentration of the epoxy resin compound used in the curable composition of the present invention may range generally from about 5 weight percent (wt %) to about 100 wt % in one embodiment, from about 10 wt % to about 100 wt % in another embodiment, and from about 20 wt % to about 80 wt % in still another

embodiment, based on the total weight of all of the components present in the curable coating composition.

The hardener compound, component (b), (also referred to as a curing agent or crosslinking agent) useful in preparing the present invention curable coating composition
5 can be selected from one or more of the following compounds: including, for example, an anhydride hardener, an amine hardener, a phenol novolac hardener, an imidazole hardener, or mixtures thereof.

Anhydride hardeners include, but are not limited to, for example, phthalic acid anhydride and derivatives thereof, nadic acid anhydride and derivatives, trimellitic acid
10 anhydride and derivatives, pyromellitic acid anhydride and derivatives thereof, benzophenonetetracarboxylic acid anhydride and derivatives thereof, dodecenylsuccinic acid anhydride and derivatives thereof, poly(ethyloctadecanedioic acid) anhydride and derivatives thereof, hexahydrophthalic anhydride, methyl hexahydrophthalic anhydride, tetrahydrophthalic anhydride, methyl tetrahydrophthalic anhydride, nadic acid anhydride,
15 methyl nadic acid anhydride, and mixtures thereof. The above anhydride hardeners can be used alone or in an admixture thereof. Methyl nadic acid anhydride is one example of a particularly hardener suitable for the present invention.

Amine hardeners include, but are not limited to, for example, dicydiamide (DICY); polyamide; phenalkamine; polyester amine; ethylenediamine (EDA);
20 diethylenetriamine (DETA); triethylenetetramine (TETA); trimethyl hexane diamine (TMDA); hexamethylene diamine (HMDA); N-(2-aminoethyl)-1,3-propanediamine (N3-Amine); N,N'-1,2-ethanediylbis-1,3-propanediamine (N4-amine); dipropylene triamine; m-xylylenediamine (mXDA); isophorone diamine (IPDA); diaminodiphenylmethane (DDM); diaminodiphenylsulfone (DDS); 2-Ethyl-6-methylaniline (MEA);
25 tris(dimethylaminomethyl)phenol (DMP-30); and mixtures thereof.

Imidazole hardeners include, but are not limited to, for example, 2-methyl imidazole, 2-ethyl-4-methylimidazole, 2-isopropylimidazole, 1-propylimidazole, 2-heptadecylimidazole, and mixtures thereof. The hardener is used to react with the epoxy groups of the epoxy resin.

30 In general, the concentration of the hardener compound used in the curable coating composition of the present invention may range generally from about 0.1 wt % to

about 60 wt % in one embodiment, from about 1 wt % to about 50 wt % in another embodiment, and from about 10 wt % to about 50 wt % in yet another embodiment, based on the total weight of the components in the curable formulation.

5 In general, the toughener compound, component (c), useful in preparing the present invention curable coating composition includes for example an amphiphilic block copolymer toughening agent which can include for example a carboxyl group terminated amphiphilic block copolymer, an epoxy group terminated amphiphilic block copolymer, and mixtures thereof.

10 In a preferred embodiment, the toughener compound, component (c), useful for preparing the curable coating composition of the present invention may include for example a carboxyl group terminated amphiphilic block copolymer (e.g., FORTEGRA 202); an epoxy group terminated amphiphilic block copolymer (e.g., an adduct of FORTEGRA 202); and mixtures thereof. The toughener compound is advantageously used to enhance corrosion and toughness performance of a thermoset (i.e., a coating) prepared from the
15 curable composition.

In general, the concentration of the amphiphilic block copolymer toughening agent used in the curable coating composition of the present invention may range generally from about 0.1 wt % to about 90 wt % in one embodiment, from about 0.1 wt % to about 30 wt % in another embodiment, and from about 1 wt % to about 29 wt % in yet another
20 embodiment, based on the total weight of the components in the curable formulation.

In preparing the curable coating composition of the present invention, optional compounds can be added to the composition. The optional compounds that may be added to the composition of the present invention may include compounds that are normally used in curable resin compositions known to those skilled in the art. The optional
25 components used in the composition preferably are used in a concentration sufficient to prepare the composition with minimal impact to the thermal and mechanical properties of the composition or to the final product made from the composition.

Optional compounds that can be added to the composition may include, for example, compounds that can be added to the composition to enhance application properties
30 (e.g., surface tension modifiers or flow aids), reliability properties (e.g., adhesion promoters), reaction rates, selectivities of the reaction, and/or catalyst lifetime.

For example, it may be advantageous to add a filler as an optional component in the coating composition. When the composition contains for example an inorganic filler, the inorganic filler can be selected from the group consisting of silica, talc, quartz, mica, and mixtures thereof. In another embodiment, the filler can be a flame
5 retardant filler which can be selected from the group consisting of aluminum trihydroxide, magnesium hydroxide, boehmite, and mixtures thereof.

In general, the concentration of the optional filler compound, when used in the curable coating composition of the present invention, may range generally from 0 wt % to about 90 wt % in one embodiment, from about 0.01 wt % to about 80 wt % in another
10 embodiment, and from about 0.01 wt % to about 70 wt % in yet another embodiment, based on the total weight of the components in the curable formulation.

Another optional compound that can be added to the composition may include, for example, a solvent. Solvents useful in the present invention may include, but are not limited to, for example, methyl ethyl ketone (MEK), dimethylformamide (DMF),
15 ethyl alcohol (EtOH), propylene glycol methyl ether (PM), propylene glycol methyl ether acetate (PMA), xylene, and mixtures thereof.

In general, the concentration of the optional solvent compound, when used in the curable coating composition of the present invention, may range generally from 0 wt % to about 80 wt % in one embodiment, from about 0.01 wt % to about 60 wt % in another
20 embodiment, and from about 0.01 wt % to about 50 wt % in yet another embodiment, based on the total weight of the components in the curable formulation.

Other optional compounds or additives that can be added to the coating composition may include, for example, dispersant additives; deformer additives; flowing additives; co-curing agents; catalysts; other solvents; other fillers; pigments; other
25 toughening agents; flexibilizing agents; processing aides; flow modifiers; adhesion promoters; diluents; stabilizers; plasticizers; curing catalysts; catalyst de-activators; other flame retardants; aromatic hydrocarbon resins; coal tar pitch; petroleum pitch; carbon nanotubes; graphene; carbon black; carbon fibers; or mixtures thereof.

Generally, the amount of the optional compounds, when used in the composition of the present invention, may be for example, from 0 wt % to about 10 wt % in
30 one embodiment, from about 0.1 wt % to about 8 wt % in another embodiment; and from about 0.1 wt % to about 5 wt % in yet another embodiment.

The thermosetting composition may further include a second thermosetting resin different from the epoxy resin (a) and different from the hardener (b). For example, the second thermosetting resin may include a polyurethane, an acrylate, and mixtures thereof. In a preferred embodiment, the optional second thermosetting resin compound
5 useful for preparing the curable coating composition of the present invention may include for example a polyurethane or an acrylate.

In general, the concentration of the second thermosetting resin compound used in the curable coating composition of the present invention may range generally from 0 wt % to about 60 wt % in one embodiment, from about 0.01 wt % to about 50 wt % in
10 another embodiment, from about 1 wt % to about 40 wt % in still another embodiment, and from about 10 wt % to about 30 wt % in yet another embodiment, based on the total weight of the components in the curable formulation.

The second thermosetting composition may further include, optionally, at least one solvent and/or may further include one or more additives chosen from the list of
15 optional additives described above. The concentration of the additives, when used, may be the concentrations as described above for optional components. The optional additives may include for example, additional flame retardants, additional toughening agents different from carboxyl group terminated or epoxy terminated amphiphilic block copolymer (c), curing inhibitors, wetting agents, colorants, thermoplastics, processing aids, dyes,
20 UV-blocking compounds, fluorescent compounds, and mixtures thereof. The above list is intended to be exemplary and not limiting.

Generally, the composition of the present invention is produced by first admixing, blending or mixing: (a) the epoxy resin described above; (b) the curing agent described above; and (c) the amphiphilic block copolymer toughening agent described
25 above; and then mixing the components for a predetermined amount of time to produce a curable coating composition which can subsequently be cured by heating. Optionally, the composition may include any one or more of the above-described optional compounds as desired.

For example, the preparation of the curable composition of the present
30 invention may be achieved by blending, in known mixing equipment, (a) at least one epoxy resin; (b) at least one curing agent; (c) at least one amphiphilic block copolymer toughening

agent; and optionally (d) any other desirable additive(s). Any of the above-mentioned optional additives may be added to the composition during the mixing or prior to the mixing to form the curable composition.

5 All the compounds of the composition are typically mixed and dispersed at a temperature enabling the preparation of an effective curable composition having the desired balance of properties for a particular application. For example, the temperature during the mixing of all components may be generally from about -10 °C to about 40 °C in one embodiment, and from about 0 °C to about 30 °C in another embodiment.

10 The preparation of composition of the present invention, and/or any of the steps thereof, may be a batch or a continuous process. The mixing equipment used in the process may be any vessel and ancillary equipment well known to those skilled in the art.

In one embodiment, the curable composition exhibits a low viscosity sufficient to allow the curable composition to be processable and handleable in conventional formulation equipment. For example, the curable composition prepared by the above
15 process advantageously exhibits a low viscosity of less than or equal to ($\leq$) about 5,000 m Pa·s at 25 °C. Generally, the viscosity of curable composition can be from about 100 m Pa·s to about 5,000 m Pa·s in one embodiment, from about 200 m Pa·s to about 4,000 m Pa·s in another embodiment, and from about 500 m Pa·s to about 3,000 m Pa·s in still another embodiment at 25 °C.

20 One embodiment of the present invention includes curing the curable composition discussed above to form a cured coating. For example, the curing of the curable composition may be carried out at a predetermined temperature and for a predetermined period of time sufficient to cure the composition to form a cured coating material.

25 To form a coating substrate, the coating composition can be first applied to the substrate by methods well known in the art such as brushing, rolling, spraying, and the like. Then, the substrate with the coating composition on the substrate can be heated to cure the composition.

30 In general, the process for producing the cured coating material of the present invention includes carrying out the curing reaction at process conditions to enable the preparation of an effective cured material having the desired balance of properties for a

particular application, particularly for forming the coating product. For example, the reaction temperature to carry out the reaction process for preparing the cured material can be in the range of from about -10 °C to about 200 °C in one embodiment, from about 10 °C to about 150 °C in another embodiment, and from about 0 °C to about 80 °C in still another embodiment.

For example, the time to carry out the reaction process for preparing the cured material may be generally from about 0.01 hour (hr) to about 14 days in one embodiment, from about 0.1 hr to about 7 days in another embodiment, and from 1 hr to about 24 hr in still another embodiment.

The preparation of the cured coating material of the present invention, and/or any of the steps thereof, may be a batch or a continuous process. The equipment employed to carry out the reaction includes equipment known to those skilled in the art.

The reaction product or cured coating of the present invention (i.e., the cross-linked coating product made from the present invention curable composition) exhibits unexpected and unique properties. For example, the cured coating exhibits better anti-corrosion properties, flexibility, impact resistance, low VOC and an enhanced adhesion better than a cured coating made from a curable composition without the toughener of the present invention. The beneficial performance properties of the cured coating are improved over conventional cured coating products made from conventional curable compositions containing conventional curing agents and catalysts; and that do not contain the amphiphilic block copolymer toughening agent of the present invention. For example, the cured coating of the present invention may advantageously be anti-corrosive. The anti-corrosive properties of the cured coating product mainly include a wet adhesion after a salt spray test, and a creep rust/disbondment and blistering after a salt spray test for 1,000 hr according to the test procedures described in ASTM B117.

In general, the cured coating of the present invention exhibits an excellent wet adhesion property, generally at least about “4B” in one embodiment after 1,000 hr salt spray test. The wet adhesion property of the cured coating material can be measured by the method described in ASTM D3359. In general, the cured coating of the present invention exhibits an improved creep rust/disbondment performance after 1,000 hr salt spray test of generally less than 15/15 mm in one embodiment and less than 5/7 mm in another

embodiment. The creep rust/disbondment performance properties of the cured coating material can be measured by the method described in ASTM D610.

In general, the cured coating of the present invention exhibits an excellent blistering performance after 1,000 hr salt spray test of at least about “8F” in one
5 embodiment. The blistering property of the cured coating material can be measured by the method described in ASTM D-714.

The cured coating of the present invention may also advantageously exhibit a high toughness property which is indicated by flexibility as well as impact strength. The flexibility property and the impact strength property may differ depending on whether a
10 clear coating product is desired or a pigmented coating product is desired. In general, the flexibility of any coating product of the present invention can be less than 13 mm, in one embodiment, and less than 5 mm in still another embodiment.

In one preferred embodiment, a cured clear coating of the present invention may exhibit a flexibility property of generally less than about 13 mm; and less than about
15 5 mm in another embodiment. In another preferred embodiment, a cured pigment coating of the present invention may exhibit a flexibility property of generally less than 38 mm in one embodiment; and less than about 15 mm in another embodiment. In other embodiments, the flexibility of a cured pigmented coating product of the present invention can be less than 5 mm.

20 The impact strength properties may differ depending on whether a clear coating product is desired or a pigmented coating product is desired. In general, the impact strength properties of any coating product of the present invention can be more than 20 centimeters times kilogram (cm•kg) in one embodiment; and more than 50 cm•kg in another embodiment.

25 In another preferred embodiment, a cured pigment coating of the present invention may exhibit impact strength properties of generally greater than about 20 cm•kg and greater than about 50 cm•kg in another embodiment.

The cured coating of the present invention may also advantageously exhibit a low VOC property. The cured coating of the present invention exhibits a low VOC
30 property of generally less than about 250 g/L in one embodiment.

Some non-limiting examples of enduse applications wherein the cured coating product of present invention may be used include, for example, coatings for the marine, steel structure, maintenance, and transportation industries.

EXAMPLES

5 The following examples and comparative examples further illustrate the present invention in detail but are not to be construed to limit the scope thereof.

In the following Examples, various materials, terms and designations are used such as for example the raw materials listed in Table I as follows:

Table I – Raw Materials

<u>Product</u>	<u>Description</u>	<u>Supplier</u>
Xylene	Solvent	Sinopharm Chemical Reagent Co.
Butanol	Solvent	Sinopharm Chemical Reagent Co.
D.E.R.331	Epoxy resin	The Dow Chemical Company
D.E.R.852	Epoxy resin	The Dow Chemical Company
D.E.R. 660X80	Epoxy resin	The Dow Chemical Company
FORTEGRA 202 adduct (F202 A)	Epoxy toughening agent	The Dow Chemical Company
FORTEGRA 202	Epoxy toughening agent	The Dow Chemical Company
Anti-terra 203	Dispersant additive	BYK
Bentone	Thickener	Elementise
Iron oxide red	Pigment	Zhejiang Huayuan Pigment Co.
Talc	Filler	Shanghai Extender Co.
Barytes	Filler	Shanghai Extender Co.
BYK066N	Defoamer	BYK
Aluminum paste	Anti-corrosive pigment	Henan Metallic Pigment Co.
Silicone 6040	Adhesion additive	Dow Corning
D.E.H.641	Phenalkamine hardener	The Dow Chemical Company
DMP30	Amine catalyst	The Dow Chemical Company

Inventive Examples 1-8 and Comparative Examples 1-6General Synthesis Procedure for FORTEGRA 202 Adduct

FORTEGRA 202 adduct (F202A) is an epoxy terminated amphiphilic block copolymer with an epoxy equivalent weight (EEW) of 360; and is prepared as follows:

5 FORTEGRA 202, 400 g, and D.E.R. 331, 600 g, is added into a 2 liter (L) flask. Then, the resulting mixture is stirred at 200 revolutions per minute (rpm), open chilling water and purge nitrogen (N₂). The temperature of the reaction mixture is raised to 120 °C and the reaction is then maintained at 120 °C for 2 hr. The epoxide equivalent weight (EEW) of the resultant mixture is tested, and if the EEW of the mixture is higher
10 than 330, the reaction is stopped. The reaction mixture is then cooled to 60 °C and a sample is poured out into a beaker. The sample is then analyzed and determined to be FORTEGRA 202 adduct.

General Synthesis Procedure for Clear Coating Formulations

The clear coating formulations described in Table II are prepared by
15 blending the components in a vessel at room temperature (about 23 °C) for about 0.5 hr.

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Table II – Formulation of Clear Coatings

Specimen Number	HSFC1 (control)	HSFC2	HSFC3	HSFC4	HSFC5	HSFC6	HSFC7	HSFC8	HSFC9	HSFC10
EXAMPLE	CE ^(a) 1	IE ^(b) 1	IE2	CE2	CE3	IE3	IE4	IE5	CE4	CE5
Part A										
D.E.R.331	0	0	0	0	0	0	23.5	28	25	23
D.E.R.660X80	0	0	0	17.5	11.6	0	0	0	0	0
ODDRAFlex LC 301	28	20.5	23.5	14	18.6	25.75	0	0	0	0
D.E.R. 852	0	0	0	0	0	0	0	0	3	5
D.E.R.791	0	0	0	0	0	0	0	0	0	0
FORTEGRA 202 adduct	0	12.5	7.5	0	0	3.75	7.5	0	0	0
FORTEGRA 202	0	0	0	0	0	0	0	3	0	0
Xylene	3	3	3	3	3	5	5	5	5	5
Butanol	1	1	1	1	1	1	1	1	1	1
Part B										
D.E.H.641	6.55	14.44	14.15	12.36	12.76	13.94	18.34	18.34	17.88	17.33
ODDRAcure 5102	4.36	0	0	0	0	0	0	0	0	0
DMP30	0.61	0.61	0.61	0.61	0.61	0.61	0.61	0.61	0.61	0.61
Total	43.52	52.05	49.76	48.47	47.57	50.05	55.95	55.95	52.49	51.94

^(a)CE = Comparative Example^(b)IE = Inventive Example

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Samples of the above formulations of Table II were then subjected to the tests described in Table III. The results of the testing are described in Table IV.

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Table III - Tests

<u>Performance</u>	<u>Testing Method</u>
Pendulum Hardness, seconds	ASTM D 4366 (1994)
Cross Cut Adhesion Test	ATSM D3002 (2002)
Impact resistance, cm.kg	DIN EN ISO 6272 (2011)
Flexibility, mm	ISO6860 (2006)
Thickness, μ m	ISO 02808 (2007)
Cone & Plate Viscosity	ASTM 4287 (1994)
Salt Spray Test, 1000h test on Q-panel	ASTM B117 (2003)

Table IV – Hardness/Impact /Flexibility Test Results of Clear Coatings

<u>Specimen Number</u>	<u>EXAMPLES</u>	<u>Hardness (s)</u>	<u>Adhesion</u>	<u>Impact (forward) (cm.kg)</u>	<u>Impact (reverse) (cm.kg)</u>	<u>Flexibility (mm)</u>
HSFC1	Comparative Example 1 (CE ^(a) 1)	134	5B	25	8	>18
HSFC2	Inventive Example 1 (IE ^(b) 1)	73	5B	106	106	<5
HSFC3	Inventive Example 2 (IE2)	91	5B	60	55	<5
HSFC4	Comparative Example 2 (CE2)	175	5B	25	8	>18
HSFC5	Comparative Example 3 (CE3)	131	5B	30	15	>18
HSFC6	Inventive Example 3 (IE3)	94	5B	50	50	<5
HSFC7	Inventive Example 4 (IE4)	151	5B	35	15	>18
HSFC8	Inventive Example 5 (IE 5)	146	5B	30	15	>18
HSFC9	Comparative Example 4 (CE4)	123	5B	20	<5	>18
HSFC10	Comparative Example 5 (CE5)	110	5B	25	<5	<5

^(a)CE = Comparative Example^(b)IE = Inventive Example

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Formulations of Comparative Example 1, Comparative Example 2, Comparative Example 3 and Inventive Example 1, Inventive Example 2 and Inventive Example 3 described in Table II above, are based on OUDRAFlex LC 301 epoxy resin.

From the performance results described in Table IV above, it can be seen that Inventive Example 1, Inventive Example 2 and Inventive Example 3 (with 1.5 %/ 3 % / 5 % added toughening agent FORTEGRA 202 adduct [in total formula], respectively) in 80 % volume solid (VS) epoxy coating formulations, FORTEGRA 202 adduct provides a significant improved flexibility and impact resistance. Formulations of Comparative Example 4, Comparative Example 5, Inventive Example 4, and Inventive Example 5 are based on D.E.R. 331 epoxy resin; and D.E.R. 852 (a flexible epoxy resin) was added in Comparative Example 4 and Comparative Example 5. Fortegra 202 adduct was added in the formulation of Inventive Example 4. Fortegra 202 was added in the formulation of Inventive Example 5. From the performance results, it can be seen that both FORTEGRA 202 and FORTEGRA 202 adduct can give good adhesion as well as better impact resistance from reverse and forward. Also, Inventive Example 4 and Inventive Example 5 show similar performance in adhesion, impact resistance and flexibility, which means that in a high solids coating formulation, FORTEGRA 202 and FORTEGRA 202 adduct give a similar improved contribution to toughness.

General Synthesis Procedure for Pigmented Coating Formulations

The pigmented coating formulations described in Table V are prepared by blending the components in a vessel and heating the mixture at room temperature for about 0.5 hr to about 1 hr.

Samples of the formulations described in Table V were then subjected to the tests described in Table III above. The results of the testing are described in Table VI.

Table V – Pigmented Formulations

<u>EXAMPLE</u>	<u>Comparative Example 6 (CE^(a)6)</u>	<u>Inventive Example 6 (IE^(b)6)</u>	<u>Inventive Example 7 (IE7)</u>	<u>Inventive Example 8 (IE8)</u>
Xylene	a high solids epoxy primer product from the market	4.11	4.11	4.11
Butanol		0.50	0.50	0.50
D.E.R. 331		0.00	0.00	29.00
OUDRAFlex LC 301		31.00	31.00	0.00
F-202(100%)		3.00	1.50	3.00
Anti-terra 203		0.31	0.31	0.31
Bentone		2.00	2.00	2.00
Iron oxide red		1.00	1.00	1.00
Talc		15.00	15.00	13.23
Barytes		17.50	17.50	17.50
BYK066N		0.30	0.30	0.30
Xylene		1.03	1.03	1.03
Aluminum paste		4.00	4.00	4.00
Silicone 6040		0.51	0.51	0.51
Butanol		2.06	2.06	2.06
Xylene		1.50	1.50	1.50
		0.00	0.00	0.00
DEH641		13.68	13.68	0.00
DMP30		0.60	0.60	0.60
Xylene		1.30	1.30	1.30
Total		99.40	97.90	81.95

^(a)CE = Comparative Example^(b)IE = Inventive Example

Table VI – Pigmented Coating Performance

<u>EXAMPLE</u>	<u>Hardness</u> (s)	<u>Adhesion</u>	<u>Impact forward</u> (cm.kg)	<u>Impact Reverse</u> (cm.kg)	<u>Flexibility</u> (mm)	<u>Thickness</u> (μ m)	<u>Viscosity, 10# 100 rpm</u> <u>Mixed (cps)</u>	<u>Wet adhesion</u> <u>ATSM D 3359</u>	<u>Creep</u> <u>rust/disbondment</u> (mm)	<u>Blistering</u> <u>(ASTM D714)</u>
Comparative Example 6 (CE ^(a) 6)	62	5B	20	2	>18	92-106	N/A	2	>30/>30	2M
Inventive Example 6 (IE ^(b) 6)	63	5B	30	4	12.3	70-106	2910	5	10/12	8F
Inventive Example 7 (IE 7)	74	5B	20	2	>18	96-116	2205	5	12/15	8F
Inventive Example 8 (IE 8)	84	5B	20	2	16	92-108	1115	5	5/7	8F

^(a)CE = Comparative Example^(b)IE = Inventive Example

Note for Table VI: Wet adhesion after salt spray test: ATSM D 3359; Salt Spray: ASTM B117 1000h test on Q-panel

CLAIMS

1. A curable coating composition comprising:

(a) at least one epoxy resin;

(b) at least one curing agent; and

(c) at least one amphiphilic block copolymer toughening agent; wherein

5 the toughening agent is a carboxyl group terminated amphiphilic block copolymer, an epoxy group terminated amphiphilic block copolymer; or mixtures thereof;

wherein the curable composition is a liquid having a low volatile organic component (VOC) property of less than about 250 g/L as measured by ASTM D2369; and

10 wherein the curable composition, when cured, provides an anticorrosive cured product having an increase in one or more properties compared to a cured product cured from a curable composition without the at least one amphiphilic block copolymer toughening agent, component (c).

2. The curable coating composition of claim 1, wherein the curable composition, when cured, provides an anticorrosive cured product having an increase in

15 (i) flexibility, (ii) impact resistance, and (iii) corrosion resistance compared to a cured product cured from a curable composition without the at least one amphiphilic block copolymer toughening agent, component (c).

3. The curable coating composition of claim 1, wherein the at least one epoxy resin is aliphatic epoxy resins, cycloaliphatic epoxy resins, bisphenol A epoxy resins,

20 bisphenol F epoxy resins, phenol novolac epoxy resins, cresol-novolac epoxy resins, biphenyl epoxy resins, polyfunctional epoxy resins, naphthalene epoxy resins, divinylbenzene dioxide, 2-glycidylphenylglycidyl ether, dicyclopentadiene-type epoxy resins, phosphorous containing epoxy resin, multi aromatic resin type epoxy resins, or mixture therefore.

4. The curable coating composition of claim 1, wherein the

25 concentration of the at least one epoxy resin is from about 5 weight percent to about 100 weight percent.

5. The curable coating composition of claim 1, wherein the at least one curing agent is an anhydride hardener, an amine hardener, a phenol novolac hardener, an imidazole hardener, or mixtures thereof.

6. The curable coating composition of claim 1, wherein the
5 concentration of the at least one curing agent is from about 0.1 weight percent to about 60 weight percent.

7. The curable coating composition of claim 1, wherein the concentration of the at least one toughening agent is from about 0.1 weight percent to about 90 weight percent.

10 8. A process for preparing a curable coating composition comprising admixing:

(a) at least one epoxy resin;

(b) at least one curing agent; and

(c) at least one amphiphilic block copolymer toughening agent; wherein
15 the toughening agent is a carboxyl group terminated amphiphilic block copolymer, an epoxy group terminated amphiphilic block copolymer; or mixtures thereof;

wherein the curable composition is a liquid having a low VOC property of less than about 250 g/L as measured by ASTM D2369; and

wherein the curable composition, when cured, provides an anticorrosive
20 cured product having an increase in one or more properties compared to a cured product cured from a curable composition without the at least one amphiphilic block copolymer toughening agent, component (c).

9. The process of claim 8, wherein the curable composition, when cured, provides an anticorrosive cured product having an increase in (i) flexibility,
25 (ii) impact resistance, and (iii) corrosion resistance compared to a cured product cured from a curable composition without the at least one amphiphilic block copolymer toughening agent, component (c).

10. A cured coating product comprising the reaction product of a curable composition including the following components:

(a) at least one epoxy resin;

(b) at least one curing agent; and

(c) at least one amphiphilic block copolymer toughening agent; wherein the toughening agent is a carboxyl group terminated amphiphilic block copolymer, an epoxy group terminated amphiphilic block copolymer; or mixtures thereof;

wherein the curable composition is a liquid having a low volatile organic component (VOC) property of less than about 250 g/L as measured by ASTM D2369; and

wherein the cured coating product is an anticorrosive cured product having an increase in one or more properties compared to a cured product cured from a curable composition without the at least one amphiphilic block copolymer toughening agent, component (c).

11. The cured coating of claim 10, wherein the cured product has an increase in (i) flexibility, (ii) impact resistance, and (iii) corrosion resistance compared to a cured product cured from a curable composition without the at least one amphiphilic block copolymer toughening agent, component (c).

12. A process for preparing a cured product comprising the steps of:

(I) preparing a curable composition by admixing:

(a) at least one epoxy resin;

(b) at least one curing agent; and

(c) at least one amphiphilic block copolymer toughening agent; wherein the toughening agent is a carboxyl group terminated amphiphilic block copolymer, an epoxy group terminated amphiphilic block copolymer; or mixtures thereof;

wherein the curable composition is a liquid having a low VOC property of less than about 250 g/L as measured by ASTM D2369; and

wherein the curable composition, when cured, provides an anticorrosive cured product having an increase in one or more properties compared to a cured product cured from a curable composition without the at least one amphiphilic block copolymer toughening agent, component (c); and

(II) heating the curable coating composition of step (I) to form a cured product.

13. The process of claim 12, wherein the cured product has an increase in (i) flexibility, (ii) impact resistance, and (iii) corrosion resistance compared to a cured product cured from a curable composition without the at least one amphiphilic block copolymer toughening agent, component (c).

14. The process of claim 12, wherein the heating step (II) is carried out at a temperature of from about -10°C to about 200°C .

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2015/080981

A. CLASSIFICATION OF SUBJECT MATTER

C08L 63/00(2006.01)i; C08L 71/02(2006.01)i; C09D 163/00(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)

C08L 63/-; C08L 71/-; C09D 163/-

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)

WPI,EPODOC,GOOGLE,CA,CNKI,CNPAT: epoxy,resin,liquid,coating,terminate?,amphiphilic,block,copolymer,cur

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2010007150 A2 (SIKA TECHNOLOGY AG, ET AL.) 21 January 2010 (2010-01-21) claims 1-12, description, page 12 lines 1-5 and 23-25, page 13 lines 3-5, page 14 lines 3-7, page 29 line 27-page 30 line 20, page 31 lines 14-16	1-14
Y	WO 2010007150 A2 (SIKA TECHNOLOGY AG, ET AL.) 21 January 2010 (2010-01-21) claims 1-12, description, page 12 lines 1-5 and 23-25, page 13 lines 3-5, page 14 lines 3-7, page 29 line 27-page 30 line 20, page 31 lines 14-16	1-14
X	WO 2015042823 A1 (DOW GLOBAL TECHNOLOGIES LLC, ET AL.) 02 April 2015 (2015-04-02) claims 1-16, description, page 3 lines 27-39, page 11 lines 6-20	1-14
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Further documents are listed in the continuation of Box C.



See patent family annex.

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“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

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Date of the actual completion of the international search

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26 August 2015

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2015/080981**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	WO 2006052730 A1 (DOW GLOBAL TECHNOLOGIES INC, ET AL.) 18 May 2006 (2006-05-18) claims 1-27	1-14

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Information on patent family members

International application No.

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