(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
17 April 2014 (17.04.2014)

WIPO | PCT

(10) International Publication Number
WO 2014/058523 A1

(51) International Patent Classification:
C09D 5/44 (2006.01) *C09D 181/04* (2006.01)
C08G 59/14 (2006.01) *C25D 5/44* (2006.01)
C08G 59/30 (2006.01) *C25D 13/22* (2006.01)
C08G 59/32 (2006.01) *C25D 13/04* (2006.01)
C09D 163/00 (2006.01) *C25D 5/50* (2006.01)

(21) International Application Number:
PCT/US2013/054262

(22) International Filing Date:
9 August 2013 (09.08.2013)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
13/649,144 11 October 2012 (11.10.2012) US

(71) Applicant: **PRC-DESOTO INTERNATIONAL, INC.** [US/US]; 12780 San Fernando Road, Sylmar, California 91342 (US).

(72) Inventors: **ANDERSON, Lawrence G.**; 4119 Northampton Drive, Allison Park, Pennsylvania 15101 (US). **FURAR, Elizabeth A.**; 371 Village Drive, Pittsburgh, Pennsylvania 15215 (US). **LINGENFELTER, Thor G.**; 411 Belle Street, Evans City, Pennsylvania 16033 (US). **MAYO, Michael A.**; 56 Rustic Ridge Drive, Pittsburgh, Pennsylvania 15239 (US). **PEFFER, Robin M.**; 176 Dwellington Drive, Valencia, Pennsylvania 16059 (US).

(74) Agents: **MEYERS, Diane R.** et al.; PPG Industries, Inc., One PPG Place, 39th Floor, Pittsburgh, Pennsylvania 15272 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

— *with international search report (Art. 21(3))*

WO 2014/058523 A1

(54) Title: COATING/SEALANT SYSTEMS, AQUEOUS RESINOUS DISPERSIONS, METHODS FOR MAKING AQUEOUS RESINOUS DISPERSIONS, AND METHODS OF ELECTROCOATING

(57) Abstract: A coating/sealant system that includes a coating and a sealant deposited over at least a portion of the coating, in which the coating includes a reaction product formed from reactants comprising a phosphated epoxy resin and a curing agent, and the sealant includes a sulfur-containing polymer.

COATING/SEALANT SYSTEMS, AQUEOUS RESINOUS DISPERSIONS, METHODS FOR MAKING AQUEOUS RESINOUS DISPERSIONS, AND METHODS OF ELECTROCOATING

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application is a continuation-in-part and claims priority to U.S. Patent Application Serial No. 13/232,093 filed September 14, 2011, which is incorporated herein by reference in its entirety.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

[0002] This invention was made with Government support under Contract No. FA8650-05-C-5010 awarded by the Air Force Research Laboratory. The United States Government may have certain rights in this invention.

FIELD OF THE INVENTION

[0003] The present invention relates to coating/sealant systems, anionic resinous dispersions, methods for making such dispersions, and methods for electrocoating using such dispersions.

BACKGROUND OF THE INVENTION

[0004] Sulfur-containing polymers are known to be well-suited for use in various applications, such as aerospace sealant compositions, due, in large part, to their fuel-resistant nature upon cross-linking. One class of sulfur-containing polymers often used in aerospace sealant compositions is polysulfides, which are polymers that have disulfide (□S□S□) linkages. Aerospace sealants that include sulfur-containing polymers, such as polysulfides, may be applied to the joint or space formed by the interface between electrically conductive substrates, such as those comprising aluminum, to which a previously deposited corrosion resistant primer coating has previously been applied. It is important that the sealant and primer coating adhere well to each other and to the substrate, though this has not always been achieved.

SUMMARY OF THE INVENTION

[0005] In certain respects, the present invention is directed to coating/sealant systems. These systems comprise a coating and a sealant deposited over at least a

portion of the coating. The coating comprises a reaction product formed from reactants comprising: (i) a phosphated epoxy resin; and (ii) a curing agent, and the sealant is deposited from a composition comprising a sulfur-containing polymer comprising a thiol-functional polysulfide.

[0006] In other respects, the present invention is directed to aqueous resinous dispersions. These dispersions comprise a base-neutralized resinous composition that comprises an ungelled phosphated epoxy resin. The ungelled phosphated epoxy resin comprises a reaction product formed from reactants comprising: (a) a polyepoxide; (b) a sulfur-functional azole; and (c) a phosphorous acid.

[0007] In yet other respects, the present invention is directed to methods of making base-neutralized aqueous resinous dispersions. These methods comprise: (a) adding a sulfur-functional azole to a composition comprising a phosphated epoxy resin derived from at least (i) a polyepoxide, and (ii) a phosphorous acid; (b) adding a base to the composition after at least a portion of the sulfur-functional azole has been added; and (c) adding water to the composition after at least a portion of the base has been added to the composition.

[0008] In still other respects, the present invention is directed to methods of electrocoating an electrically conductive substrate serving as an anode in an electrical circuit comprising the anode and a cathode that are immersed in an aqueous resinous dispersion comprising passing electric current between the anode and the cathode to cause a resinous composition to deposit on the anode. In these methods, the dispersion comprises an anionic resin comprising a reaction product formed from reactants comprising: (a) a polyepoxide; (b) a sulfur-functional azole; and (c) a phosphorous acid.

[0009] The present invention is also directed to, *inter alia*, related coated substrates, including aerospace vehicles comprising a substrate coated with a composition described herein and/or a coating/sealant system described herein.

DETAILED DESCRIPTION OF EMBODIMENTS OF THE INVENTION

[0010] For purposes of the following detailed description, it is to be understood that the invention may assume various alternative variations and step sequences, except where expressly specified to the contrary. Moreover, other than in

any operating examples, or where otherwise indicated, all numbers expressing, for example, quantities of ingredients used in the specification and claims are to be understood as being modified in all instances by the term "about". Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[0011] Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard variation found in their respective testing measurements.

[0012] Also, it should be understood that any numerical range recited herein is intended to include all sub-ranges subsumed therein. For example, a range of "1 to 10" is intended to include all sub-ranges between (and including) the recited minimum value of 1 and the recited maximum value of 10, that is, having a minimum value equal to or greater than 1 and a maximum value of equal to or less than 10.

[0013] As indicated above, certain embodiments of the present invention are directed to coating/sealant systems. As used herein, the term "coating/sealant system" refers to a combination that includes a layer of coating and a sealant deposited over at least a portion of the coating. As used herein, the term "coating" refers to a substantially continuous polymer layer supported on a substrate, which may or may not have a uniform thickness. As used herein, the term "**sealant**" refers to a solid elastomer that, when applied to an aperture (such as the joint or space formed by the interface between two parts), has the ability to resist atmospheric conditions, such as moisture and temperature, and at least partially block the transmission of materials, such as water, fuel, and/or other liquids and gasses, which might otherwise occur at the aperture. Sealants, therefore, are often applied to a peripheral edge surface of a component part for the purpose of hindering material transport to or from such a part. In certain embodiments, the coating/sealant systems of the present invention are

useful on aerospace fuel tanks. Thus, in certain embodiments of the present invention, the sealant is "fuel-resistant", which, as used herein, refers to a cured sealant that has a percent volume swell of not greater than 40%, in some cases not greater than 25%, in some cases not greater than 20% after immersion for one week at 140°F (60°C) and ambient pressure (1 atmosphere) in jet reference fluid (JRF) type 1 according to methods similar to those described in ASTM D792 or AMS 3269a, incorporated herein by reference. Jet reference fluid JRF type 1, as employed herein for determination of fuel resistance, has the following composition (see AMS 2629, issued Jul. 1, 1989), §3.1.1 et seq., available from SAE (Society of Automotive Engineers, Warrendale, PA) (that is incorporated herein by reference):

Toluene	28 ± 1% by volume
Cyclohexane (technical)	34 ± 1% by volume
Isooctane	38 ± 1% by volume
Tertiary dibutyl disulfide (doctor sweet)	1 ± 0.005% by volume

[0014] The coating/sealant systems of the present invention can be deposited upon any of a variety of substrates. In certain embodiments, however, the substrate is electrically conductive, such as is the case with substrates comprising titanium, stainless steel, aluminum, as well as electrically conductive composite materials, such as polymeric materials containing a sufficient amount of conductive filler, such as carbon black. As will be appreciated, the substrate can optionally be pretreated with a corrosion-inhibiting treatment, such as anodizing or deposition of a conversion coating composition (such as is described in United States Patent Application Publication No. 2010-0243108 A1 at [0014]-[0019], the cited portion of which being incorporated herein by reference), as long as the substrate maintains its electrical conductivity. In some embodiments, the substrate is only cleaned and deoxidized . prior to application of the coating/sealant systems of the present invention. Such cleaning and deoxidizing is described in the foregoing United States Patent Application Publication No. 2010-0243108 at [0014]-[0017].

[0015] In certain embodiments of the present invention, the substrate is embodied in the form of a component part of an aircraft, such as, for example, a wing, a fuselage, or a tail assemblage. More specifically, the substrate may be embodied as any of a variety of aircraft parts, such as, for example, an aileron, a wing edge

(leading or trailing) or spar, slat, spoiler, flap, rudder, fin, horizontal stabilizer, elevator, tail, tube, seat track, floor track, strut, longeron, skin, rib, bulkhead, wheel, stringer, helicopter rotor blade, (including spar and outer surface), or any of a variety of flanges, hinges, clips, and fasteners, such as rivets, bolts, nuts, that connect parts together.

[0016] As previously indicated, the coating/sealant systems of the present invention comprise a coating comprising a reaction product formed from reactants comprising a phosphated epoxy resin. As used herein, the term "phosphated epoxy resin" refers to an ungelled resin derived from at least a polyepoxide and a phosphorous acid.

[0017] Suitable polyepoxides include any compound or a mixture of compounds having more than 1.0 epoxy groups per molecule. Several polyepoxides are known in the art. Examples of the polyepoxides can be found in the Handbook of Epoxy Resins, Lee and Neville, 1967, McGraw-Hill Book Company.

[0018] In certain embodiments of the present invention, the polyepoxide comprises a polyglycidyl ether of a polyphenol, such as bisphenol A. As will be appreciated, such polyepoxides can be produced by etherification of a polyphenol with an epichlorohydrin in the presence of an alkali. Suitable polyphenols include, without limitation, 1,1-bis(4-hydroxyphenyl)ethane; 2,2-bis(4-hydroxyphenyl)propane; 1,1-bis(4-hydroxyphenyl)isobutane; 2,2-bis(4-hydroxytertiarybutylphenyl) propane; bis(2-hydroxynaphthyl)methane; 1,5-dihydroxynaphthalene; 1,1-bis(4-hydroxy-3-allylphenyl)ethane; and 4,4-bis(4'-hydroxyphenyl)valeric acid. Another useful class of polyepoxides is produced similarly from polyphenol resins.

[0019] In addition to the polyepoxides described above, there can also be employed addition polymerization polymers containing pendant epoxy groups. Such polymers can be made by copolymerizing a variety of polymerizable ethylenically unsaturated monomers at least one of which is an epoxy containing monomer, e.g., glycidyl acrylate or glycidyl methacrylate.

[0020] A suitable ethylenically unsaturated monomer that does not contain a group that is reactive with the epoxy group can be employed as a comonomer. Exemplary such monomers include α,β-ethylenically unsaturated monomers, such as

unsaturated carboxylic acid esters of saturated alcohols containing from 1 to about 8 carbon atoms, and monovinyl aromatic monomers such as styrene and vinyl toluene.

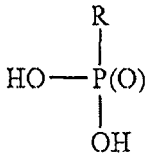
[0021] In certain embodiments, the polyepoxide has an epoxy equivalent weight of 172 to 5000, such as 300 to 1000.

[0022] In addition to the polyepoxide(s), the reaction mixture can contain a monomeric monoepoxide such as monoglycidyl ethers of alcohols and phenols, such as phenyl glycidyl ether, and glycidyl esters of monocarboxylic acids such as glycidyl neodecanoate.

[0023] In certain embodiments, the phosphorous acid that is reacted with the polyepoxide comprises a phosphoric acid, such as, for example, a 100 percent orthophosphoric acid or a phosphoric acid aqueous solution such as is referred to as an 85 percent phosphoric acid. Other forms of phosphoric acid such as superphosphoric acid, diphosphoric acid and triphosphoric acid can be employed herein. Also, the polymeric or partial anhydrides of phosphoric acids can be employed. In some embodiments, aqueous phosphoric acids that are of about 70 to 90 percent and preferably about 85 percent phosphoric acid are employed.

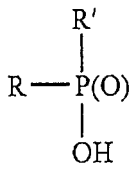
[0024] In some embodiments, the phosphorous acid that is reacted with the polyepoxide consists essentially of a phosphoric acid. In other words, in these embodiments, the phosphoric acid is present in an amount of at least 98 mole %, at least 99% mole %, or, in some cases, 100 mole %, based on the total moles of phosphorous acid that is reacted with the polyepoxide.

[0025] Alternatively, in addition to, or in lieu of, the phosphoric acid, phosphonic acids and/or phosphinic acids can be reacted with the polyepoxide. Examples of phosphonic acids are organophosphonic acids of the structure:



wherein R is organic radical such as those having a total of 1-30, such as 6-18 carbons. R can be aliphatic, aromatic or mixed aliphatic/aromatic and can be an unsubstituted hydrocarbon or a substituted hydrocarbon.

[0026] Examples of phosphinic acids are organophosphinic acids of the structure:



wherein R and R' are each independently hydrogen or an organic radical. Examples of such radicals are those having a total of 1-30, such as 6-18 carbons. The organic component of the phosphinic acid (R, R') can be aliphatic, aromatic or mixed aliphatic/aromatic. R and R' can be an unsubstituted hydrocarbon or a substituted hydrocarbon.

[0027] Representative suitable organophosphonic acids and organophosphinic acids are: 3-amino propyl phosphonic acid, 4-methoxyphenyl phosphonic acid, benzylphosphonic acid, butylphosphonic acid, carboxyethylphosphonic acid, diphenylphosphinic acid, dodecylphosphonic acid, ethylidenediphosphonic acid, heptadecylphosphonic acid, methylbenzylphosphinic acid, naphthylmethylphosphinic acid, octadecylphosphonic acid, octylphosphonic acid, pentylphosphonic acid, methylphenylphosphinic acid, phenylphosphonic acid, styrene phosphonic acid, dodecyl bis-1,12-phosphonic acid, poly(ethylene glycol) phosphonic acid, including mixtures thereof.

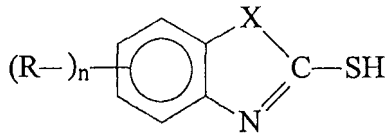
[0028] In some embodiments of the present invention, the phosphorous acid comprises a mixture of: (a) a phosphoric acid; and (b) an organophosphonic acid and/or an organophosphinic acid. In these embodiments, as will be appreciated, the resulting phosphated epoxy resin comprises a mixture of reaction products formed from reactants comprising: (i) a polyepoxide; (ii) a phosphoric acid; and (iii) an organophosphonic acid and/or an organophosphinic acid. As will be appreciated, such a mixture of reaction products may include a phosphated epoxy resin in which the phosphated portion is derived solely from phosphoric acid, a phosphated epoxy resin in which the phosphated portion is derived solely from organophosphonic and/or organophosphinic acid, and/or a phosphated epoxy resin in which the phosphated portion is derived from both a phosphoric acid and/or organophosphonic and/or organophosphinic acid. In certain embodiments, the relative amounts of the polyepoxide and the phosphorus acids that are reacted with one another are: for each

equivalent of epoxy, there are 0.1 to 0.8 moles of phosphoric acid and from 0.01 to 0.4 moles of organophosphonic and/or organophosphinic acid with the molar ratio of phosphoric to organophosphonic and/or organophosphinic acid being within the range of 1:0.01 to 0.5. The phosphated epoxy resin often has an acid value of 10 to 60, such as 15 to 50, based on resin solids.

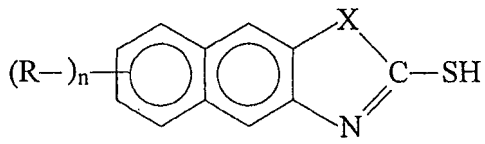
[0029] In certain embodiments of the present invention, the reactants used to manufacture the phosphated epoxy resin further comprise a sulfur-functional azole. As used herein, "azole" means a 5-membered heterocyclic compound that contains in the heterocyclic ring two double bonds, a nitrogen atom, at least one other non-carbon atom (such as another nitrogen atom, a oxygen atom or a sulfur atom), and one or more carbon atoms. Exemplary azoles include, without limitation, diazoles, triazoles, tetrazoles, oxazoles, oxadiazoles, oxatriazoles, thiazoles, thiadiazoles, and thiatriazoles. As used herein, "sulfur-functional azole" means an azole that includes at least one sulfur atom external to the azole ring.

[0030] In certain embodiments, the sulfur-functional azole comprises a mercaptoarylimidazole, mercaptoaryloxazole, and/or a mercaptoarylthiazole.

[0031] More particularly, in certain embodiments, the mercaptoarylimidazole, mercaptoaryloxazole, or mercaptoarylthiazole is represented by the structure (I) or (II) or a tautomer thereof:



(I)



(II)

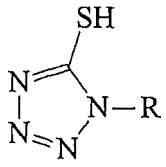
wherein: (i) X represents a nitrogen atom, an oxygen atom, or a sulfur atom; (ii) R represents hydroxyl, hydrogen, aryl, alkyl, aralkyl, or a halogen atom; and (iii) n is an integer of 0 to 4.

[0032] Specific examples of compounds according to structure (I), which are suitable for use in the present invention, include mercaptobenzimidazole, mercaptomethylbenzimidazole, mercaptohydroxybenzimidazole, mercaptoiodobenzimidazole, mercaptochlorobenzimidazole,

mercaptotetrahydroxybutylphenylimidazole, mercaptobenzoxazole, mercaptomethylbenzoxazole, mercaptohydroxybenzoxazole, mercaptoiodobenzoxazole, mercaptochlorobenzoxazole, mercaptotetrahydroxybutylphenyloxazole, mercaptobenzothiazole, mercaptomethylbenzothiazole, mercaptohydroxybenzothiazole, mercaptoiodobenzothiazole, mercaptochlorobenzothiazole, mercaptotetrahydroxybutylphenylthiazole, mercaptohydroxybenzothiazole and the like, including mixtures thereof.

[0033] Specific examples of compounds according to structure (II), which are suitable for use in the present invention, include mercaptonaphthoimidazole, mercaptochloronaphthoimidazole, mercaptohydroxynaphthoimidazole, mercaptomethylnaphthoimidazole, mercaptonaphthothiazole, mercaptoiodonaphthothiazole, mercaptohydroxynaphthothiazole, mercaptomethylnaphthothiazole and the like, including mixtures thereof. Such compounds are disclosed in U.S. Patent No. 5,498,502 at col. 4, lines 8-40, the cited portion of which being incorporated herein by reference.

[0034] Also suitable are sulfur-functional azoles that contain three or more nitrogen atoms in the heterocyclic ring, *i.e.*, triazoles and tetrazoles. In some embodiments, the sulfur-functional azole comprises a sulfur-functional tetrazole according to the formula (III):



(III)

wherein R represents an organic radical, such as those having a total of 1 to 30, such as 1-18 or 6-18 or 1-6 carbon atoms. R can be aliphatic, aromatic, or mixed aliphatic/aromatic and can be unsubstituted hydrocarbon or a substituted hydrocarbon.

[0035] Specific examples of such compounds, according to formula (III) are 5-mercapto-1-methyltetrazole, 1-ethyl-5-mercaptotetrazole, 1-cyclopropyl-5-mercaptotetrazole, 1-allyl-5-mercaptotetrazole, 1-benzyl-5-mercaptotetrazole, 1-(2-methoxyethyl)-5-mercaptotetrazole, and phenyl-1H-tetrazole 5-thiol.

[0036] Examples of the sulfur-functional triazoles include 5-phenyl-1H-1,2,4-triazole-3-thiol, 3-mercapto-1,5-diphenyl-1,2,4-triazole, 3-mercapto-1,2,4-triazole, 3-mercapto-4-methyl-1,2,4-triazole, 3-mercapto-1-phenyl-1,2,4-triazole, 5-mercapto-1-phenyl-1,2,4-triazole, and 5-mercapto-1,2,4-triazole-3-acetic acid, 3,5-dimercapto-1,2,4-triazole, 3,5-dimercapto-1-phenyl-1,2,4-triazole, and 3,5-dimercapto-1,4-diphenyl-1,2,4-triazole.

[0037] Examples of sulfur-functional oxazoles include: 2-mercaptoxazolo[4,5]pyridine; 2-mercaptoxazole, 5-nitro-2-mercaptobenzoxazole; 5-chloro-mercaptoxazole; 2-mercapto-5-phenyloxazole; 2-mercapto-4,5-dimethyloxazole; 2-mercapto-4,5-diphenyloxazole; 6-amino-mercaptobenzoxazole; 2-mercaptobenzoxazole; 2-thioxo-4-oxazolidinone.

[0038] Examples of sulfur-functional thiazoles include: 2-mercaptothiazole; 4, 5-diphenyl-2-mercaptothiazole; 4-methy-2-mercaptolthiazole; 4,5-dimethyl-2-mercaptothiazole; thio-rhodanine; 2-mercapto -4-phenylthiazole; 5-thiorhodanine acetic acid; rhodaninic acid.

[0039] Examples of sulfur-functional thiadiazoles include: 5-ethyl-2-mercapto-1,3,4-thiadiazole, dimercapto-1,3,4-thiadiazole; 5-phenylmethyl-2-mercapto-1,3,4-thiadiazole; 5-aminomethyl-2-mercapto-1,3,4-thiadiazole; 2-sulfonamide-1,3,4-thiadiazole-2-thiol; 5-(propylthio)-2-mercapto-1, 3,4-thiadiazole; 2-mercapto-1,3,4-thiadiazole; 5,5 thio bis(1,3,4-thiadiazole-2-thiol); 5-phenyl 2-mercapto-1,3,4-thiadiazole; 5-amino-1,3,4 thiadiazole-2-thiol.

[0040] In certain embodiments, the relative amounts of the polyepoxide and the sulfur-functional azole that are reacted with one another are for each equivalent of epoxy, there are 0.01 to 0.25 mole of thiol.

[0041] In certain embodiments, in addition to the reactants described above, the reactants used to manufacture the phosphated epoxy resin may further comprise a compound having two functional groups reactive with epoxy groups, such as, diols, diphenols (including Bisphenol A), dicarboxylic acids, dithiols, and/or diamines, to name a few.

[0042] Suitable methods for preparing the phosphated epoxy resins described herein are illustrated by the Examples. In some cases, a sulfur-functional azole is first reacted with the polyepoxide and resulting reaction product with the phosphorus

acid(s). Such reactions are often conducted in organic solvent as described in the Examples.

[0043] Alternatively, suitable aqueous resinous dispersions can be produced by a method in which (a) a sulfur-functional azole (such as any of those described earlier) is added to a composition comprising a phosphated epoxy resin derived from at least (i) a polyepoxide (such as any of those described earlier), and (ii) a phosphorous acid (such as any of those described earlier); (b) a base (such as any of those described earlier) is added to the composition after at least a portion of the sulfur-functional azole has been added; and (c) water is added to the composition after at least a portion of the base has been added to the composition. In some cases, base is not added until after a majority (>50% by weight) of the total amount of sulfur-functional azole desired has been added to the composition. In still other cases, base is not added until after at least 90% by weight of the total amount of sulfur-functional azole desired as been added to the composition. In still other cases, base is not added until all of the total amount of sulfur-functional azole desired has been added to the composition. In some cases, water is not added until after a majority (>50% by weight) of the total amount of base desired has been added to the composition. In still other cases, water is not added until after at least 90% by weight of the total amount of base desired as been added to the composition. In still other cases, water is not added until all of the total amount of base desired has been added to the composition.

[0044] In certain embodiments of the present invention, the phosphated epoxy resin is present in the form of an aqueous dispersion of the phosphated epoxy resin in a continuous medium primarily or principally comprising water. For example, in certain embodiments, the continuous phase is at least 80 weight percent water, based on the total weight of the continuous medium. In certain embodiments, the amount of organic solvent present in the aqueous dispersion is less than 20 weight percent, such as less than 10 weight percent, or, in some cases, less than 5 weight percent, or, in yet other cases, less than 2 weight percent, with the weight percents being based on the total weight of the continuous phase.

[0045] In adapting the phosphated epoxy resin to be dispersed in a water-based continuous medium, it is neutralized with a base. Suitable bases include both organic or inorganic bases. Illustrative examples of suitable bases are ammonia,

monoalkylamines, dialkylamines, or trialkylamines such as ethylamine, propylamine, dimethylamine, dibutylamine and cyclohexylamine; monoalkanolamine, dialkanolamine or trialkanolamine such as ethanolamine, diethanolamine, triethanolamine, propanolamine, isopropanolamine, diisopropanolamine, dimethylethanolamine and diethylethanolamine; morpholine, e.g., N-methylmorpholine or N-ethylmorpholine. The percent of neutralization is such as would make the resin(s) water-dispersible and electrophoretic. Typically, the resin(s) are at least partially neutralized from 20 to 200 percent, 40 to 150 percent, such as 60 to 120 percent neutralization.

[0046] As a result, certain embodiments of the present invention are directed to aqueous resinous dispersions comprising a base-neutralized resinous composition, wherein the resinous composition comprises an ungelled phosphated epoxy resin comprising the reaction product of reactants comprising: (a) a polyepoxide; (b) a sulfur-functional azole; and (c) a phosphorous acid.

[0047] As previously indicated, in the coating/sealant systems of the present invention, the coating comprises a cured reaction product of reactants comprising the phosphated epoxy resin (such as any of those described above); and (ii) a curing agent. Therefore, certain embodiments of the aqueous resinous dispersions described above further comprise a curing agent.

[0048] Suitable curing agents include, but are not necessarily limited to, aminoplast resins and phenolplast resins. Suitable aminoplast resins are condensation products of an aldehyde, e.g., formaldehyde, acetaldehyde, crotonaldehyde, and benzaldehyde and an amino or amido group containing material such as urea, melamine, and benzoguanamine. Products obtained from the reaction of alcohols and formaldehyde with melamine, urea and benzoguanamine are often used.

[0049] Illustrative but non-limiting examples of useful aminoplast resins are those available under the trademark CYMEL from Cytec Industries and RESIMENE from Solutia Inc. Specific examples are CYMEL 1130 and 1156 and RESIMENE 750 and 753.

[0050] The relative amounts of the (a) phosphated epoxy resin and (b) curing agent is from 50 to 90, such as 60 to 75 percent by weight phosphated epoxy resin, and from 10 to 50, such as 25 to 40 percent by weight, curing agent based on solids

weight of (a) and (b). In some embodiments of the present invention, the phosphated epoxy resin is present in an amount of at least 40 percent by weight, at least 50 percent by weight, such as at least 60 percent by weight, based on the total resin solids weight of the liquid composition from which the coating is formed.

[0051] In preparing the final coating composition, the above ingredients can be admixed in water in any convenient manner. Typical coating additives such as pigments, fillers, corrosion inhibitors, anti-oxidants, flow control agents, surfactants and the like can also be employed.

[0052] Suitable corrosion inhibitors are azoles, such as benzotriazole, 5-methyl benzotriazole, 2–amino thiazole, and the sulfur-functional azoles described earlier with respect to preparation of the phosphated epoxy resin (when employed as a corrosion inhibitor, it is desired that at least some of the azole be "free", *i.e.*, not polymerized). Other suitable corrosion inhibitors include, but are not limited to, zinc phosphate, such as zinc orthophosphate, zinc metaborate, barium metaborate monhydrate, calcium ion-exchanged silica, colloidal silica, synthetic amorphous silica, and molybdates, such as calcium molybdate, zinc molybdate, barium molybdate, strontium molybdate, and mixtures thereof. Suitable calcium ion-exchanged silica is commercially available from W. R. Grace & Co. as SHIELDEX® AC3 and/or SHIELDEX® C303. Suitable amorphous silica is available from W. R. Grace & Co. under the tradename SYLOID®. Suitable zinc phosphate is commercially available from Heubach as HEUCOPHOS ZP-10.

[0053] Chrome-containing corrosion inhibitors are also suitable. Examples of such corrosion inhibitors are calcium chromate, magnesium chromate, strontium chromate and/or barium chromate.

[0054] In certain embodiments, the corrosion inhibitor(s), if present, are in the aqueous dispersion in amounts as low as 0.001 percent such as 0.001 to 10% by weight based on total weight of the aqueous dispersion. The composition often has a solids content of 5 to 25 percent, such as 5 to 15 percent.

[0055] In certain embodiments, the coating is deposited onto the substrate via an anionic electrodeposition process. In such a process, an electrically conductive substrate (such as any of those described earlier), serving as an anode in an electrical circuit comprising the anode and a cathode, is immersed in an aqueous resinous

dispersion comprising a base-neutralized resinous composition of the type described above. An electric current is passed between the anode and the cathode to cause the resinous composition to deposit on the anode.

[0056] The electrodeposition bath often has an operating bath conductivity of 200 to 3000 micromhos per centimeter, such as 500 to 1500 micromhos per centimeter. The residence time of the substrate being coated in the bath is often from 30 to 120 seconds.

[0057] After electrocoating, the substrate is removed and then baked in an oven at a temperature and over a period sufficient to effect cure. Often, the coated substrate is baked at temperatures of 225°F or lower, such as 200°F or lower for 20 to 60 minutes. In some cases, the substrate is cured at 180°F for 20 minutes to produce hard, solvent resistant and non-tacky film. If desired, the electrocoated substrates can be baked at higher temperatures of, say, 350°F.

[0058] As previously indicated, the coating/sealant systems of the present invention comprise a sealant deposited over at least a portion of the coating. In these embodiments of the present invention, the sealant is deposited from a composition comprising a sulfur-containing polymer. As used herein, the term "sulfur-containing polymer" refers to any polymer having at least one sulfur atom.

[0059] In certain embodiments, the sulfur-containing polymer comprises a polysulfide. Indeed, it has been discovered, surprisingly, that sealants formed from compositions comprising a polysulfide can adhere particularly well to certain coatings formed from an aqueous resinous dispersion comprising a base-neutralized resinous composition, wherein the resinous composition comprises an ungelled phosphated epoxy resin comprising the reaction product of reactants comprising: (a) a polyepoxide; (b) a sulfur-functional azole; and (c) a phosphorous acid, as described above.

[0060] As used herein, the term "polysulfide" refers to a polymer that contains one or more disulfide linkages, *i.e.*, □[S□S]□ linkages, in the polymer backbone and/or in the terminal or pendant positions on the polymer chain. Often, the polysulfide polymer will have two or more sulfur-sulfur linkages. Suitable polysulfides are commercially available from Akzo Nobel under the name THIOPLAST. THIOPLAST products are available in a wide range of molecular

weights ranging, for example, from less than 1100 to over 8000, with molecular weight being the average molecular weight in grams per mole. In some cases, the polysulfide has a number average molecular weight of 1,000 to 4,000. The crosslink density of these products also varies, depending on the amount of crosslinking agent used. The "□SH" content, i.e., mercaptan content, of these products can also vary. The mercaptan content and molecular weight of the polysulfide can affect the cure speed of the polymer, with cure speed increasing with molecular weight.

[0061] In some embodiments of the present invention, in addition to or in lieu of, a polysulfide as previously described, the sealant is deposited from a composition comprising a polymeric mixture comprising: (a) from 90 mole percent to 25 mole percent of mercaptan terminated disulfide polymer of the formula $HS(RSS)_mR'SH$; and (b) from 10 mole percent to 75 mole percent of diethyl formal mercaptan terminated polysulfide polymer of the formula $HS(RSS)_nRSH$, wherein R is $□C_2H_4□O□CH_2□O□C_2H_4□$; R' is a divalent member selected from alkyl of from 2 to 12 carbon atoms, alkyl thioether of from 4 to 20 carbon atoms, alkyl ether of from 4 to 20 carbon atoms and one oxygen atom, alkyl ether of from 4 to 20 carbon atoms and from 2 to 4 oxygen atoms each of which is separated from the other by at least 2 carbon atoms, alicyclic of from 6 to 12 carbon atoms, and aromatic lower alkyl; and the value of m and n is such that the diethyl formal mercaptan terminated polysulfide polymer and the mercaptan terminated disulfide polymer have an average molecular weight of from 1,000 to 4,000, such as 1,000 to 2,500. Such polymeric mixtures are described in U.S. Patent No. 4,623,711 at col. 4, line 18 to col. 8, line 35, the cited portion of which being incorporated herein by reference. In some cases, R' in the above formula is$□CH_2□CH_2□$; $□C_2H_4□O□C_2H_4□$; $□C_2H_4□S□C_2H_4□$; $□C_2H_4□O□C_2H_4□O□C_2H_4□$; or $□CH_2□C_6H_4□CH_2□$.

[0062] In addition to or in lieu of a polysulfide, the sulfur-containing polymer may comprise a polythioether. As used herein, the term "polythioether" refers to a polymer comprising at least one thioether linkage, *i.e.*, □[□C□S□C□]□, in the polymer backbone and/or in the terminal or pendant positions on the polymer chain. Often, polythioethers have from 8 to 200 of these linkages. Polythioethers suitable for use in the present invention include, for example, those that includes a structure

having the formula (IV):

$$—R^1—[—S—(CH_2)_2—O—[—R^2—O—]_m—(CH_2)_2—S—R^1]_n— \quad (IV)$$

wherein: (1) R^1 denotes a C_{2-6} n-alkylene, C_{3-6} branched alkylene, C_{6-8} cycloalkylene or C_{6-10} alkylcycloalkylene group, $—[(—CH_2—)_p—X—]_q—(—CH_2—)_r—$, or $—[(—CH_2—)_p—X—]_q—(—CH_2—)_r—$ in which at least one $—CH_2—$ unit is substituted with a methyl group; (2) R^2 denotes a C_{2-6} n-alkylene, C_{2-6} branched alkylene, C_{6-8} cycloalkylene or C_{6-10} alkylcycloalkylene group, or $—[(—CH_2—)_p—X—]_q—(—CH_2—)_r—$, X denotes one selected from the group consisting of O, S and $—NR^6—$, R^6 denotes H or methyl; (3) m is a rational number from 0 to 10; (4) n is an integer from 1 to 60; (5) p is an integer from 2 to 6; (6) q is an integer from 1 to 5, and (7) r is an integer from 2 to 10. Such polythioethers are described in U.S. Patent No. 6,172,179 at col. 2, line 29 to col. 4, line 34, the cited portion of which being incorporated herein by reference. Examples of suitable polythioethers are available from PRC-Desoto International, Inc., under the trademark PERMAPOL, such as PERMAPOL P-3.1e or PERMAPOL P-3.

[0063] In certain embodiments of the present invention, the sealant is deposited from a composition comprising a polymer blend comprising: (a) a polysulfide as described above; (b) a polythioether that includes a structure having the formula (III); (c) a polymeric mixture of the type described above, such as is obtained from the reaction of a polysulfide, an organic dimercaptan, such as dimercapto diethyl sulfide, and an amine. In some embodiments, the weight ratio of (a) and (b) in such polymer blends is 10:90 to 90:10, such as 50:50. Such polymer blends are described in U.S. Patent No. 7,524,564 at col. 1, lines 51 to col. 2, line 67, the cited portion of which being incorporated herein by reference.

[0064] In certain embodiments, the sulfur-containing polymer, or blend thereof, is present in the composition from which the sealant is formed in an amount of at least 30 weight percent, such as least 40 weight percent, or, in some cases, at least 45 weight percent, based on the total weight of non-volatile components in the composition. In certain embodiments, the sulfur-containing polymer, or blend thereof, is present in the composition from which the sealant is formed in an amount of no more than 90 weight percent, such as no more than 80 weight percent, or, in

some cases, no more than 75 weight percent, based on the weight of all non-volatile components of the composition.

[0065] In certain embodiments, the composition from which the sealant is formed also comprises a curing agent. Curing agents useful in certain compositions of the invention (particularly in the case in which a thiol-functional sulfur-containing polymer is used) include epoxy resins, for example, hydantoin diepoxide, diglycidyl ether of bisphenol-A, diglycidyl ether of bisphenol-F, Novolactype epoxides, and any of the epoxidized unsaturated and phenolic resins, as well as unsaturated compounds, such as acrylic and methacrylic esters of commercially available polyols, unsaturated synthetic or naturally occurring resin compounds, triallylcyanurate, and olefinic terminated derivatives of the polythioethers of the present invention.

[0066] In addition, in the case where a thiol-functional sulfur-containing polymer is used, useful cures can be obtained through oxidative coupling of the thiol groups using organic and inorganic peroxides (e.g., MnO_2) known to those skilled in the art.

[0067] Fillers useful in the certain embodiments of the compositions from which the sealant is deposited include those commonly used in the art, including conventional inorganic fillers, such as carbon black and calcium carbonate ($CaCO_3$), as well as lightweight fillers. Suitable lightweight fillers include, for example, those described in United States Patent No. 6,525,168 at col. 4, lines 23-55, the cited portion of which being incorporated herein by reference. In certain embodiments, the compositions include 5 to 60 weight percent of the filler or combination of fillers, such as 10 to 50 weight percent, based on the total weight of the composition.

[0068] In addition to the foregoing ingredients, the sealant composition can optionally include one or more of the following: colorants, thixotropes, accelerators, retardants, adhesion promoters, solvents and masking agents, among other components.

[0069] Thixotropes, for example silica, are often used in an amount from 0.1 to 5 weight percent, based on the total weight of the composition.

[0070] Cure catalysts known to the art, such as amines, often are present in an amount from 0.1 to 5 weight percent, based on the total weight of the composition. Specific examples of useful catalysts are, without limitation, 1,4-diaza-

bicyclo[2.2.2]octane (DABCO®, commercially available from Air Products, Chemical Additives Division, Allentown, PA) and DMP-30® (an accelerant composition including 2,4,6-tris(dimethylaminomethyl)phenol, commercially available from Rohm and Haas, Philadelphia, PA).

[0071] Retardants, such as stearic acid, likewise often are used in an amount from 0.1 to 5 weight percent, based on the total weight of the composition. Adhesion promoters, if employed, are often present in amount from 0.1 to 15 weight percent, based on the total weight of the composition. Suitable adhesion promoters include phenolics, such as METHYLON phenolic resin available from Occidental Chemicals, and organosilanes, such as epoxy, mercapto or amino functional silanes, such as Silquest A-187 and Silquest A-1100 available from Momentive Performance Materials. Masking agents, such as pine fragrance or other scents, which are useful in covering any low level odor of the composition, are often present in an amount from 0.1 to 1 weight percent, based on the total weight of the composition.

[0072] In certain embodiments, the sealant composition comprises a plasticizer which, in at least some cases, may allow the composition to include sulfur-containing polymer(s) which have a higher T_g than would ordinarily be useful in an aerospace sealant. That is, use of a plasticizer may effectively reduce the T_g of the composition, and thus increase the low-temperature flexibility of the cured polymerizable composition beyond that which would be expected on the basis of the T_g of the sulfur-containing polymer alone. Plasticizers that are useful in certain embodiments of the compositions of the present invention include, for example, phthalate esters, chlorinated paraffins, and hydrogenated terphenyls. The plasticizer or combination of plasticizers often constitute 1 to 40 weight percent, such as 1 to 10 weight percent of the composition. In certain embodiments, depending on the nature and amount of the plasticizer(s) used in the composition, thioethers of the invention which have T_g values up to -50°C, such as up to -55°C, can be used.

[0073] In certain embodiments, the sealant composition can further comprise one or more organic solvents, such as isopropyl alcohol, in an amount ranging from, for example, 0 to 15 percent by weight on a basis of total weight of the composition, such as less than 15 weight percent and, in some cases, less than 10 weight percent.

[0074] The coating/sealants systems of the present invention can, in at least some cases, exhibit excellent interlayer adhesion as well as adhesion to the substrate. In some embodiments of the present invention, the coating/sealant systems of the present invention exhibit an average peel strength of at least 150N/25mm, such as at least 200N/25mm, and a % cohesive of at least 50%, such as at least 90%, or, in some cases, 100%, when measured according to AS 5127/1B as described in the Examples herein.

[0075] These and other aspects of the claimed invention are further illustrated by the following non-limiting examples.

EXAMPLES

Example 1: Preparation of Aqueous Resinous Dispersion

[0076] A 12-liter round bottom 4-neck flask was equipped with a stirrer with bearing, a water-cooled condenser, a thermocouple probe with nitrogen inlet adapter and an electrically-heated mantle. The flask was charged with 2949.8 grams (7.845 mole) of bisphenol A diglycidyl ether (equivalent weight 188), 948.8 grams (4.162 mole) of bisphenol A, 418.9 grams of 2-n-butoxyethanol, and 335.3 grams 2-ethylhexanol. Under a nitrogen blanket, this was stirred and heated to 115°C. At 115°C, 2.9 grams of ethyl triphenylphos-phonium iodide (available from Sigma-Aldrich) was added. This was heated until an exotherm began, and the reaction mixture was maintained at or above 165°C for 60 minutes. To the reaction mixture was added 383.3 grams of Ektasolve EEH (available from Eastman Chemical Company) and 83.6 grams of 2-ethylhexanol as it was cooled to 90°C. At 90°C, a mixture of 67.9 grams (0.430 mole) of phenylphosphonic acid, 115.6 grams (1.003 mole) of 85% o-phosphoric acid, and 24.7 grams of Ektasolve EEH was added. After the exotherm, the reaction mixture was held at 120°C for 30 minutes, and then it was cooled to 100°C. At 100°C, 257.6 grams of deionized water was added over about an hour, and the reaction mixture was held at 100°C afterwards for 2 hours. At that point, it was cooled to 90°C and 324.2 grams (2.437 mole) of diisopropanolamine and 1487.2 grams of Cymel 1130 (available from Cytec Industries, Inc.) were added. The mixture was held at 90°C for 30 minutes. Of this material, 7000 grams was stirred into 5511.4 grams of deionized water, followed by the addition of 1317.0 grams more

deionized water. To this was added 366.4 grams of 2-hexoxyethanol, 225.5 grams of Optifilm 400 (available from Eastman Chemical Company), and 5.5 grams of Tektronic 150R1 (available from the BASF Corporation). Subsequently 1045.5 grams of deionized water was added to yield a dispersion evidencing 39.4% solids after 1 hour at 110°C.

Example 2: Preparation of Aqueous Resinous Dispersion

[0077] A 3-liter round bottom 4-neck flask was equipped with a stirrer with bearing, a water-cooled condenser, a thermocouple probe with nitrogen inlet adapter and an electrically-heated mantle. The flask was charged with 705 grams (3.75 mole) of bisphenol A diglycidyl ether (equivalent weight 188), 222.6 grams (1.952 mole) of bisphenol A, 39 grams (0.237 mole) of mercaptomethylbenzoimidazole (available from Sigma-Aldrich), and 180.3 grams of 2-n-butoxyethanol. Under a nitrogen blanket, this was stirred and heated to 115°C. At 115°C, 0.7 grams of ethyl triphenylphosphonium iodide (available from Sigma-Aldrich) was added. This was heated until an exotherm began, and the reaction mixture was maintained at or above 165°C for 60 minutes. To the reaction mixture was added 112 grams of 2-n-butoxyethanol as it was cooled to 90°C. At 90°C, 27.6 grams of 85% o-phosphoric acid was added. After the exotherm, the reaction mixture was held at 120°C for 30 minutes, and then it was cooled to 100°C. At 100°C, 61.6 grams of deionized water was added over about an hour, and the reaction mixture was held at 100°C afterwards for 2 hours. At that point, it was cooled to 90°C and 63.8 grams of diisopropanolamine, 330.5 grams of Cymel 1130 (available from Cytec Industries, Inc.) and 40.1 grams of mercaptomethylbenzoimidazole were added. The mixture was held at 90°C for 30 minutes. Of this material, 1650 grams was stirred into 1350 grams of deionized water, followed by the addition of 315.8 grams deionized water, then finally 390.1 grams of deionized water. The final dispersion evidenced 30.3% solids after 1 hour at 110°C.

Example 3: Preparation of Aqueous Resinous Dispersion

[0078] A 3-liter round bottom 4-neck flask was equipped with a stirrer with bearing, a water-cooled condenser, a thermocouple probe with nitrogen inlet adapter

and an electrically-heated mantle. The flask was charged with 450 grams (2.39 mole) of bisphenol A diglycidyl ether (equivalent weight 188), 142.1 grams (1.25 mole) of bisphenol A, 15.9 grams (0.135 mole) of phenyl-1H-tetrazole 5-thiol (available from Sigma-Aldrich) and 115.1 grams of 2-n-butoxyethanol. Under a nitrogen blanket, this was stirred and heated to 115°C. At 115°C, 0.5 grams of ethyl triphenylphosphonium iodide (available from Sigma-Aldrich) was added. This was heated until an exotherm began, and the reaction mixture was maintained at or above 165°C for 60 minutes. To the reaction mixture was added 71.2 grams of 2-n-butoxyethanol as it was cooled to 90°C. At 90°C, 17.6 grams of 85% o-phosphoric acid was added. After the exotherm, the reaction mixture was held at 120°C for 30 minutes, and then it was cooled to 100°C. At 100°C, 39.3 grams of deionized water was added over about an hour, and the reaction mixture was held at 100°C afterwards for 2 hours. At that point, it was cooled to 90°C and 40.7 grams of diisopropanolamine , 211.0 grams of Cymel 1130 (available from Cytec Industries, Inc.) and 26.1 grams phenyl-1H-tetrazole-5-thiol was added. The mixture was held at 90°C for 30 minutes. Of this material, 1000 grams was stirred into 814 grams of deionized water and the dispersion agitated for 1 hour, followed by the addition of 190.9 grams deionized water, then finally 235.9 grams of deionized water. The final dispersion evidenced 36.1% solids after 1 hour at 110°C.

Example 4: Preparation of Aqueous Resinous Dispersion

[0079] A 3-liter round bottom 4-neck flask was equipped with a stirrer with bearing, a water-cooled condenser, a thermocouple probe with nitrogen inlet adapter and an electrically-heated mantle. The flask was charged with 727.9 parts (3.87 mole) of bisphenol A diglycidyl ether (equivalent weight 188), 229.8 grams (2.02 mole) of bisphenol A and 186.1 grams of 2-n-butoxyethanol. Under a nitrogen blanket, this was stirred and heated to 115°C. At 115°C, 0.7 grams of ethyl triphenylphosphonium iodide (available from Sigma-Aldrich) was added. This was heated until an exotherm began, and the reaction mixture was maintained at or above 165°C for 60 minutes. To the reaction mixture was added 115.2 grams of 2-n-butoxyethanol as it was cooled to 90°C. At 90°C, 42.2 grams of 2-mercaptobenzothiazole was added and the reacton maintained for 30 minutes. To the reaction mixture 28.5 grams of 85% o-phosphoric

acid was added. After the exotherm, the reaction mixture was held at 120°C for 60 minutes, and then it was cooled to 100°C. At 100°C, 63.6 grams of deionized water was added over about an hour, and the reaction mixture was held at 100°C afterwards for 2 hours. At that point, it was cooled to 90°C and 65.8 grams of diisopropanolamine , and 341.3 grams of Cymel 1130 (available from Cytec Industries, Inc.) were added. The mixture was held at 90°C for 30 minutes. Of this material, 1600 grams was stirred into 1267.4 grams of deionized water water and the dispersion agitated for 1 hour, followed by the addition of 301.8 grams deionized water, then finally 372.8 grams of deionized water. The final dispersion evidenced 34.0% solids after 1 hour at 110°C.

Examples 5-8: Preparation of Coating Compositions

[0080] Coating compositions were prepared using the ingredients and amounts (parts by weight) listed in Table 1. The pH and conductivity of the final composition is also set forth in Table 1.

Table 1

Ingredients	Example 5	Example 6	Example 7	Example 8
Dispersion of Example 1	1632.7	--	--	--
Dispersion of Example 2	--	1294.1	--	--
Dispersion of Example 3	--	--	1565.8	--
Dispersion of Example 4	--	--	--	1120.1
Pigment Paste[1]	331.1	217.8	306.8	217.8
Deionized water	1836.2	988.1	1727.5	1162.1
pH[2]	8.61	8.81	8.45	8.65
Conductivity (Ω^{-1})[3]	867	710	927	964

[1]Grey pigment paste, ACPP-1120, available from PPG Industries, Inc., 51.4% solids.
[2] Measured with an ACCUMET pH meter commercially available from Fisher Scientific
[3] Measured with a conductivity meter commercially available from YSI, Inc

[0081] In each case, the dispersion was added to a gallon container. Under agitation the pigment paste was added to the dispersion along with the deionized water. Final bath solids were about 20% with a pigment to resin ratio of 0.2:1.0. Fifty percent of the total bath was removed by ultrafiltration and replaced with deionized water.

Test Substrates

[0082] Aluminum 2024-T3 bare panels were cleaned by immersing in a solution of RIDOLINE 298, an alkaline cleaner available from Henkel Corporation, for two minutes at 130°F. After alkaline cleaning, the panels were immersed in tap water rinse for one minute at ambient conditions. The panels were then immersed in a solution of DEOXIDIZER 6/16, an acidic deoxidizer available from Henkel Corporation, for two minutes and thirty seconds at ambient conditions. After the acid deoxidation, the panels were immersed in tap water for one minute at ambient conditions followed by a final spray rinse of deionized water. The panels were air dried prior to use.

[0083] The coating compositions of Examples 5, 6, 7, and 8 were deposited onto clean and deoxidized panels that were 2 ¾" by 6". This was done by heating the coating compositions of Examples 5 and 6 to 75°F (24°C) and Examples 7 and 8 to 90°F (32°C). The panels were immersed in a bath of the coating composition under agitation and then impressed with 85 to 275 volts for 90 seconds and thermally cured for 30 minutes at 200°F (93°C) to achieve a film thickness of about 0.8 mils.

[0084] Sealant adhesion was evaluated using PR-1776 M B-2 sealant, commercially available from PRC-DeSoto International, Inc. Panels were prepared per AS5127/1B with the following modifications: aluminum foil strips were used in place of the wire screen or fabric reinforcement. The foil strips were 0.005" thick measuring 1" wide by 12" long. Foil preparation included scuff abrading with grey SCOTCH BRITE pads(TM), solvent cleaning with solvent per AS5127/1B, and application of PR-148 adhesion promoter commercially available from PRC-DeSoto International, Inc., per manufacturer's instructions. Panels were cured for 14 days at 77°F and 50% relative humidity and then tested for peel strength per AS5127/1B. Results are set forth in Table 2.

Table 2

Example	Peel Strength[1] Reading 1 N/25mm	Peel Strength[1] Reading 2 N/25mm	Peel Strength[1] Reading 3 N/25mm	Peel Strength[1] Reading 4 N/25mm	Average Peel Strength N/25mm	% Cohesive[2]
5	52	57	42	38	47	0
6	182	215	222	228	212	100
7	115	164	163	184	157	30
8	198	212	204	204	205	99

[1] Peel strength is a measurement of the force required to pull the foil strip away from the substrate

[2] % Cohesive refers to the portion of the surface area of the substrate to which the sealant remains adhered after the foil strip is pulled away from the substrate (result is reported as average of four readings).

Example 9: Preparation of Aqueous Resinous Dispersion

[0085] A 12-liter round bottom 4-neck flask was equipped with a stirrer with bearing, a water-cooled condenser, a thermocouple probe with nitrogen inlet adapter and an electrically-heated mantle. The flask was charged with 2337.4 grams (6.216 mole) of bisphenol A diglycidyl ether (equivalent weight 188), 751.9 grams (3.298 mole) of bisphenol A, 332.0 grams of 2-n-butoxyethanol, and 265.7 grams 2-ethylhexanol. Under a nitrogen blanket, this was stirred and heated to 115°C. At 115°C, 2.3 grams of ethyl triphenylphos-phonium iodide (available from Sigma-Aldrich) was added. This was heated until an exotherm began, and the reaction mixture was maintained at or above 165°C for 60 minutes. To the reaction mixture was added 303.8 grams of Ektasolve EEH (available from Eastman Chemical Company) and 66.2 grams of 2-ethylhexanol as it was cooled to 90°C. At 90°C, a mixture of 53.8 grams (0.340 mole) of phenylphosphonic acid, 91.6 grams (0.794 mole) of 85% o-phosphoric acid, and 19.6 grams of Ektasolve EEH was added. After the exotherm, the reaction mixture was held at 120°C for 30 minutes, and then it was cooled to 100°C. At 100°C, 204.1 grams of deionized water was added over about an hour, and the reaction mixture was held at 100°C afterwards for 2 hours. At that point, it was cooled to 90°C and 256.9 grams (1.932 mole) of diisopropanolamine, 1178.5 grams of Cymel 1130 (available from Cytec Industries, Inc.), and 136.1 grams (1.144 mole) of 2-mercaptobenzothiazole were added. The mixture was held at 90°C for 30 minutes. Of this material, 5600 grams was stirred into 4484.5 grams of

deionized water, followed by the addition of 1061.5 grams more deionized water. To this was added 295.4 grams of 2-hexoxyethanol, 181.8 grams of Optifilm 400 (available from Eastman Chemical Company), and 4.4 grams of Tektronic 150R1 (available from the BASF Corporation). Subsequently, 842.7 grams of deionized water was added to yield a dispersion evidencing 38.6% solids after 1 hour at 110°C.

Example 10: Preparation of Aqueous Resinous Dispersion

[0086] A 12-liter round bottom 4-neck flask was equipped with a stirrer with bearing, a water-cooled condenser, a thermocouple probe with nitrogen inlet adapter and an electrically-heated mantle. The flask was charged with 2102.9 grams (5.593 mole) of bisphenol A diglycidyl ether (equivalent weight 188), 663.9 grams (2.912 mole) of bisphenol A, 118.3 grams (0.707 mole) of 2-mercaptobenzothiazole, and 537.7 grams of 2-n-butoxyethanol. Under a nitrogen blanket, this was stirred and heated to 115°C. At 115°C, 2.1 grams of ethyl triphenylphosphonium iodide (available from Sigma-Aldrich) was added. This was heated until an exotherm began, and the reaction mixture was maintained at or above 165°C for 60 minutes. To the reaction mixture was added 332.9 grams of 2-n-butoxyethanol as it was cooled to 90°C. At 90°C, 82.4 grams (0.715 mole) of 85% o-phosphoric acid was added. After the exotherm, the reaction mixture was held at 120°C for 30 minutes, and then it was cooled to 100°C. At 100°C, 183.7 grams of deionized water was added over about an hour, and the reaction mixture was held at 100°C afterwards for 2 hours. At that point, it was cooled to 90°C and 190.2 grams (1.430 mole) of diisopropanolamine and 985.9 grams of Cymel 1130 (available from Cytec Industries, Inc.) were added. The mixture was held at 90°C for 30 minutes. Of this material, 4800 grams was stirred into 3926.5 grams of deionized water, followed by the addition of 918.6 grams deionized water, then finally 1134.7 grams of deionized water. The final dispersion evidenced 37.1% solids after 1 hour at 110°C.

Example 11: Preparation of Aqueous Resinous Dispersion

[0087] A 3000 ml round bottom 4-neck flask was equipped with a stirrer with bearing, a water-cooled condenser, a thermocouple probe with nitrogen inlet adapter and an electrically-heated mantle. The flask was charged with 400.8 grams (1.0660

mole) of bisphenol A diglycidyl ether (equivalent weight 188), 128.9 grams (0.565 mole) of bisphenol A, and 102.5 grams of 2-n-butoxyethanol. Under a nitrogen blanket, this was stirred and heated to 115°C. At 115°C, 0.4 grams of ethyl triphenylphosphonium iodide (available from Sigma-Aldrich) was added. This was heated until an exotherm began, and the reaction mixture was maintained at or above 165°C for 60 minutes. To the reaction mixture was added 66.8 grams of 2-n-butoxyethanol as it was cooled to 90°C. At 90°C, 19.1 grams (0.166 mole) of 85% o-phosphoric acid was added. After the exotherm, the reaction mixture was held at 120°C for 30 minutes, and then it was cooled to 100°C. At 100°C, 35.0 grams of deionized water was added over about 45 minutes, and the reaction mixture was held at 100°C afterwards for 2 hours. At that point, it was cooled to 90°C and 53.5 grams (0.402 mole) of diisopropanolamine, 202.1 grams of Cymel 1130 (available from Cytec Industries, Inc.), and 90.9 grams of the adduct of Example 12 were added. The mixture was held at 90°C for 30 minutes. Of this material, 900 grams was stirred into 708.6 grams of deionized water, followed by the addition of 169.3 grams deionized water, then finally 209.2 grams of deionized water. The final dispersion evidenced 38.7% solids after 1 hour at 110°C.

Example 12: Preparation of Adduct

[0088] A 1-liter round bottom 4-neck flask was equipped with a stirrer with bearing, a water-cooled condenser, a thermocouple probe with nitrogen inlet adapter and an electrically-heated mantle. The flask was charged, in order, with 40.2 grams mercaptobenzothiazole, 92.5 grams EPON 828 and 192.0 grams methyl amyl ketone. The reaction was heated to 50°C and held for 1 hour. Temperature was increased until refluxing occurred (116°C). The reaction was held for 6 hours and the condenser replaced with a distillation head and condenser. The heating mantle was set for 118°C and volatile components were removed (173g) until the set temp was reached. The final material was 86% solids and the desired product was confirmed by nuclear magnetic resonance.

Examples 13-15: Preparation of Coating Compositions

[0089] Coating compositions was prepared using the ingredients and amounts (parts by weight) listed in Table 3. The pH and conductivity of the final composition is also set forth in Table 3.

Table 3

Ingredients	Example 13	Example 14	Example 15
Dispersion of Example 9	1546.8	--	--
Dispersion of Example 10	--	2212.4	--
Dispersion of Example 11	--	--	1543.6
Pigment Paste[1]	331.1	455.0	331.1
Deionized water	1922.2	2555.1	1925.4
pH[2]	8.34	8.69	8.25
Conductivity (Ω^{-1})[3]	974	807	985

[0090] In each case, the dispersion was added to a gallon container. Under agitation the pigment paste was added to the dispersion along with the deionized water. Final bath solids were about 20% with a pigment to resin ratio of 0.2:1.0. Fifty percent of the total bath was removed by ultrafiltration and replaced with deionized water.

Test Substrates

[0091] Aluminum 2024-T3 bare panels were cleaned by immersing in a solution of RIDOLINE 298, an alkaline cleaner available from Henkel Corporation, for two minutes at 130°F. After alkaline cleaning, the panels were immersed in tap water rinse for one minute at ambient conditions. The panels were then immersed in a solution of DEOXIDIZER 6/16, an acidic deoxidizer available from Henkel Corporation, for two minutes and thirty seconds as ambient conditions. After the acid deoxidation, the panels were immersed in tap water for one minute at ambient conditions followed by a final spray rinse of deionized water. The panels were air dried prior to use.

[0092] The coating compositions of Examples 5, 13, 14, and 15 were deposited onto clean and deoxidized panels that were 2 ¾" by 6". This was done by heating the coating compositions of Example 5 and 13 to 75°F (24°C) and Examples 14 and 15 to 90°F (32°C). The panels were immersed in a bath of the coating composition under agitation and then impressed with 85 to 275 volts for 90 seconds

and thermally cured for 30 minutes at 200°F (93°C), with the exception of Example 15 which was cured for 60 minutes, to achieve a film thickness of about 0.8 mils.

[0093] Sealant adhesion was evaluated using PR-1776 M B-2 sealant, commercially available from PRC-DeSoto International, Inc. Panels were prepared per AS5127/1B with the following modifications: aluminum foil strips were used in place of the wire screen or fabric reinforcement. The foil strips were 0.005" thick measuring 1" wide by 12" long. Foil preparation included scuff abrading with grey SCOTCH BRITE pads(TM), solvent cleaning with solvent per AS5127/1B, and application of PR-148 adhesion promoter commercially available from PRC-DeSoto International, Inc., per manufacturer's instructions. Panels were cured for 14 days at ambient temperature and humidity conditions and then tested for peel strength per AS5127/1B. Results are set forth in Table 4.

Table 4

Example	Panel #	Peel Strength[1] Reading 1 N/25mm	Peel Strength[1] Reading 1 N/25mm	Peel Strength[1] Reading 1 N/25mm	Peel Strength[1] Reading 1 N/25mm	Average Peel Strength N/25mm	% Cohesive[2]
5	A	92	78	55	74	75	0
	B	51	97	80	71	75	0
13	A	71	64	47	42	56	3
	B	64	75	46	48	58	2
14	A	234	227	238	204	226	100
	B	156	165	167	161	162	100
15	A	46	51	59	53	52	0
	B	46	67	58	74	61	5

[1] Peel strength is a measurement of the force required to pull the foil strip away from the substrate

[2] % Cohesive refers to the portion of the surface area of the substrate to which the sealant remains adhered after the foil strip is pulled away from the substrate (result is reported as average of four readings).

Example 16: Preparation of Aqueous Resinous Dispersion

[0094] A 3-liter round bottom 4-neck flask was equipped with a stirrer with bearing, a water-cooled condenser, a thermocouple probe with nitrogen inlet adapter and an electrically-heated mantle. The flask was charged with 727.9 parts (3.87 mole) of bisphenol A diglycidyl ether (equivalent weight 188), 229.8 grams (2.02 mole) of bisphenol A and 186.1 grams of 2-n-butoxyethanol. Under a nitrogen blanket, this was stirred and heated to 115°C. At 115°C, 0.7 grams of ethyl triphenylphosphonium

iodide (available from Sigma-Aldrich) was added. This was heated until an exotherm began, and the reaction mixture was maintained at or above 165°C for 60 minutes. To the reaction mixture was added 115.2 grams of 2-n-butoxyethanol as it was cooled to 90°C. At 90°C, 28.5 grams of 85% o-phosphoric acid was added and after the exotherm, the reaction mixture was held at 120°C for 30 minutes. To the reaction mixture 41.0 grams of 2-mercaptobenzothiazole was added and the reaction maintained at 120°C for 30 minutes, and then it was cooled to 100°C. At 100°C, 63.6 grams of deionized water was added over about an hour, and the reaction mixture was held at 100°C afterwards for 2 hours. At that point, it was cooled to 90°C and 65.8 grams of diisopropanolamine, and 341.3 grams of Cymel 1130 (available from Cytec Industries, Inc.) were added. The mixture was held at 90°C for 30 minutes. Of this material, 1608 grams was stirred into 1295.3 grams of deionized water and the dispersion agitated for 1 hour, followed by the addition of 305.6 grams deionized water, then finally 377.5 grams of deionized water. The final dispersion evidenced 34.0% solids after 1 hour at 110°C.

Example 17: Preparation of Coating Compositions

[0095] A coating composition was prepared using the ingredients and amounts (parts by weight) listed in Table 5. The pH and conductivity of the final composition is also set forth in Table 5.

Table 5

Ingredients	Example B
Dispersion of Example 16	1577.9
Pigment Paste[1]	331.1
Deionized water	1891.1
pH[2]	8.56
Conductivity (Ω^{-1})[3]	973

[1]Grey pigment paste, ACPP-1120, available from PPG Industries, Inc., 51.4% solids.
[2] Measured with an ACCUMET pH meter commercially available from Fisher Scientific
[3] Measured with a conductivity meter commercially available from YSI, Inc

[0096] In each case, the dispersion was added to a gallon container. Under agitation the pigment paste was added to the dispersion along with the deionized water. Final bath solids were about 20% with a pigment to resin ratio of 0.2:1.0.

Fifty percent of the total bath was removed by ultrafiltration and replaced with deionized water.

Test Substrates

[0097] Aluminum 2024-T3 bare panels were cleaned by immersing in a solution of RIDOLINE 298, an alkaline cleaner available from Henkel Corporation, for two minutes at 130°F. After alkaline cleaning, the panels were immersed in tap water rinse for one minute at ambient conditions. The panels were then immersed in a solution of DEOXIDIZER 6/16, an acidic deoxidizer available from Henkel Corporation, for two minutes and thirty seconds at ambient conditions. After the acid deoxidation, the panels were immersed in tap water for one minute at ambient conditions followed by a final spray rinse of deionized water. The panels were air dried prior to use.

[0098] The coating composition of Example 17 was deposited onto clean and deoxidized panels that were 2 ¾" by 6". This was done by heating the coating composition of Example 17 to 90°F (32°C). The panels were immersed in a bath of the coating composition under agitation and then impressed with 85 to 275 volts for 90 seconds and thermally cured for 30 minutes at 200°F (93°C) to achieve a film thickness of about 0.8 mils.

[0099] Sealant adhesion was evaluated using PR-1776 M B-2 sealant, commercially available from PRC-DeSoto International, Inc. Panels were prepared per AS5127/1B with the following modifications: aluminum foil strips were used in place of the wire screen or fabric reinforcement. The foil strips were 0.005" thick measuring 1" wide by 12" long. Foil preparation included scuff abrading with grey SCOTCH BRITE pads(TM), solvent cleaning with solvent per AS5127/1B, and application of PR-148 adhesion promoter commercially available from PRC-DeSoto International, Inc., per manufacturer's instructions. Panels were cured for 14 days at 77°F and 50% relative humidity and then tested for peel strength per AS5127/1B. Results are set forth in Table 6.

Table 6

Example	Peel Strength[1] Reading 1 N/25mm	Peel Strength[1] Reading 2 N/25mm	Peel Strength[1] Reading 3 N/25mm	Peel Strength[1] Reading 4 N/25mm	Average Peel Strength N/25mm	% Cohesive[2]
17	171	184	190	203	187	85

[1] Peel strength is a measurement of the force required to pull the foil strip away from the substrate

[2] % Cohesive refers to the portion of the surface area of the substrate to which the sealant remains adhered after the foil strip is pulled away from the substrate (result is reported as average of four readings).

[0100] Whereas particular embodiments of this invention have been described above for purposes of illustration, it will be evident to those skilled in the art that numerous variations of the details of the present invention may be made without departing from the invention as defined in the appended claims.

WHAT IS CLAIMED IS:

1. A method for making a base-neutralized aqueous resinous dispersion comprising:

(a) adding a sulfur-functional azole to a composition comprising a phosphated epoxy resin derived from at least (i) a polyepoxide, and (ii) a phosphorous acid;

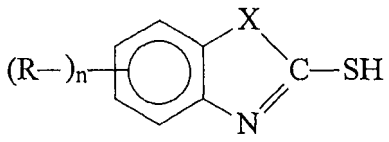
(b) adding a base to the composition after at least a portion of the sulfur-functional azole has been added; and

(c) adding water to the composition after at least a portion of the base has been added to the composition.

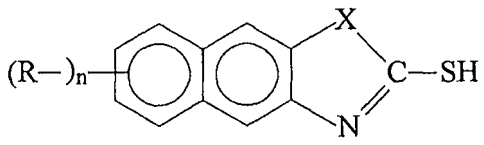
2. The method of claim 1, wherein base is added after at least 50% by weight of the total amount of sulfur-functional azole desired has been added to the dispersion.

3. The method of claim 1, wherein the sulfur-functional azole comprises a mercaptoarylimidazole, a mercaptoaryloxazole, and/or a mercaptoarylthiazole.

4. The method of claim 3, wherein the mercaptoarylimidazole, mercaptoaryloxazole, or mercaptoarylthiazole is represented by the structure (I) or (II):



(I)

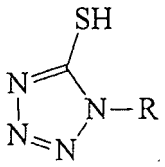


(II)

wherein: (i) X represents N, O or S; (ii) R represents hydroxyl, hydrogen, aryl, alkyl, aralkyl, or a halogen atom; and (iii) n is an integer of 0 to 4.

5. The method of claim 1, wherein the sulfur-functional azole comprises a tetrazole.

6. The method of claim 5, wherein the tetrazole is represented by the structure:



wherein R represents an organic radical having a total of 1 to 3 carbon atoms.

7. The method of claim 6, wherein R is a phenyl group.

8. The method of claim 1, wherein the sulfur-functional azole is present in an amount of 0.01 to 0.25 mole of thiol to one equivalent of epoxy.

9. The method of claim 1, wherein the phosphorous acid comprises a mixture comprising:

(1) a phosphoric acid; and

(2) an organophosphonic acid and/or an organophosphinic acid.

10. The method of claim 9, wherein the mixture comprises from 0.1 to 0.8 mole of phosphoric acid to one equivalent of epoxy and from 0.01 to 0.4 mole of phosphonic and/or an organophosphinic acid per equivalent of epoxy.

11. The method of claim 1, further comprising adding a curing agent to the aqueous resinous dispersion.

12. The method of claim 11, wherein the curing agent comprises an aminoplast.

13. The method of claim 1, wherein the phosphated epoxy resin is present in an amount of at least 50 percent by weight, based on the total resin solids weight of the dispersion.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/054262

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D5/44 C08G59/14 C08G59/30 C08G59/32 C09D163/00
C09D181/04 C25D5/44 C25D13/22 C25D13/04 C25D5/50
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09D C08G

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011/008625 A1 (PEFFER ROBIN M [US] ET AL) 13 January 2011 (2011-01-13) (a)(b)(c); claims 1,7,12,13 paragraph [0079]; examples I-III	1-4,9-13
X	WO 2010/117479 A1 (PRC DESOTO INT INC [US]; KARABIN RICHARD F [US]; KAYLO ALAN J [US]; MC) 14 October 2010 (2010-10-14) (a)(b)(c); claims 1,4,5; examples I,II	1-4,9-13
X	WO 2009/023690 A1 (PPG IND OHIO INC [US]) 19 February 2009 (2009-02-19) (a)(b)(c); claims 1-12 sentence 5, paragraph 0019 - sentence 6	1-4,9-13

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
7 October 2013	14/10/2013

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

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/054262

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 086 092 A (SCHUPP HANS [DE] ET AL) 4 February 1992 (1992-02-04) claim 1; example 1	1-13
A	US 4 360 614 A (CASTELLUCCI NICHOLAS T ET AL) 23 November 1982 (1982-11-23) claim 1; example 1	1-13
X,P	WO 2013/052190 A2 (PRC DESOTO INT INC [US]; VALKO JOSEPH T [US]; PEFFER ROBIN M [US]; MAY) 11 April 2013 (2013-04-11) examples 1-9	1-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2013/054262

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2011008625 A1	13-01-2011	AU 2011299355 A1	21-03-2013
		CA 2810505 A1	15-03-2012
		CN 103180489 A	26-06-2013
		EP 2614179 A1	17-07-2013
		KR 20130079529 A	10-07-2013
		SG 188429 A1	30-04-2013
		US 2011008625 A1	13-01-2011
		WO 2012033700 A1	15-03-2012
WO 2010117479 A1	14-10-2010	CA 2754819 A1	14-10-2010
		CN 102369246 A	07-03-2012
		EP 2414463 A1	08-02-2012
		JP 2012522129 A	20-09-2012
		KR 20120001792 A	04-01-2012
		RU 2011143773 A	10-05-2013
		US 2010243108 A1	30-09-2010
		WO 2010117479 A1	14-10-2010
WO 2009023690 A1	19-02-2009	AU 2008286932 A1	19-02-2009
		CA 2696158 A1	19-02-2009
		CN 101778881 A	14-07-2010
		DK 2178942 T3	02-09-2013
		EP 2178942 A1	28-04-2010
		EP 2497792 A1	12-09-2012
		ES 2423754 T3	24-09-2013
		JP 5133415 B2	30-01-2013
		JP 2010537044 A	02-12-2010
		JP 2012246571 A	13-12-2012
		KR 20100054829 A	25-05-2010
		RU 2010109390 A	20-09-2011
		US 2009045071 A1	19-02-2009
		WO 2009023690 A1	19-02-2009
US 5086092 A	04-02-1992	BR 8806395 A	22-08-1989
		DE 3741161 A1	15-06-1989
		EP 0319792 A1	14-06-1989
		ES 2028241 T3	01-07-1992
		JP H02110170 A	23-04-1990
		US 5086092 A	04-02-1992
US 4360614 A	23-11-1982	NONE	
WO 2013052190 A2	11-04-2013	US 2013065057 A1	14-03-2013
		WO 2013052190 A2	11-04-2013

(19)中华人民共和国国家知识产权局

(12)发明专利申请

(10)申请公布号 CN 104797663 A
(43)申请公布日 2015.07.22

(21)申请号 201380060004.2
(22)申请日 2013.08.09
(30)优先权数据
13/649,144 2012.10.11 US
(85)PCT国际申请进入国家阶段日
2015.05.18
(86)PCT国际申请的申请数据
PCT/US2013/054262 2013.08.09
(87)PCT国际申请的公布数据
WO2014/058523 EN 2014.04.17
(71)申请人 PRC-迪索托国际公司
地址 美国加利福尼亚
(72)发明人 L·G·安德森 E·A·弗拉尔
T·G·林根菲尔特 M·A·玛尤
R·M·派弗尔 J·T·沃克
(74)专利代理机构 中国国际贸易促进委员会专利商标事务所 11038
代理人 孙悦
(51)Int.Cl.
C09D 5/44(2006.01)
C08G 59/14(2006.01)
C08G 59/30(2006.01)
C08G 59/32(2006.01)
C09D 163/00(2006.01)
C09D 181/04(2006.01)
C25D 5/44(2006.01)
C25D 13/22(2006.01)
C25D 13/04(2006.01)
C25D 5/50(2006.01)

权利要求书1页 说明书18页

(54)发明名称

涂层/密封剂体系,含水树脂分散体,制造含水树脂分散体的方法,和电涂方法

(57)摘要

一种涂层/密封剂体系,其包括涂层和沉积在该涂层的至少一部分上的密封剂,在其中该涂层包括由包含磷酸化的环氧树脂和固化剂的反应物所形成的反应产物,并且该密封剂包括含硫的聚合物。

CN 104797663 A

1. 一种制造碱中和的含水树脂分散体的方法，其包括：

(a) 将硫官能化的唑类加入到组合物中，该组合物包含得自至少 (i) 多环氧化物和 (ii) 亚磷酸的磷酸化的环氧树脂；

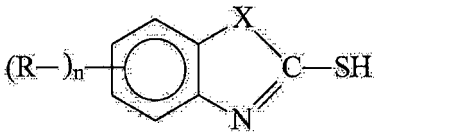
(b) 在已经加入了至少一部分的硫官能化的唑类之后，将碱加入该组合物中；和

(c) 在至少一部分的碱已经加入该组合物之后，将水加入该组合物中。

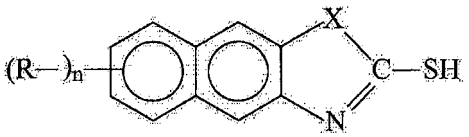
2. 权利要求 1 的方法，其中在所期望的硫官能化的唑类的总量的至少 50 重量% 已经加入到该分散体中之后，加入碱。

3. 权利要求 1 的方法，其中该硫官能化的唑类包括巯基芳基咪唑、巯基芳基噁唑和 / 或巯基芳基噻唑。

4. 权利要求 3 的方法，其中该巯基芳基咪唑、巯基芳基噁唑或者巯基芳基噻唑是用结构 (I) 或 (II) 来表示的：



(I)

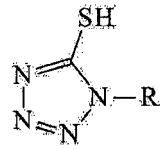


(II)

其中：(i) X 表示 N、O 或 S；(ii) R 表示羟基、氢、芳基、烷基、芳烷基或卤素原子；和 (iii) n 是 0-4 的整数。

5. 权利要求 1 的方法，其中该硫官能化的唑类包括四唑。

6. 权利要求 5 的方法，其中该四唑是用下面的结构表示：



其中 R 表示具有总共 1-3 个碳原子的有机基团。

7. 权利要求 6 的方法，其中 R 是苯基。

8. 权利要求 1 的方法，其中该硫官能化的唑类的存在量是相对于 1 当量的环氧基 0.01-0.25mol 的硫醇。

9. 权利要求 1 的方法，其中该亚磷酸包含混合物，该混合物包含：

(1) 磷酸；和

(2) 有机膦酸和 / 或有机次膦酸。

10. 权利要求 9 的方法，其中该混合物包含相对于 1 当量的环氧基 0.1-0.8mol 的磷酸，和每当量环氧基 0.01-0.4mol 的膦酸和 / 或有机次膦酸。

11. 权利要求 1 的方法，其进一步包括将固化剂加入到该含水树脂分散体中。

12. 权利要求 11 的方法，其中该固化剂包括氨基塑料。

13. 权利要求 1 的方法，其中该磷酸化的环氧树脂的存在量是至少 50 重量%，基于该分散体的总树脂固体重量。

涂层 / 密封剂体系，含水树脂分散体，制造含水树脂分散体的方法，和电涂方法

[0001] 交叉参考的相关申请

[0002] 本申请是 2011 年 9 月 14 日提交的美国专利申请系列号 13/232093 的部分继续，并且要求它的优选权，其在此以其全部引入作为参考。

[0003] 关于联邦资助研究的声明

[0004] 本发明是经空军研究实验室批准，在合同号 FA8650-05-C-5010 下由政府资助进行的。美国政府在本发明中会具有某些权利。

发明领域

[0005] 本发明涉及涂层 / 密封剂体系，阴离子树脂分散体，制造这样的分散体的方法和使用这样的分散体电涂的方法。

[0006] 发明背景

[0007] 已知含硫聚合物非常适用于不同的应用，例如航空航天密封剂组合物，这主要归因于它们在交联后获得的耐燃料性。经常用于航空航天密封剂组合物中的一类含硫的聚合物是聚硫化物，其是具有二硫化物 (-S-S-) 连接基的聚合物。包括含硫的聚合物例如聚硫化物的航空航天密封剂可以施用到通过导电基底例如包含铝的那些基底之间的界面所形成的结合处或者空间，在所述基底上已经事先施涂了事先沉积的耐腐蚀底漆涂层。重要的是该密封剂和底漆涂层彼此良好粘附和附着到基底上，但是这并非总是能够实现。

发明内容

[0008] 在某些方面，本发明涉及涂层 / 密封剂体系。这些体系包含涂层和沉积在该涂层的至少一部分上的密封剂。该涂层包含由反应物形成的反应产物，该反应物包含 :(i) 磷酸化的环氧树脂 ;和 (ii) 固化剂，并且该密封剂是从包含含硫的聚合物 (其包含硫醇官能化的聚硫化物) 的组合物来沉积的。

[0009] 在其它方面，本发明涉及含水树脂分散体。这些分散体包含碱中和的树脂组合物，其包含未凝胶化的磷酸化的环氧树脂。该未凝胶化的磷酸化的环氧树脂包含由反应物形成的反应产物，该反应物包含 :(a) 多环氧化物 ;(b) 硫官能化的唑类 ;和 (c) 亚磷酸。

[0010] 在仍然的其它方面，本发明涉及制造碱中和的含水树脂分散体的方法。这些方法包括 :(a) 将硫官能化的唑类加入到包含磷酸化的环氧树脂的组合物中，该磷酸化的环氧树脂得自至少 (i) 多环氧化物，和 (ii) 亚磷酸 ;(b) 在至少一部分的该硫官能化的唑类已经加入后，将碱加入该组合物中 ;和 (c) 在至少一部分的碱已经加入该组合物后，将水加入该组合物。

[0011] 在仍然的其它方面，本发明涉及电涂浸入在含水树脂分散体中的导电基底的方法，该导电基底充当包含阳极和阴极的电回路的阳极，该方法包括在该阳极和阴极之间输送电流，来引起树脂组合物沉积到该阳极上。在这些方法中，该分散体包含阴离子树脂，其包含由包含下面的反应物所形成的反应产物 :(a) 多环氧化物 ;(b) 硫官能化的唑类 ;和

(c) 亚磷酸。

[0012] 本发明还尤其涉及相关的涂覆基底等，其包括航空航天器，其包含用这里所述的组合物和 / 或这里所述的涂层 / 密封剂体系涂覆的基底。

具体实施方式

[0013] 为了下面的详细说明的目的，应当理解本发明可以采用不同的备选的变化和步骤次序，除了其中有明确的相反规定之外。此外，除了在任何操作实施例中，或者在另有规定之处，否则表示例如说明书和权利要求中所用的成分的量的全部数字被理解为在全部的情况中是用术语“约”修正的。因此，除非有相反的指示，否则下面的说明书和附加的权利要求中阐明的数字参数是约数，其可以根据本发明所寻求获得的期望的性能而变化。最起码，和并非打算使用等价原则来限制权利要求的范围，每个数字参数应当至少按照所报告的有效数字的位数和通过使用通常的四舍五入技术来解释。

[0014] 虽然阐明本发明宽的范围的数字范围和参数是约数，但是在具体实施例中所述的数值是尽可能精确来报告的。但是任何数值本质上包含了由它们各自的测试测量中存在的标准偏差所必然形成的某些误差。

[0015] 同样，应当理解这里所述的任何数字范围目的是包括处于其中的全部的子范围。例如范围“1-10”目的是包括在所述的最小值 1 和所述的最大值 10 之间（并包括端值）的全部子范围，即，具有最小值等于或者大于 1 和最大值等于或者小于 10。

[0016] 如上所述，本发明的某些实施方案涉及涂层 / 密封剂体系。此处使用的术语“涂层 / 密封剂体系”指的是一种组合，其包括涂料层和沉积在该涂层的至少一部分上的密封剂。此处使用的术语“涂层”指的是一种负载于基底上的基本连续的聚合物层，其可以或者可以不具有均匀厚度。此处使用的术语“密封剂”指的是固体弹性体，其当施用到孔（例如通过两个部件之间的界面形成的结合处或者空间）时，具有抵抗大气条件例如湿气和温度的能力，并且至少部分地阻挡材料例如水、燃料和 / 或其它液体和气体的透过，否则其会在该孔处发生。密封剂因此经常施用到部件的外围边缘表面上，来阻止材料传输到这样的部件或者传输自这样的部件。在某些实施方案中，本发明的涂层 / 密封剂体系可用于航空航天燃料槽。因此在本发明的某些实施方案中，该密封剂是“耐燃料的”，作为此处使用的，其指的是根据类似于在此引入作为参考的 ASTM D792 或者 AMS 3269a 中所述的那些的方法，固化的密封剂在 140 °F（60℃）和环境压力（1 大气压）在喷气机参照流体（JRF）类型 1 中浸泡 1 周后，体积溶胀百分比不大于 40%，在一些情况中不大于 25%，在一些情况中不大于 20%。喷气机参照流体 JRF 类型 1（其在此用于测定耐燃料性）具有下面的组成（参见 AMS 2629，1989 年 7 月 1 日公布），§ 3.1.1 以及其以下，获自 SAE(Society of Automotive Engineers，Warrendale，PA)（其在此引入作为参考）：

[0017]

甲苯	28 ± 1 体积%
环己烷(工业级)	34 ± 1 体积%
异辛烷	38 ± 1 体积%
叔二丁基二硫化物	1 ± 0.005 体积%

[0018] （脱除硫醇的 (doctor sweet)）

[0019] 本发明的涂层 / 密封剂体系可以沉积到任何的多种基底上。但是在某些实施方案中，该基底是导电的，例如是基底包含钛、不锈钢、铝、以及导电复合材料例如含有足量的导电填料例如炭黑的聚合型材料的情况。如将理解的，该基底可以任选地用腐蚀抑制处理来预处理，所述腐蚀抑制处理例如阳极化或者沉积转化涂料组合物（例如描述在美国专利申请公开号 2010-0243108A1 的 [0014]-[0019] 中，其引用部分在此引入作为参考），只要该基底保持它的导电性就行。在一些实施方案中，在施用本发明的涂层 / 密封剂体系之前，仅仅将该基底清洁和脱氧化。这样的清洁和脱氧化描述在前述美国专利申请公开号 2010-0243108 的 [0014]-[0017] 中。

[0020] 在本发明的某些实施方案中，该基底体现为飞机部件的形式，例如机翼、机身或者尾部装配。更具体地，该基底可以体现为任何的多种飞机零件，例如副翼、机翼边缘（前缘或者后缘）或者翼梁、缝翼、扰流板、襟翼、方向舵、垂直尾翼、水平稳定器、升降舵、尾部、管、座位轨道、地板轨道、压杆、纵梁、外壳、翼肋、隔板、轮子、纵向加强条、直升机旋翼桨叶、（包括翼梁和外表面）、或者任何的多种法兰、铰链、夹子和紧固件例如铆钉、螺栓、螺母，其将零件连接在一起。

[0021] 如前所述，本发明的涂层 / 密封剂体系包含涂层，其包含由包含磷酸化的环氧树脂的反应物所形成的反应产物。此处使用的术语“磷酸化的环氧树脂”指的是未凝胶化的树脂，其得自至少多环氧化物和亚磷酸。

[0022] 合适的多环氧化物包括具有大于 1.0 个环氧基团 / 分子的任何化合物或者化合物的混合物。几种多环氧化物是本领域已知的。多环氧化物的例子可以在 Handbook of Epoxy Resins, Lee 和 Neville, 1967, McGraw-Hill Book Company 中找到。

[0023] 在本发明的某些实施方案中，该多环氧化物包括多酚的多缩水甘油醚，例如双酚 A。如将理解的，这样的多环氧化物可以通过多酚与表氯醇在碱存在下醚化来生产。合适的多酚包括但不限于 1, 1- 双 (4- 羟基苯基）乙烷 ;2, 2- 双 (4- 羟基苯基）丙烷 ;1, 1- 双 (4- 羟基苯基）异丁烷 ;2, 2- 双 (4- 羟基叔丁基苯基）丙烷 ;双 (2- 羟基萘基）甲烷 ;1, 5- 二羟基萘 ;1, 1- 双 (4- 羟基 -3- 烯丙基苯基）乙烷 ;和 4, 4- 双 (4' - 羟基苯基）戊酸。另一种有用种类的多环氧化物是类似的由多酚树脂来生产的。

[0024] 除了上述的多环氧化物之外，还可以使用含有侧接环氧基团的加聚的聚合物。这样的聚合物可以通过多种可聚合的烯属不饱和单体（其至少之一是含环氧的单体，例如丙烯酸缩水甘油酯或者甲基丙烯酸缩水甘油酯）共聚来制造。

[0025] 一种合适的烯属不饱和单体（其不包含与环氧基团有反应性的基团）可以用作共聚单体。示例性的这样的单体包括 α, β - 烯属不饱和单体，例如含有 1- 约 8 个碳原子的饱和醇的不饱和羧酸酯，和单乙烯基芳族单体例如苯乙烯和乙烯基甲苯。

[0026] 在某些实施方案中，该多环氧化物的环氧当量是 172-5000，例如 300-1000。

[0027] 除了多环氧化物之外，该反应混合物可以包含单体单环氧化物例如醇和酚的单缩水甘油醚，例如苯基缩水甘油醚，和单羧酸的缩水甘油酯例如新癸酸缩水甘油酯。

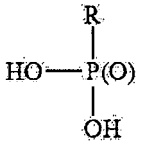
[0028] 在某些实施方案中，与该多环氧化物反应的亚磷酸包含磷酸，例如 100％正磷酸或者例如被称作 85％磷酸的磷酸水溶液。其它形式的磷酸例如过磷酸、二磷酸和三磷酸可以在此使用。同样，可以使用磷酸的偏酐或聚合型酐。在一些实施方案中，使用具有约 70-90％

和优选约 85％磷酸的磷酸水溶液。

[0029] 在一些实施方案中，与多环氧化物反应的亚磷酸基本上由磷酸组成。换言之，在这些实施方案中，磷酸的存在量是至少 98mol％，至少 99％ mol％，或者在一些情况中 100mol％，基于与多环氧化物反应的亚磷酸的总摩尔数。

[0030] 作为磷酸的备选项或者除了其之外或者代替其，膦酸和 / 或次膦酸可以与多环氧化物反应。膦酸的例子是具有下面结构的有机膦酸：

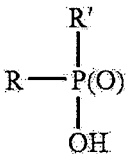
[0031]



[0032] 其中 R 是有机基团例如具有总共 1-30，例如 6-18 个碳的那些。R 可以是脂肪族的、芳族的或者混合的脂肪族的 / 芳族的，并且可以是未取代的烃或者取代的烃。

[0033] 次膦酸的例子是具有下面结构的有机次膦酸：

[0034]



[0035] 其中 R 和 R’ 每个独立的是氢或者有机基团。这样的基团的例子是具有总共 1-30，例如 6-18 个碳的那些。次膦酸的有机组分 (R，R’) 可以是脂肪族的，芳族的或者混合的脂肪族的 / 芳族的。R 和 R’ 可以是未取代的烃或取代的烃。

[0036] 代表性的合适的有机膦酸和有机次膦酸是：3- 氨基丙基膦酸、4- 甲氧基苯基膦酸、苄基膦酸、丁基膦酸、羧乙基膦酸、二苯基次膦酸、十二烷基膦酸、亚乙基二膦酸、十七烷基膦酸、甲基苄基次膦酸、萘基甲基次膦酸、十八烷基膦酸、辛基膦酸、戊基膦酸、甲基苯基次膦酸、苯基膦酸、苯乙烯膦酸、十二烷基双 -1，12- 膦酸、聚 (乙二醇) 膦酸，包括其混合物。

[0037] 在本发明的一些实施方案中，该亚磷酸包含下面的组分的混合物：(a) 磷酸；和 (b) 有机膦酸和 / 或有机次膦酸。在这些实施方案中，如将理解的，所形成的磷酸化的环氧树脂包含由反应物形成的反应产物的混合物，该反应物包含：(i) 多环氧化物；(ii) 磷酸；和 (iii) 有机膦酸和 / 或有机次膦酸。如将理解的，这样的反应产物的混合物可以包括磷酸化的环氧树脂 (在其中磷酸化的部分仅仅得自磷酸)，磷酸化的环氧树脂 (在其中磷酸化的部分仅仅得自有机膦酸和 / 或有机次膦酸) 和 / 或磷酸化的环氧树脂 (在其中磷酸化的部分得自磷酸和 / 或有机膦酸和 / 或有机次膦酸二者)。在某些实施方案中，彼此反应的多环氧化物和亚磷酸的相对量是：对于每当量的环氧基，存在着 0.1-0.8mol 的磷酸和 0.01-0.4mol 的有机膦酸和 / 或有机次膦酸，并且磷酸与有机膦酸和 / 或有机次膦酸的摩尔比是 1 :0.01-0.5。该磷酸化的环氧树脂经常具有 10-60，例如 15-50 的酸值，基于树脂固体。

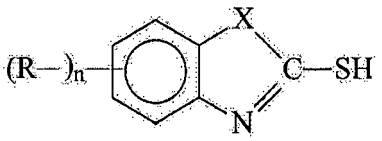
[0038] 在本发明的某些实施方案中，用于制造磷酸化的环氧树脂的反应物进一步包含硫官能化的唑类。此处使用的“唑”表示 5 元杂环化合物，其包含在该杂环中的两个双键、一个

氮原子、至少一个其它的非碳原子（例如另一氮原子、氧原子或硫原子），和一个或多个碳原子。示例性的唑包括但不限于二唑、三唑、四唑、噁唑、噁二唑、噁三唑、噻唑、噻二唑和噻三唑。此处使用的“硫官能化的唑类”表示这样的唑，其在唑环之外包括至少一个硫原子。

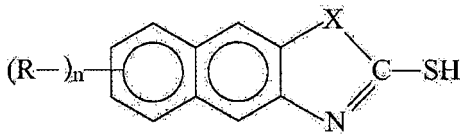
[0039] 在某些实施方案中，该硫官能化的唑类包含巯基芳基咪唑、巯基芳基噁唑和/或巯基芳基噻唑。

[0040] 更具体地，在某些实施方案中，该巯基芳基咪唑、巯基芳基噁唑或者巯基芳基噻唑是用结构（I）或（II）或者其互变异构体来表示的：

[0041]



(I)



(II)

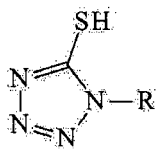
[0042] 其中：(i)X表示氮原子、氧原子或硫原子；(ii)R表示羟基、氢、芳基、烷基、芳烷基或卤素原子；和(iii)n是0-4的整数。

[0043] 适用于本发明的根据结构（I）的化合物具体的例子包括巯基苯并咪唑、巯基甲基苯并咪唑、巯基羟基苯并咪唑、巯基碘苯并咪唑、巯基氯苯并咪唑、巯基四羟基丁基苯基咪唑、巯基苯并噁唑、巯基甲基苯并噁唑、巯基羟基苯并噁唑、巯基碘苯并噁唑、巯基氯苯并噁唑、巯基四羟基丁基苯基噁唑、巯基苯并噻唑、巯基甲基苯并噻唑、巯基羟基苯并噻唑、巯基碘苯并噻唑、巯基氯苯并噻唑、巯基四羟基丁基苯基噻唑、巯基羟基苯并噻唑等，包括其混合物。

[0044] 适用于本发明的根据结构（II）的化合物具体的例子包括巯基萘并咪唑、巯基氯萘并咪唑、巯基羟基萘并咪唑、巯基甲基萘并咪唑、巯基萘并噻唑、巯基碘萘并噻唑、巯基羟基萘并噻唑、巯基甲基萘并噻唑等，包括其混合物。这样的化合物公开在美国专利号5498502的第4栏第8-40行，其引用部分在此引入作为参考。

[0045] 同样合适的是硫官能化的唑类，其在杂环环中包含3或更多个氮原子，即，三唑和四唑。在一些实施方案中，该硫官能化的唑类包含根据式（III）的硫官能化的四唑：

[0046]



(III)

[0047] 其中R表示有机基团，例如具有总共1-30，例如1-18或6-18或1-6个碳原子的那些。R可以是脂肪族的，芳族的或者混合的脂肪族的/芳族的，并且可以是未取代的烃或取代的烃。

[0048] 根据式（III）的这样的化合物具体的例子是5-巯基-1-甲基四唑、1-乙基-5-巯基四唑、1-环丙基-5-巯基四唑、1-烯丙基-5-巯基四唑、1-苄基-5-巯基四唑、1-(2-甲

氧基乙基)-5-巯基四唑、和苯基-1H-四唑5-硫醇。

[0049] 该硫官能化的三唑的例子包括5-苯基-1H-1,2,4-三唑-3-硫醇、3-巯基-1,5-二苯基-1,2,4-三唑、3-巯基-1,2,4-三唑、3-巯基-4-甲基-1,2,4-三唑、3-巯基-1-苯基-1,2,4-三唑、5-巯基-1-苯基-1,2,4-三唑、和5-巯基-1,2,4-三唑-3-乙酸、3,5-二巯基-1,2,4-三唑、3,5-二巯基-1-苯基-1,2,4-三唑、和3,5-二巯基-1,4-二苯基-1,2,4-三唑。

[0050] 硫官能化的噁唑的例子包括:2-巯基噁唑[4,5]吡啶;2-巯基噁唑、5-硝基-2-巯基苯并噁唑;5-氯-巯基噁唑;2-巯基-5-苯基噁唑;2-巯基-4,5-二甲基噁唑;2-巯基-4,5-二苯基噁唑;6-氨基-巯基苯并噁唑;2-巯基苯并噁唑;2-硫代-4-噁唑烷酮。

[0051] 硫官能化的噻唑的例子包括:2-巯基噻唑;4,5-二苯基-2-巯基噻唑;4-甲基-2-巯基噻唑;4,5-二甲基-2-巯基噻唑;硫代罗丹明;2-巯基-4-苯基噻唑;5-硫代罗丹明乙酸;罗丹明酸。

[0052] 硫官能化的噻二唑的例子包括:5-乙基-2-巯基-1,3,4-噻二唑、二巯基-1,3,4-噻二唑;5-苯基甲基-2-巯基-1,3,4-噻二唑;5-氨基甲基-2-巯基-1,3,4-噻二唑;2-磺酰胺-1,3,4-噻二唑-2-硫醇;5-(丙基硫)-2-巯基-1,3,4-噻二唑;2-巯基-1,3,4-噻二唑;5,5硫代双(1,3,4-噻二唑-2-硫醇);5-苯基2-巯基-1,3,4-噻二唑;5-氨基-1,3,4-噻二唑-2-硫醇。

[0053] 在某些实施方案中,彼此反应的多环氧化物和硫官能化的唑类的相对量是对于每当量的环氧基,存在着0.01-0.25mol的硫醇。

[0054] 在某些实施方案中,除了上述反应物之外,用于制造磷酸化的环氧树脂的反应物可以进一步包含这样的化合物,其具有两个与环氧基团有反应性的官能团,例如二醇、二酚(包括双酚A)、二羧酸、二硫醇和/或二胺是可以提及的几个。

[0055] 合适的制备这里所述的磷酸化的环氧树脂的方法描述在实施例中。在一些情况中,硫官能化的唑类首先与多环氧化物反应,并且所形成的反应产物与亚磷酸反应。这样的反应经常在有机溶剂中进行,如实施例所述。

[0056] 备选地,合适的含水树脂分散体可以通过这样的方法生产,在其中(a)将硫官能化的唑类(例如任何前述的那些)加入到组合物,该组合物包含得自至少(i)多环氧化物(例如任何前述的那些),和(ii)亚磷酸(例如任何前述的那些)的磷酸化的环氧树脂;(b)在至少一部分的该硫官能化的唑类已经加入后,将碱(例如任何前述的那些)加入该组合物中;和(c)在至少一部分的碱已经加入该组合物中之后,向该组合物中加入水。在一些情况中,不加入碱,直到期望的硫官能化的唑类总量的大部分(>50重量%)已经加入该组合物后为止。在仍然的其它情况中,不加入碱,直到期望的硫官能化的唑类的总量的至少90重量%已经加入该组合物后为止。在仍然的其它情况中,不加入碱,直到全部总量的期望的硫官能化的唑类已经加入该组合物后为止。在一些情况中,不加入水,直到所期望碱的总量的大部分(>50重量%)已经加入该组合物后为止。在仍然的其它情况中,不加入水,直到期望的碱的总量的至少90重量%已经加入该组合物后为止。在仍然的其它情况中,不加入水,直到全部总量的期望的碱已经加入该组合物后为止。

[0057] 在本发明的某些实施方案中,该磷酸化的环氧树脂是以磷酸化的环氧树脂的含水分散体的形式存在的,该含水分散体在主要或大部分含水的连续介质中。例如在某些实施

方案中，该连续相是至少 80 重量%的水，基于连续介质的总重量。在某些实施方案中，有机溶剂在该含水分散体中的存在量小于 20 重量%，例如小于 10 重量%，或者在一些情况中小于 5 重量%，或者在仍然的其它情况中小于 2 重量%，并且该重量%是基于连续相的总重量。

[0058] 为了将磷酸化的环氧树脂分散在基于水的连续介质中，将它用碱中和。合适的碱包括有机或无机碱二者。合适的碱的示例性的例子是氨，单烷基胺，二烷基胺或者三烷基胺例如乙基胺、丙基胺、二甲基胺、二丁基胺和环己基胺；单烷醇胺，二烷醇胺或者三烷醇胺例如乙醇胺、二乙醇胺、三乙醇胺、丙醇胺、异丙醇胺、二异丙醇胺、二甲基乙醇胺和二乙基乙醇胺；吗啉例如 N- 甲基吗啉或 N- 乙基吗啉。中和百分比是这样的，以使得所述树脂是水可分散的和电泳的。典型地，将树脂至少部分地中和到 20-200%，40-150%，例如 60-120%的中和比。

[0059] 因此，本发明的某些实施方案涉及含水树脂分散体，其包含碱中和的树脂组合物，其中该树脂组合物包含未凝胶化的磷酸化的环氧树脂，其包含反应物的反应产物，该反应物包含：(a) 多环氧化物；(b) 硫官能化的唑类；和 (c) 亚磷酸。

[0060] 如前所述，在本发明的涂层 / 密封剂体系中，该涂层包含反应物的固化的反应产物，该反应物包含磷酸化的环氧树脂（例如上述的任何那些）；和 (ii) 固化剂。所以，上述的含水树脂分散体的某些实施方案进一步包含固化剂。

[0061] 合适的固化剂包括但不必限于氨基塑料树脂和酚醛塑料树脂。合适的氨基塑料树脂是醛例如甲醛、乙醛、巴豆醛和苯甲醛与含氨基或酰胺基的材料例如尿素、三聚氰胺和苯并胍胺的缩合产物。经常使用获自醇和甲醛与三聚氰胺、尿素和苯并胍胺反应的产物。

[0062] 有用的氨基塑料树脂的示例性但非限制性的例子是以商标名 CYMEL 市售自 Cytec Industries 和以商标名 RESIMENE 市售自 Solutia Inc. 的那些。具体的例子是 CYMEL 1130 和 1156 和 RESIMENE 750 和 753。

[0063] (a) 磷酸化的环氧树脂和 (b) 固化剂的相对量是 50-90，例如 60-75%重量的磷酸化的环氧树脂，和 10-50，例如 25-40%重量的固化剂，基于 (a) 和 (b) 的固体重量。在本发明的一些实施方案中，该磷酸化的环氧树脂的存在量是至少 40%重量，至少 50%重量，例如至少 60%重量，基于形成涂层的液体组合物的总树脂固体重量。

[0064] 在制备最终的涂料组合物中，上述成分可以以任何方便的方式与水掺混。也可以使用典型的涂料添加剂例如颜料、填料、腐蚀抑制剂、抗氧化剂、流动控制剂、表面活性剂等。

[0065] 合适的腐蚀抑制剂是唑类，例如苯并三唑，5- 甲基苯并三唑，2- 氨基噻唑，和前述关于制备磷酸化的环氧树脂的硫官能化的唑类（当用作腐蚀抑制剂时，期望的是至少一些所述的唑是“游离的”，即，没有聚合）。其它合适的腐蚀抑制剂包括但不限于磷酸锌例如正磷酸锌，偏硼酸锌，偏硼酸钡单水合物，钙离子交换的二氧化硅，胶体二氧化硅，合成的非晶二氧化硅，和钼酸盐例如钼酸钙、钼酸锌、钼酸钡、钼酸锶及其混合物。合适的钙离子交换的二氧化硅是作为 **SHIELDEX®** AC3 和 / 或 **SHIELDEX®** C303 市售自 W. R. Grace&Co. 的。合适的非晶二氧化硅是以商标名 **SYLOID®** 市售自 W. R. Grace&Co. 的。合适的磷酸锌是作为 HEUCOPHOS ZP-10 市售自 Heubach 的。

[0066] 含铬的腐蚀抑制剂也是合适的。这样的腐蚀抑制剂的例子是铬酸钙、铬酸镁、铬酸锶和/或铬酸钡。

[0067] 在某些实施方案中，该腐蚀抑制剂在存在时，在含水分散体中的量低到0.001%例如0.001-10重量%，基于含水分散体的总重量。该组合物经常的固含量是5-25%，例如5-15%。

[0068] 在某些实施方案中，将涂料经由阴离子电沉积方法沉积到基底上。在这样的方法中，将导电基底（例如上述的任何那些，其充当包含阳极和阴极的电路中的阳极）浸入含水树脂分散体中，该分散体包含了上述类型的碱中和的树脂组合物。将电流在该阳极和阴极之间送过，来引起该树脂组合物沉积到阳极上。

[0069] 电沉积浴经常具有200-3000微欧姆/厘米，例如500-1500微欧姆/厘米的运行浴传导率。该涂覆的基底在浴液中的驻留时间经常是30-120秒。

[0070] 在电涂后，除去基底，然后在一定温度并且以足以进行固化的温度在炉子中焙烤基底。经常地，该涂覆的基底是在225℉或更低的温度，例如200℉或更低的温度焙烤20-60分钟。在一些情况中，该基底在180℉固化20分钟来产生硬的、耐溶剂的和不发粘的膜。如果期望，该电涂的基底可以在较高的温度焙烤，比如350℉。

[0071] 如前所述，本发明的涂层/密封剂体系包含沉积在至少一部分的该涂层上的密封剂。在本发明的这些实施方案中，该密封剂是从包含含硫的聚合物的组合物中沉积的。此处使用的术语“含硫的聚合物”指的是具有至少一个硫原子的任何聚合物。

[0072] 在某些实施方案中，该含硫的聚合物包含聚硫化物。确实地，已经令人惊讶地发现，由包含聚硫化物的组合物形成的密封剂可以特别良好的附着到由含水树脂分散体所形成的某些涂层上，该含水分散体包含碱中和的树脂组合物，其中该树脂组合物包含未凝胶化的磷酸化的环氧树脂，其包含反应物的反应产物，该反应物包含：(a)多环氧化物；(b)硫官能化的唑类；和(c)亚磷酸，如上所述。

[0073] 此处使用的术语“聚硫化物”指的是这样的聚合物，其在聚合物主链中和/或在聚合物链上的端部或侧部位置上包含一个或多个二硫化物连接，即-[S-S]-连接基。经常地，该聚硫化物聚合物将具有两个或更多个硫-硫连接基。合适的聚硫化物是以名称THIOPLAST市售自Akzo Nobel。THIOPLAST产品是以宽的分子量范围来获得的，例如从小于1100到超过8000，并且分子量是平均分子量，单位为g/mol。在一些情况中，该聚硫化物的数均分子量是1000-4000。这些产物的交联密度也是变化的，这取决于交联剂的用量。这些产物的“-SH”含量（即，硫醇含量）也可以变化。聚硫化物的硫醇含量和分子量会影响聚合物的固化速率，并且固化速率伴随着分子量而增加。

[0074] 在本发明的一些实施方案中，除了前述聚硫化物之外或者代替前述聚化物，密封剂是从包含聚合型混合物的组合物中沉积的，该聚合型混合物包含：(a)90mol%-25mol%的式$HS(RSS)_mR'SH$的硫醇封端的二硫化物聚合物；和(b)10mol%-75mol%的式$HS(RSS)_nRSH$的二乙基甲缩醛硫醇封端的聚硫醚聚合物，其中R是$-C_2H_4-O-CH_2-O-C_2H_4-$；R'是选自下面的二价基团：2-12个碳原子的烷基，4-20个碳原子的烷基硫醚，4-20个碳原子和1个氧原子的烷基醚，4-20个碳原子和2-4氧原子（其每个是通过至少2个碳原子来彼此隔开的）的烷基醚，6-12个碳原子的脂环族化合物，和芳族低级烷基；并且m和n的值是这样的，以使得二乙基甲缩醛硫醇封端的聚硫醚聚合物和硫醇端接的二硫化物聚合物的平均分

子量是 1000-4000，例如 1000-2500。这样的聚合型混合物描述在美国专利号 4623711 的第 4 栏第 18 行到第 8 栏第 35 行中，其引用部分在此引入作为参考。在一些情况中，上式中的 R' 是 $-CH_2-CH_2-$；$-C_2H_4-O-C_2H_4-$；$-C_2H_4-S-C_2H_4-$；$-C_2H_4-O-C_2H_4-O-C_2H_4-$；或者 $-CH_2-C_6H_4-CH_2-$。

[0075] 除了聚硫化物之外或者代替聚硫化物，该含硫的聚合物可以包含聚硫醚。此处使用的术语“聚硫醚”指的是这样的聚合物，其在聚合物主链中和 / 或在聚合物链上的端部或侧部位置上包含至少一个硫醚连接基，即，-[-C-S-C-]-。经常地，聚硫醚具有 8-200 个这些连接基。适用于本发明的聚硫醚包括例如包括具有式 (IV) 的结构的那些：

[0076] $-R^1-[-S-(CH_2)_2-O-[-R^2-O-]_m-(CH_2)_2-S-R^1]_n-$ (IV)

[0077] 其中：(1) R^1 表示 C_{2-6} 正亚烷基，C_{3-6} 支化的亚烷基，C_{6-8} 环亚烷基或 C_{6-10} 烷基环亚烷基、$-[(-CH_2-)_p-X-]_q-(-CH_2-)_r-$、或者 $-[(-CH_2-)_p-X-]_q-(-CH_2-)_r-$、其中至少一个 $-CH_2-$ 单元是用甲基取代的；(2) R^2 表示 C_{2-6} 正亚烷基、C_{2-6} 支化的亚烷基、C_{6-8} 环亚烷基或 C_{6-10} 烷基环亚烷基、或者 $-[(-CH_2-)_p-X-]_q-(-CH_2-)_r-$，X 表示选自 O、S 和 $-NR^6-$ 之一，R^6 表示 H 或甲基；(3) m 是 0-10 的有理数；(4) n 是 1-60 的整数；(5) p 是 2-6 的整数；(6) q 是 1-5 的整数，和 (7) r 是 2-10 的整数。这样的聚硫醚描述在美国专利号 6172179 第 2 栏第 29 行到第 4 栏第 34 行，其引用部分在此引入作为参考。合适的聚硫醚的例子是以商标名 PERMAPOL，例如 PERMAPOL P-3.1e 或者 PERMAPOL P-3 获自 PRC-Desoto International，Inc.。

[0078] 在本发明的某些实施方案中，该密封剂是从包含聚合型共混物的组合物中沉积的，该聚合型共混物包含：(a) 上述的聚硫化物；(b) 包括具有式 (III) 的结构的聚硫醚；(c) 上述类型的聚合型混合物，例如获自聚硫化物、有机二硫醇例如二巯基二乙基硫化物，和胺的反应。在一些实施方案中，这样的聚合型共混物中 (a) 和 (b) 的重量比是 10 :90-90 :10，例如 50 :50。这样的聚合型共混物描述在美国专利号 7524564 第 1 栏第 51 行到第 2 栏第 67 行，其引用部分在此引入作为参考。

[0079] 在某些实施方案中，该含硫的聚合物或者其共混物在形成密封剂的组合物中的存在量是至少 30 重量%，例如至少 40 重量%，或者一些情况中是至少 45 重量%，基于组合物中非挥发性组分的总重量。在某些实施方案中，该含硫的聚合物或者其共混物在形成密封剂的组合物中的存在量不大于 90 重量%，例如不大于 80 重量%，或者在一些情况中不大于 75 重量%，基于组合物中全部非挥发性组分的重量。

[0080] 在某些实施方案中，形成密封剂的组合物还包含固化剂。可用于本发明的某些组合物中的密封剂（特别是在其中使用硫醇官能化的含硫聚合物的情况中）包括环氧树脂例如乙内酰脲二环氧化物，双酚 A 的二缩水甘油醚，双酚 F 的二缩水甘油醚，酚醛树脂清漆类型的环氧化物，和任何环氧化的不饱和树脂和酚醛树脂，以及不饱和化合物例如市售多元醇的丙烯酸酯和甲基丙烯酸酯、不饱和的合成或天然存在的树脂化合物、三烯丙基氰尿酸酯、和本发明的聚硫醚的烯烃封端的衍生物。

[0081] 另外，在其中使用硫醇官能化的含硫聚合物的情况中，有用的固化可以通过硫醇基团的氧化性偶联，使用本领域技术人员已知的有机和无机过氧化物（例如 MnO_2）来获得的。

[0082] 可用于某些实施方案的组合物（密封剂从该组合物中沉积）的填料包括本领域通常使用的那些，包括常规的无机填料例如炭黑和碳酸钙 ($CaCO_3$)，以及轻量填料。合适的轻量填料包括例如描述在美国专利号 6525168 第 4 栏第 23-55 行中的那些，其引用部分在此

引入作为参考。在某些实施方案中，该组合物包括 5-60 重量%的填料或者填料的组合，例如 10-50 重量%，基于该组合物的总重量。

[0083] 除了前述成分之外，该密封剂组合物可以任选地包括下面的一种或多种：着色剂、触变剂、加速剂、阻滞剂、附着力促进剂、溶剂和掩蔽剂等其它组分。

[0084] 触变剂例如二氧化硅经常的用量是 0.1-5 重量%，基于该组合物的总重量。

[0085] 本领域已知的固化催化剂例如胺经常的存在量是 0.1-5 重量%，基于该组合物的总重量。有用的催化剂的具体的例子是，但不限于，1,4- 二氮杂 - 双环 [2.2.2] 辛烷（**DABCO®**，市售自 Air Product, Chemical Additives Division, Allentown, PA）和 **DMP-30®**（一种包括 2,4,6- 三（二甲基氨基甲基）酚的加速剂组合物，市售自 Rohm and Haas, Philadelphia, PA）。

[0086] 阻滞剂例如硬脂酸同样经常的用量是 0.1-5 重量%，基于该组合物的总重量。附着力促进剂（如果使用的话）经常的存在量是 0.1-15 重量%，基于该组合物的总重量。合适的附着力促进剂包括酚醛树脂，例如获自 Occidental Chemicals 的 METHYLON 酚醛树脂，和有机硅烷例如环氧、巯基或者氨基官能化硅烷，例如获自 Momentive Performance Material 的 Silquest A-187 和 Silquest A-1100。掩蔽剂例如松树香味剂或者其它香味剂（其可用于遮盖所述组合物的任何低水平气味）经常的存在量是 0.1-1 重量%，基于该组合物的总重量。

[0087] 在某些实施方案中，该密封剂组合物包含增塑剂，其在至少一些情况下可以使得所述组合物包括这样的含硫聚合物，其 T_g 高于航空航天密封剂中通常使用的那些。即，使用增塑剂可有效地降低组合物的 T_g，和因此使得固化的可聚合组合物的低温挠性增加超过基于单独的含硫聚合物的 T_g 所预期的低温挠性。可用于本发明组合物的某些实施方案中的增塑剂包括例如邻苯二甲酸酯、氯化石蜡和氢化三联苯。增塑剂或者增塑剂的组合物经常构成组合物的 1-40 重量%，例如 1-10 重量%。在某些实施方案中，取决于组合物中所用的增塑剂的性质和用量，可以使用本发明的硫醚，其 T_g 值高到 -50℃，例如高到 -55℃。

[0088] 在某些实施方案中，该密封剂组合物可以进一步包含一种或多种有机溶剂例如异丙醇，其量是例如 0-15% 重量，基于该组合物的总重量，例如小于 15 重量%和在一些情况中小于 10 重量%。

[0089] 本发明的涂层 / 密封剂体系在至少一些情况中会表现出优异的层间附着性以及对基底的附着性。在本发明的一些实施方案中，当根据这里的实施例所述的 AS 5127/1B 来测量时，本发明的涂层 / 密封剂体系表现出平均剥离强度是至少 150N/25mm，例如至少 200N/25mm，和粘着性%是至少 50%，例如至少 90% 或者在一些情况中是 100%。

[0090] 要求保护的本发明的这些和其它方面通过下面的非限定性实施例来进一步说明。

[0091] 实施例

[0092] 实施例 1：制备含水树脂分散体

[0093] 使 12L 圆底四颈烧瓶装备有搅拌器，并且带有轴承，水冷却的冷凝器，热电偶探头和氮气入口接头和电加热罩。向该烧瓶中装入 2949.8g(7.845mol) 的双酚 A 二缩水甘油醚（当量 188），948.8g(4.162mol) 的双酚 A，418.9g 的 2- 正丁氧基乙醇和 335.3g 的 2- 乙基己醇。在氮气层下，将其搅拌和加热到 115℃。在 115℃，加入 2.9g 的乙基三苯基碘化

鏻（获自 Sigma-Aldrich）。将其加热直到放热开始，并且将该反应混合物在 165℃或以上保持 60 分钟。向该反应混合物中加入 383.3g 的 Ektasolve EEH（获自 Eastman Chemical Company）和 83.6g 的 2- 乙基己醇（在它冷却到 90℃时）。在 90℃，加入 67.9g(0.430mol) 的苯基膦酸，115.6g(1.003mol) 的 85％正磷酸和 24.7g 的 Ektasolve EEH 的混合物。在放热后，将该反应混合物在 120℃保持 30 分钟，然后将它冷却到 100℃。在 100℃，将 257.6g 去离子水在约 1 小时内加入，并且之后将该反应混合物在 100℃保持 2 小时。在那个点，将它冷却到 90℃和加入 324.2g(2.437mol) 的二异丙醇胺和 1487.2g 的 Cymel 1130（获自 Cytec Industries，Inc.）。将该混合物在 90℃保持 30 分钟。将 7000g 的这种材料搅拌到 5511.4g 的去离子水中，随后加入 1317.0g 更多的去离子水。向其中加入 366.4g 的 2- 己氧基乙醇，225.5g 的 Optifilm400（获自 Eastman Chemical Company）和 5.5g 的 Tektronic 150RI（获自 BASFCorporation）。随后加入 1045.5g 去离子水来产生分散体，其在 110℃和 1 小时后显示为 39.4％固体。

[0094] 实施例 2：制备含水树脂分散体

[0095] 使 3L 圆底四颈烧瓶装备有搅拌器，并且带有轴承，水冷却的冷凝器，热电偶探头和氮气入口接头和电加热罩。向该烧瓶中装入 705g(3.75mol) 的双酚 A 二缩水甘油醚（当量 188），222.6g(1.952mol) 的双酚 A，39g(0.237mol) 的巯基甲基苯并咪唑（获自 Sigma-Aldrich）和 180.3g 的 2- 正丁氧基乙醇。在氮气层下，将其搅拌和加热到 115℃。在 115℃，加入 0.7g 的乙基三苯基碘化鏻（获自 Sigma-Aldrich）。将其加热直到放热开始，并且将该反应混合物在 165℃或以上保持 60 分钟。向该反应混合物中加入 112g 的 2- 正丁氧基乙醇（在它冷却到 90℃时）。在 90℃，加入 27.6g 的 85％正磷酸。在放热后，将该反应混合物在 120℃保持 30 分钟，然后将它冷却到 100℃。在 100℃，将 61.6g 的去离子水在约 1 小时中加入，并且之后将该反应混合物在 100℃保持 2 小时。在那个点，将它冷却到 90℃和加入 63.8g 的二异丙醇胺，330.5g 的 Cymel 1130（获自 Cytec Industries，Inc.）和 40.1g 的巯基甲基苯并咪唑。将该混合物在 90℃保持 30 分钟。将 1650g 的这种材料搅拌到 1350g 去离子水中，随后加入 315.8g 去离子水，然后最后加入 390.1g 去离子水。最终的分散体在 110℃和 1 小时后显示为 30.3％固体。

[0096] 实施例 3：制备含水树脂分散体

[0097] 使 3L 圆底四颈烧瓶装备有搅拌器，并且带有轴承，水冷却的冷凝器，热电偶探头和氮气入口接头和电加热罩。向该烧瓶中装入 450g(2.39mol) 的双酚 A 二缩水甘油醚（当量 188），142.1g(1.25mol) 的双酚 A，15.9g(0.135mol) 的苯基 -1H- 四唑 5- 硫醇（获自 Sigma-Aldrich）和 115.1g 的 2- 正丁氧基乙醇。在氮气层下，将其搅拌和加热到 115℃。在 115℃，加入 0.5g 的乙基三苯基碘化鏻（获自 Sigma-Aldrich）。将其加热直到放热开始，并且将该反应混合物在 165℃或以上保持 60 分钟。向该反应混合物中加入 71.2g 的 2- 正丁氧基乙醇（在它冷却到 90℃时）。在 90℃，加入 17.6g 的 85％正磷酸。在放热后，将该反应混合物在 120℃保持 30 分钟，然后将它冷却到 100℃。在 100℃，将 39.3g 的去离子水在约 1 小时中加入，并且之后将该反应混合物在 100℃保持 2 小时。在那个点，将它冷却到 90℃和加入 40.7g 的二异丙醇胺，211.0g 的 Cymel 1130（获自 Cytec Industries，Inc.）和 26.1g 苯基 -1H- 四唑 -5- 硫醇。将该混合物在 90℃保持 30 分钟。将 1000g 的这种材料搅拌到 814g 去离子水中，并且将该分散体搅拌 1 小时，随后加入 190.9g 去离子水，然后最后

加入 235.9g 去离子水。最终的分散体在 110℃和 1 小时后显示为 36.1%固体。

[0098] 实施例 4 :制备含水树脂分散体

[0099] 使 3L 圆底四颈烧瓶装备有搅拌器，并且带有轴承，水冷却的冷凝器，热电偶探头和氮气入口接头和电加热罩。向该烧瓶中装入 727.9 份 (3.87mol) 的双酚 A 二缩水甘油醚 (当量 188)，229.8g(2.02mol) 的双酚 A 和 186.1g 的 2- 正丁氧基乙醇。在氮气层下，将其搅拌和加热到 115℃。在 115℃，加入 0.7g 的乙基三苯基碘化鏻 (获自 Sigma-Aldrich)。将其加热直到放热开始，并且将该反应混合物在 165℃或以上保持 60 分钟。向该反应混合物中加入 115.2g 的 2- 正丁氧基乙醇 (在它冷却到 90℃时)。在 90℃，加入 42.2g 的 2- 巯基苯并噻唑，并且将该反应保持 30 分钟。向该反应混合物中加入 28.5g 的 85%正磷酸。在放热后，将该反应混合物在 120℃保持 60 分钟，然后将它冷却到 100℃。在 100℃，将 63.6g 的去离子水在约 1 小时中加入，并且之后将该反应混合物在 100℃保持 2 小时。在那个点，将它冷却到 90℃和加入 65.8g 的二异丙醇胺和 341.3g 的 Cymel 1130(获自 Cytec Industries, Inc.)。将该混合物在 90℃保持 30 分钟。将 1600g 的这种材料搅拌到 1267.4g 去离子水中，并且将该分散体搅拌 1 小时，随后加入 301.8g 去离子水，然后最后加入 372.8g 去离子水。最终的分散体在 110℃和 1 小时后显示为 34.0%固体。

[0100] 实施例 5-8 :制备涂料组合物

[0101] 涂料组合物是使用表 1 所列的成分和用量 (重量份) 来制备的。最终组合物的 pH 和导电率也列于表 1 中。

[0102] 表 1

[0103]

成分	实施例 5	实施例 6	实施例 7	实施例 8
实施例 1 的分散体	1632.7	--	--	--
实施例 2 的分散体	--	1294.1	--	--
实施例 3 的分散体	--	--	1565.8	--
实施例 4 的分散体	--	--	--	1120.1
颜料糊 [1]	331.1	217.8	306.8	217.8
去离子水	1836.2	988.1	1727.5	1162.1
pH[2]	8.61	8.81	8.45	8.65
导电率 (Ω^{-1})[3]	867	710	927	964

[0104] [1]灰色颜料糊，ACPP-1120，获自 PPG Industries, Inc.，51.4%固体。

[0105] [2]用 ACCUMET pH 计测量，其市售自 Fisher Scientific

[0106] [3]用电导率计测量，其市售自 YSI, Inc

[0107] 在每种情况中，将分散体加入到加仑容器中。在搅拌下，将颜料糊与去离子水一

起加入该分散体中。最终浴固体是约 20%，并且颜料与树脂比是 0.2 :1.0。通过超滤除去 50%的总浴液，并且用去离子水代替。

[0108] 测试基底

[0109] 将铝 2024-T3 裸板在 130 ℉通过浸入到 RIDOLINE 298 溶液（一种碱性清洁剂，获自 Henkel Corporation）中 2 分钟来清洁。在碱清洁之后，在环境条件将该面板浸入到自来水冲洗中 1 分钟。然后在环境条件将该面板浸入 DEOXIDIZER 6/16 溶液（一种酸性脱氧剂，获自 Henkel Corporation）两分钟三十秒。在酸脱氧之后，在环境条件将该面板浸入自来水中 1 分钟，随后进行去离子水最终喷淋冲洗。在使用前将该面板空气干燥。

[0110] 将实施例 5、6、7 和 8 的涂料组合物沉积到清洁的和脱氧的 2 $^{3}/_{4}$"×6"面板上。这是通过将实施例 5 和 6 的涂料组合物加热到 75 ℉（24℃）和将实施例 7 和 8 的涂料组合物加热到 90 ℉（32℃）来进行的。在搅拌下将该面板浸入所述涂料组合物浴中，然后施加 85-275 伏特 90 秒，并且在 200 ℉（93℃）热固化 30 分钟来实现约 0.8 密耳的膜厚。

[0111] 密封剂附着性是使用市售自 PRC-DeSoto International，Inc. 的 PR-1776 M B-2 密封剂来评价的。面板是根据 AS5127/1B 来制备的，具有下面的改变：使用铝箔条代替金属丝网筛或者织物增强件。该箔条是 0.005"厚，尺寸是 1"宽乘 12"长。箔制备包括用灰色 SCOTCH BRITE 垫 (TM) 拖磨，用溶剂根据 AS5127/1B 进行溶剂清洗，和根据制造商的说明使用市售自 PRC-DeSoto International，Inc. 的 PR-148 附着力促进剂。将面板在 77 ℉和 50%相对湿度固化 14 天，然后根据 AS5127/1B 测试剥离强度。结果在表 2 中给出。

[0112] 表 2

[0113]

实施例	剥离强度[1]读数 1 N/25mm	剥离强度[1]读数 2 N/25mm	剥离强度[1]读数 3 N/25mm	剥离强度[1]读数 4 N/25mm	平均剥离强度 N/25mm	%粘着[2]
5	52	57	42	38	47	0
6	182	215	222	228	212	100
7	115	164	163	184	157	30
8	198	212	204	204	205	99

[0114] [1]剥离强度是将箔条从基底上拉开所需的力的度量

[0115] [2]%粘着指的是在箔条从基底上拉开之后，密封剂保持粘着在其上的基底的表面积的部分（结果是作为四个读数的平均值来报告的）。

[0116] 实施例 9：制备含水树脂分散体

[0117] 使 12L 圆底四颈烧瓶装备有搅拌器，并且带有轴承，水冷却的冷凝器，热电偶探头和氮气入口接头和电加热罩。向该烧瓶中装入 2337.4g(6.216mol) 的双酚 A 二缩水甘油醚（当量 188），751.9g(3.298mol) 的双酚 A，332.0g 的 2-正丁氧基乙醇和 265.7g 的 2-乙基己醇。在氮气层下，将其搅拌和加热到 115℃。在 115℃，加入 2.3g 的乙基三苯基碘化鏻（获自 Sigma-Aldrich）。将其加热直到放热开始，并且将该反应混合物在 165℃或以上保持 60 分钟。向该反应混合物中加入 303.8g 的 Ektasolve EEH（获自 Eastman Chemical Company）和 66.2g 的 2-乙基己醇（在它冷却到 90℃时）。在 90℃，加入 53.8g(0.340mol) 的苯基膦酸，91.6g(0.794mol) 的 85%正磷酸和 19.6g 的 Ektasolve EEH。在放热之后，将该反应混

合物在120℃保持30分钟，然后将它冷却到100℃。在100℃，将204.1g的去离子水在约1小时中加入，并且之后将该反应混合物在100℃保持2小时。在那个点，将它冷却到90℃和加入256.9g(1.932mol)的二异丙醇胺，1178.5g的Cymel 1130(获自Cytec Industries，Inc.)和136.1g(1.144mol)的2-巯基苯并噻唑。将该混合物在90℃保持30分钟。将5600g的这种材料搅拌到4484.5g的去离子水中，随后加入1061.5g更多的去离子水。向其中加入295.4g的2-己氧基乙醇，181.8g的Optifilm 400(获自Eastman Chemical Company)和4.4g的Tektronic 150R1(获自BASF Corporation)。随后，加入842.7g的去离子水来产生分散体，其在110℃和1小时后显示为38.6%的固体。

[0118] 实施例10：制备含水树脂分散体

[0119] 使12L圆底四颈烧瓶装备有搅拌器，并且带有轴承，水冷却的冷凝器，热电偶探头和氮气入口接头和电加热罩。向该烧瓶中装入2102.9g(5.593mol)的双酚A二缩水甘油醚(当量188)，663.9g(2.912mol)的双酚A，118.3g(0.707mol)的2-巯基苯并噻唑和537.7g的2-正丁氧基乙醇。在氮气层下，将其搅拌和加热到115℃。在115℃，加入2.1g的乙基三苯基碘化鏻(获自Sigma-Aldrich)。将其加热直到放热开始，并且将该反应混合物在165℃或以上保持60分钟。向该反应混合物中加入332.9g的2-正丁氧基乙醇(在它冷却到90℃时)。在90℃，加入82.4g(0.715mol)的85%正磷酸。在放热后，将该反应混合物在120℃保持30分钟，然后将它冷却到100℃。在100℃，将183.7g的去离子水在约1小时加入，并且之后将该反应混合物在100℃保持2小时。在那个点，将它冷却到90℃和加入190.2g(1.430mol)的二异丙醇胺和985.9g的Cymel 1130(获自Cytec Industries，Inc.)。将该混合物在90℃保持30分钟。将4800g的这种材料搅拌到3926.5g去离子水中，随后加入918.6g去离子水，然后最后加入1134.7g的去离子水。最终的分散体在110℃和1小时后显示为37.1%的固体。

[0120] 实施例11：制备含水树脂分散体

[0121] 使3000ml圆底四颈烧瓶装备有搅拌器，并且带有轴承，水冷却的冷凝器，热电偶探头和氮气入口接头和电加热罩。向该烧瓶中装入400.8g(1.0660mol)的双酚A二缩水甘油醚(当量188)，128.9g(0.565mol)的双酚A和102.5g的2-正丁氧基乙醇。在氮气层下，将其搅拌和加热到115℃。在115℃，加入0.4g的乙基三苯基碘化鏻(获自Sigma-Aldrich)。将其加热直到放热开始，并且将该反应混合物在165℃或以上保持60分钟。向该反应混合物中加入66.8g的2-正丁氧基乙醇(在它冷却到90℃时)。在90℃，加入19.1g(0.166mol)的85%正磷酸。在放热后，将该反应混合物在120℃保持30分钟，然后将它冷却到100℃。在100℃，将35.0g的去离子水在约45分钟中加入，并且之后将该反应混合物在100℃保持2小时。在那个点，将它冷却到90℃和加入53.5g(0.402mol)的二异丙醇胺，202.1g的Cymel 1130(获自Cytec Indus tries，Inc.)和90.9g的实施例12的加合物。将该混合物在90℃保持30分钟。将900g的这种材料搅拌到708.6g去离子水中，随后加入169.3g去离子水，然后最后加入209.2g去离子水。最终的分散体在110℃和1小时后显示为38.7%的固体。

[0122] 实施例12：制备加合物

[0123] 使1L圆底四颈烧瓶装备有搅拌器，并且带有轴承，水冷却的冷凝器，热电偶探头和氮气入口接头和电加热罩。向该烧瓶中依次装入40.2g巯基苯并噻唑，92.5g的EPON828

和 192.0g 甲基戊基酮。将该反应加热到 50℃并保持 1 小时。升温，直到发生回流（116℃）。将该反应保持 6 小时，并且用蒸馏头和冷凝器来代替冷凝器。将加热罩设定为 118℃和除去挥发性组分（173g），直到达到设定温度。最终的材料是 86％固体，将所期望的产物通过核磁共振来确认。

[0124] 实施例 13-15：制备涂料组合物

[0125] 涂料组合物是使用表 3 所列的成分和用量（重量份）来制备的。最终组合物的 pH 和导电率也列于表 3 中。

[0126] 表 3

[0127]

成分	实施例 13	实施例 14	实施例 15
实施例 9 的分散体	1546.8	---	---
实施例 10 的分散体	---	2212.4	---
实施例 11 的分散体	---	---	1543.6
颜料糊[1]	331.1	455.0	331.1
去离子水	1922.2	2555.1	1925.4
pH[2]	8.34	8.69	8.25
导电率（Ω^{-1}）[3]	974	807	985

[0128] 在每种情况中，将分散体加入到加仑容器中。在搅拌下，将颜料糊与去离子水一起加入该分散体中。最终浴固体是约 20％，并且颜料与树脂比是 0.2：1.0。通过超滤除去 50％的总浴液，并且用去离子水代替。

[0129] 测试基底

[0130] 将铝 2024-T3 裸板在 130 ℉通过浸入到 RIDOLINE 298 溶液（一种碱性清洁剂，获自 Henkel Corporation）中 2 分钟来清洁。在碱清洁之后，在环境条件将该面板浸入到自来水冲洗中 1 分钟。然后在环境条件将该面板浸入 DEOXIDIZER 6/16 溶液（一种酸性脱氧剂，获自 Henkel Corporation）两分钟三十秒。在酸脱氧之后，在环境条件将该面板浸入自来水中 1 分钟，随后进行去离子水最终喷淋冲洗。在使用前将该面板空气干燥。

[0131] 将实施例 5、13、14 和 15 的涂料组合物沉积到清洁的和脱氧的 2 $^{3}/_{4}$”×6”面板上。这是通过将实施例 5 和 13 的涂料组合物加热到 75 ℉（24℃）和将实施例 14 和 15 的涂料组合物加热到 90 ℉（32℃）来进行的。在搅拌下将该面板浸入所述涂料组合物浴中，然后施加 85-275 伏特 90 秒，并且在 200 ℉（93℃）热固化 30 分钟来实现约 0.8 密耳的膜厚，例外是实施例 15，其固化了 60 分钟。

[0132] 密封剂附着性是使用市售自 PRC-DeSoto International，Inc. 的 PR-1776 M B-2 密封剂来评价的。面板是根据 AS5127/1B 来制备的，具有下面的改变：使用铝箔条代替金属丝网筛或者织物增强件。该箔条是 0.005”厚，尺寸是 1”宽乘 12”长。箔制备包括用灰色

SCOTCH BRITE 垫(TM)拖磨，用溶剂根据 AS5127/1B 进行溶剂清洗，和根据制造商的说明使用市售自 PRC-DeSoto International，Inc. 的 PR-148 附着力促进剂。将面板在环境温度和湿度条件下固化 14 天，然后根据 AS5127/1B 测试剥离强度。结果在表 4 中给出。

[0133] 表 4

[0134]

实施例	面板#	剥离强度[1]读数 1 N/25mm	剥离强度[1]读数 1 N/25mm	剥离强度[1]读数 1 N/25mm	剥离强度[1]读数 1 N/25mm	平均剥离强度 N/25mm	%粘着[2]
5	A	92	78	55	74	75	0
	B	51	97	80	71	75	0
13	A	71	64	47	42	56	3
	B	64	75	46	48	58	2
14	A	234	227	238	204	226	100
	B	156	165	167	161	162	100
15	A	46	51	59	53	52	0
	B	46	67	58	74	61	5

[0135] [1]剥离强度是将箔条从基底上拉开所需的力的度量

[0136] [2]%粘着指的是在箔条从基底上拉开之后，密封剂保持粘着在其上的基底的表面积的部分（结果是作为四个读数的平均值来报告的）。

[0137] 实施例 16：制备含水树脂分散体

[0138] 使 3L 圆底四颈烧瓶装备有搅拌器，并且带有轴承，水冷却的冷凝器，热电偶探头和氮气入口接头和电加热罩。向该烧瓶中装入 727.9 份 (3.87mol) 的双酚 A 二缩水甘油醚（当量 188），229.8g(2.02mol) 的双酚 A 和 186.1g 的 2- 正丁氧基乙醇。在氮气层下，将其搅拌和加热到 115℃。在 115℃，加入 0.7g 的乙基三苯基碘化鏻（获自 Sigma-Aldrich）。将其加热直到放热开始，并且将该反应混合物在 165℃或以上保持 60 分钟。向该反应混合物中加入 115.2g 的 2- 正丁氧基乙醇（在它冷却到 90℃时）。在 90℃，加入 28.5g 的 85% 正磷酸，并且在放热后，将该反应混合物在 120℃保持 30 分钟。向该反应混合物中加入 41.0g 的 2- 巯基苯并噻唑，并且将该反应在 120℃保持 30 分钟，然后将它冷却到 100℃。在 100℃，将 63.6g 的去离子水在约 1 小时中加入，和之后将该反应混合物在 100℃保持 2 小时。在那个点，将它冷却到 90℃和加入 65.8g 的二异丙醇胺和 341.3g 的 Cymel 1130（获自 Cytec Industries，Inc.）。将该混合物在 90℃保持 30 分钟。将 1608g 的这种材料搅拌到 1295.3g 去离子水中，并且将该分散体搅拌 1 小时，随后加入 305.6g 去离子水，然后最后加入 377.5g 去离子水。最终的分散体在 110℃和 1 小时后显示为 34.0% 的固体。

[0139] 实施例 17：制备涂料组合物

[0140] 涂料组合物是使用表 5 所列的成分和用量（重量份）来制备的。最终组合物的 pH 和导电率也列于表 5 中。

[0141] 表 5

[0142]

成分	实施例 B
实施例 16 的分散体	1577.9
颜料糊[1]	331.1
去离子水	1891.1
pH[2]	8.56
电导率 (Ω^{-1})[3]	973

[0143] [1]灰色颜料糊，ACPP-1120，获自 PPG Industries，Inc.，51.4%固体。

[0144] [2]用 ACCUMET pH 计测量，其市售自 Fisher Scientific

[0145] [3]用电导率计测量，其市售自 YSI，Inc

[0146] 在每种情况中，将分散体加入到加仑容器中。在搅拌下，将颜料糊与去离子水一起加入该分散体中。最终浴固体是约 20%，并且颜料与树脂比是 0.2 :1.0。通过超滤除去 50%的总浴液，并且用去离子水替代。

[0147] 测试基底

[0148] 将铝 2024-T3 裸板在 130 °F 通过浸入到 RIDOLINE 298 溶液（一种碱性清洁剂，获自 Henkel Corporation）中 2 分钟来清洁。在碱清洁之后，在环境条件将该面板浸入到自来水冲洗中 1 分钟。然后在环境条件将该面板浸入 DEOXIDIZER 6/16 溶液（一种酸性脱氧剂，获自 Henkel Corporation）两分钟三十秒。在酸脱氧之后，在环境条件将该面板浸入自来水中 1 分钟，随后进行去离子水最终喷淋冲洗。在使用前将该面板空气干燥。

[0149] 将实施例 17 的涂料组合物沉积到清洁的和脱氧的 2 $^{3}/_{4}$”×6”面板上。这是通过将实施例 17 的涂料组合物加热到 90 °F（32℃）来进行的。在搅拌下将该面板浸入所述涂料组合物浴中，然后施加 85-275 伏特 90 秒，并且在 200 °F（93℃）热固化 30 分钟来实现约 0.8 密耳的膜厚。

[0150] 密封剂附着性是使用市售自 PRC-DeSoto International，Inc. 的 PR-1776 M B-2 密封剂来评价的。面板是根据 AS5127/1B 来制备的，具有下面的改变：使用铝箔条代替金属丝网筛或者织物增强件。该箔条是 0.005”厚，尺寸是 1”宽乘 12”长。箔制备包括用灰色 SCOTCH BRITE 垫 (TM) 拖磨，用溶剂根据 AS5127/1B 进行溶剂清洗，和根据制造商的说明使用市售自 PRC-DeSoto International，Inc. 的 PR-148 附着力促进剂。将面板在 77 °F 和 50% 相对湿度下固化 14 天，然后根据 AS5127/1B 测试剥离强度。结果在表 6 中给出。

[0151] 表 6

[0152]

实施例	剥离强度[1]读数 1 N/25mm	剥离强度[1]读数 2 N/25mm	剥离强度[1]读数 3 N/25mm	剥离强度[1]读数 4 N/25mm	平均剥离强度 N/25mm	%粘着[2]
17	171	184	190	203	187	85

[0153] [1]剥离强度是将箔条从基底上拉开所需的力的度量

[0154] ^{2}%粘着指的是在箔条从基底上拉开之后，密封剂保持粘着在其上的基底的表面积的部分（结果是作为四个读数的平均值来报告的）。

[0155] 虽然上面出于说明的目的已经描述了本发明具体的实施方案，但是对本领域技术人员来说显然可以对本发明作出细节的诸多变化，而不脱离附加的权利要求所定义的本发明。