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(54) **ELECTRODEPOSITABLE COATING COMPOSITIONS AND RELATED METHODS**

ELEKTROTAUHLACKIERUNGEN UND ENTSPRECHENDE VERFAHREN

COMPOSITIONS DE REVETEMENT POUVANT ETRE APPLIQUEES PAR ELECTRODEPOSITION
ET PROCEDES ASSOCIES

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Description

BACKGROUND OF THE INVENTION

I. FIELD OF THE INVENTION

[0001] The present invention relates to cationic electrodepositable coating compositions comprising a hydroxyl group-containing cationic resin, a blocked polyisocyanate curing agent, and an organotin catalyst; to methods of preparing such compositions; and to methods for applying such compositions.

II. TECHNICAL CONSIDERATIONS

[0002] The application of a coating by electrodeposition involves deposition of a film-forming composition to an electrically conductive substrate under the influence of an applied electrical potential. Electrodeposition has gained prominence in the coating industry because in comparison with non-electrophoretic coating methods, electrodeposition provides higher paint utilization, excellent corrosion resistance and low environmental contamination. Early attempts at commercial electrodeposition processes used anionic electrodeposition where the workpiece to be coated serves as the anode. However, cationic electrodeposition has become increasingly popular and today is the most prevalent method of electrodeposition.

[0003] Many cationic electrodeposition compositions in use today are based on active hydrogen-containing resins derived from a polyepoxide and a capped or blocked polyisocyanate curing agent. Typically, these cationic electrodeposition compositions also contain organotin catalysts to lower the temperature at which the blocking agent is released from blocked polyisocyanate and to activate cure of the electrodeposition composition.

[0004] Common organotin catalysts include dialkyltin oxides, for example, dibutyltin oxide, dioctyltin oxide and dimethyltin oxide, and derivatives thereof, such as dibutyltin dicarboxylates and dibutyltin mercaptides. Although effective to some degree in promoting cure of the electrodeposition composition, the use of such catalysts in cationic electrodeposition compositions can present several drawbacks. For example, most of the common dialkyltin oxides are high melting, amorphous solid materials which must be introduced into the composition in the form of a catalyst paste prepared by dispersing the solid catalyst into a pigment wetting resin under extremely high shear conditions. Preparation of stable catalyst pastes can be very costly and time intensive.

[0005] Further, it has been noted that some of the aforementioned organotin catalysts can cause a multitude of surface defects in the cured electrodeposited coating composition. For example, dibutyltin oxide dispersions can flocculate in the electrodeposition bath, resulting in oversized dibutyltin oxide agglomerates or particles which can settle in areas of the electrodeposition tank where agitation is poor. This flocculation phenomenon constitutes a loss of catalyst from the coating composition resulting in poor cure response. Moreover, the flocculate particles can settle in the uncured electrodeposited coating causing localized "hot spots" or pinholes in the surface of the cured coating. Also, electrodeposition bath stability can be adversely affected with the use of some organotin catalysts. It has been observed that soft, floating foams can form from a mixture of organotin catalyst, polyisocyanate curing agent and microscopic air bubbles.

[0006] Known in the art for use as catalysts in cationic electrodepositable coating compositions are the condensation products of dialkyltin oxides, such as dibutyltin oxide, and hydroxyl compounds such as aliphatic alcohols, alkanolamines, and phenols. These catalysts purportedly are storage stable and the organophilic molecule segments thereof enable them to stay in the resinous phase and, thus, in the dewatered film.

[0007] Also, known in the art for use as catalysts in cationic electrodepositable coating compositions are dialkyltin aromatic carboxylic acid salts prepared by reacting a dialkyltin oxide, such as dibutyltin oxide, with an aromatic carboxylic acid. Such catalysts are said to be more compatible with the resinous binder system, provide improved bath stability, and yield a coated film free from defects such as cratering and seeding. Further, a catalytic effect can be observed at lower temperatures than with the corresponding dialkyltin oxides, and cured films have improved corrosion resistance. Such catalysts can also be used in conjunction with bismuth and/or zirconium compounds to provide a cationic electrocoating composition having superior corrosion resistance, low-temperature curability and good electrodeposition bath stability.

[0008] Carboxylic acid and mercapto derivatives of dialkyltin oxides, for example diorganotin bis-carboxylates and diorganotin bis-mercaptides are also known in the art as catalysts for cationic electrodepositable coating compositions. The diorganotin bis-carboxylates can be prepared by reacting a dialkyltin oxide with the appropriate hydroxy-carboxylic acid or mercaptan. It is alleged that the use of such compounds as catalysts in cationic electrodepositable compositions can prevent problems associated with catalyst volatility and provide emulsion stability by becoming chemically bound via hydroxy-functionality to one or more of the composition components. However, with lower carboxylic acid derivatives, such as acetate, formate and laurate, the organotin derivative can hydrolyze and form the corresponding diorganotin oxide precipitate. The liberation of these low molecular weight carboxylic acids also can lower the throwpower of the

electrodepositable composition, and can increase corrosion of the anode. Cautious incorporation of higher carboxylic acid derivatives such as dibutyltin dioleate, provide electrodeposition coating compositions with improved stability, however free acid from the at least partial hydrolysis of these organotin compounds can negatively affect coating performance when applied over galvanized steel substrates. It has been noted that with these higher carboxylic acid derivatives, the higher acid can remain in the film after curing, and can migrate to the zinc-electrodeposition coating interface causing adhesion loss and poor corrosion resistance.

[0009] Alkyltin diacetyl acetonates, for example dibutyltin diacetyl acetate, have been employed as catalysts for curing components of cationic electrodeposition coatings containing a blocked polyisocyanate curing agent. Such catalysts typically are added in solution to a blend of an epoxy amine adduct and a blocked polyisocyanate curing agent, prior to dispersion into water. The alkyltin diacetyl acetate catalysts purportedly are readily dispersed and remain dispersed in aqueous electrocoating baths. The art teaches that such materials are hydrolytically stable for extended periods of time under conventional electrocoating conditions. However, in practice, it is known in the art that some hydrolysis can occur, resulting in reformation of the dialkyltin oxide and the acetyl acetate. The acetyl acetate can react readily with any primary amine present in the cationic composition as a result of the reaction of a ketimine-containing compound with epoxy groups of a main film-forming resin, thereby forming high molecular weight species. In such instances, coating appearance can be adversely affected due to the presence of dialkyltin oxide precipitates and particles of the high molecular weight species resulting from reaction of primary amine and acetyl acetate.

[0010] Triorganotin compounds are known for use as catalysts in electrodepositable coating compositions comprised of an active hydrogen-containing resin and a blocked polyisocyanate curing agent. For example, it is known to use triorganotin compounds such as bis (tributyltin) oxide, bis (triocetyl tin) oxide, bis (tributyltin) sulfide, and bis (triocetyl tin) adipate, which preferably are in liquid form at room temperature. These materials are easily incorporated into the electrodepositable composition and have good catalytic activity even at relatively low levels and at temperatures below 150°C. Such triorganotin compound, however, have been observed to have poor cure response when used in conjunction with resinous components having phenolic hydroxyl groups. Moreover, some trialkyltin compounds, for example, tributyltin compounds, are known to be volatile at typical curing temperatures. Also, some trialkyltin compounds can be toxic. Further, many triorganotin compounds typically have the disadvantage of high cost.

[0011] In view of the foregoing, it would be advantageous to provide a cationic electrodepositable coating composition containing an organotin catalyst which overcomes the problems encountered with prior art compositions containing such catalysts as discussed above. These problems are solved by the electrodepositable compositions of the present invention wherein the organotin catalyst can be incorporated into the resinous phase without the necessity of a grinding or milling operation. Such compositions demonstrate improved storage stability and cure response at lower cure temperatures, without compromising cured film appearance and performance properties.

[0012] EP 0 509 437 discloses an electrocoating composition comprising a polyisocyanate curing agent blocked with a blocking agent such as an aliphatic alcohol or an ether alcohol compound and a dioctyltin oxide curing catalyst. EP 0 509 437 does not disclose 1,2 glycol as a blocking agent for the polyisocyanate curing agent.

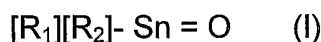
[0013] US 4 785 068 discloses a cationic electrodeposition paint composition comprising a methyl ethyl ketoxime blocked polyisocyanate compound as a curing agent and dioctyl tin oxide as a curing catalyst.

[0014] WO 98/07795 discloses an electrodepositable coating composition comprising a dioctyltin oxide curing catalyst and a polyisocyanate curing agent capped with a lower aliphatic alcohol or a glycol ether.

SUMMARY OF THE INVENTION

[0015] In one embodiment, the present invention is directed to an improved electrodepositable coating composition comprising a resinous phase dispersed in an aqueous medium, the resinous phase comprising: (a) an active hydrogen-containing, cationic salt group-containing resin; and (b) a polyisocyanate curing agent at least partially blocked with a blocking agent comprising one or more 1,2-glycols.

[0016] The improvement comprises the inclusion in the electrodepositable coating composition of an organotin catalyst for effecting cure between the resin (a) and the curing agent (b). The organotin catalyst is or is derived from a dialkyltin compound having the following structure (I):



where R_1 and R_2 are the same or different, and each independently represents a monovalent hydrocarbon group wherein the sum of the carbon atoms in R_1 and R_2 is greater than 8. The catalyst is present in the electrodepositable coating composition in an amount sufficient to effect cure of the electrodepositable composition at a temperature at or below 340°F (171.1°C).

[0017] In accordance with the present invention further provided is an improved method for preparing an electrodepositable coating composition comprising a resinous phase dispersed in an aqueous medium, the resinous phase comprising: (a) an active hydrogen-containing, cationic salt group-containing resin; (b) a polyisocyanate curing agent at least partially blocked with a blocking agent comprising one or more 1,2-glycols and (c) an organotin catalyst for effecting the cure of the resin (a) and the curing agent (b). The method comprises the steps of (1) preparing the resin (a) from a mixture of reactive components; (2) preparing the at least partially blocked polyisocyanate curing agent (b) separate from the resin (a) by reacting a polyisocyanate and a blocking agent; (3) admixing the resin (a) and the curing agent (b) to form a resinous admixture; (4) blending an organic and/or inorganic acid with the resinous admixture to form an acidified admixture; and (5) dispersing the acidified admixture of (4) in an aqueous medium. The improvement comprises incorporating the organotin catalyst (c) into the mixture of reactive components during the preparation of the resin (a) in step (1), wherein the catalyst (c) is or is derived from a dialkyltin compound having the structure (I) above where R_1 and R_2 are as described above for that structure, the catalyst being present in the electrodepositable coating composition in an amount sufficient to effect cure of the composition at a temperature at or below 340°F (171.1°C).

[0018] The present invention also is directed to an improved method of electrocoating a conductive substrate serving as a cathode in an electrical circuit comprising said cathode and an anode, said cathode and anode being immersed in an aqueous electrocoating composition. The method comprises passing electric current between said cathode and anode to cause deposition of the electrocoating composition onto the substrate as a substantially continuous film, the aqueous electrocoating composition comprising a resinous phase dispersed in an aqueous medium. The resinous phase comprises: (a) an active hydrogen group-containing, cationic group-containing electrodepositable resin, and (b) a polyisocyanate curing agent at least partially blocked with a blocking agent comprising one or more 1,2-glycols.

[0019] The improvement comprises the inclusion in the electrocoating composition of an organotin catalyst for effecting cure between the resin (a) and the curing agent (b), where the catalyst is or is derived from a dialkyltin compound having the structure (I) where R_1 and R_2 are as described above for that structure. The catalyst is present in the electrocoating composition in an amount sufficient to effect cure of the electrocoating composition at a temperature at or below 340°F (171.1°C).

DETAILED DESCRIPTION OF THE INVENTION

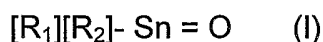
[0020] Other than in the operating examples, or where otherwise indicated, all numbers expressing quantities of ingredients, reaction conditions and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated 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 sought 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.

[0021] 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 values, however, inherently contain certain errors necessarily resulting from the standard deviation found in their respective testing measurements.

[0022] 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.

[0023] As previously mentioned, the present invention is directed to an improved electrodepositable coating composition comprising a resinous phase dispersed in an aqueous medium, the resinous phase comprising: (a) an active hydrogen-containing, cationic salt group-containing resin; and (b) an at least partially blocked polyisocyanate curing agent. The improvement comprises the inclusion in the electrodepositable coating composition of an organotin catalyst for effecting cure between the resin (a) and the curing agent (b).

[0024] The organotin catalyst is or is derived from a dialkyltin compound having the following structure (I):



where R_1 and R_2 are the same or different, and each independently represents a monovalent hydrocarbon group wherein the sum of the carbon atoms of R_1 and R_2 is greater than 8.

[0025] In one embodiment of the present invention, R_1 and R_2 can be the same or different, and each independently represents a monovalent hydrocarbon group having at least 4 carbon atoms, provided that at least one of R_1 and R_2

represents a monovalent hydrocarbon group having greater than 4 carbon atoms. The catalyst is present in the electrodepositable coating composition in an amount sufficient to effect cure of the electrodepositable composition at a temperature at or below 340°F (171.1 °C).

[0026] As used herein, a "monovalent hydrocarbon group" means a monovalent group having a backbone repeat unit based exclusively on carbon. As used herein, "monovalent" refers to a substituent group that, as a substituent group, forms only one single, covalent bond. As used herein, "hydrocarbon groups" are intended to encompass both branched and unbranched hydrocarbon groups. Thus, when referring to a "monovalent hydrocarbon group," the hydrocarbon group can be branched or unbranched, acyclic or cyclic, saturated or unsaturated, and can contain from 1 to 24 (or in the case of an aromatic group from 3 to 24) carbon atoms. Nonlimiting examples of such hydrocarbon groups include alkyl, alkoxy, aryl, alkaryl, and alkoxyaryl groups. Nonlimiting examples of lower alkyl groups include, for example, methyl, ethyl, propyl, and butyl groups. As used herein, "lower alkyl" refers to alkyl groups having from 1 to 6 carbon atoms. One or more of the hydrogen atoms of the hydrocarbon can be substituted with heteroatoms. As used herein, "heteroatoms" means elements other than carbon, for example, oxygen, nitrogen, and halogen atoms.

[0027] In an embodiment of the present invention, one or both of R_1 and R_2 can represent a monovalent hydrocarbon group having greater than 4 carbon atoms, and typically 8 or more carbon atoms.

[0028] Non-limiting examples of organotin catalysts suitable for use in the cationic electrodepositable coating compositions of the present invention include dibenzyltin oxide, dioctyltin oxide, diisopentyltin oxide, dihexyltin oxide, diisoamyltin oxide, and mixtures thereof. In a particular embodiment of the present invention, the organotin catalyst comprises dioctyltin oxide and/or its derivatives, for example, dioctyltin acetate which is the reaction product of dioctyltin oxide with one mole of acetic acid.

[0029] As previously mentioned, derivatives of the dialkyltin compound having the structure (I) above are also suitable as catalysts for the electrodepositable coating composition of the present invention. Suitable such derivatives include but are not limited to dialkyltin carboxylates, for example the condensation products of dioctyltin oxide and carboxylic acids, for example short chain carboxylic acids such as acetic, lactic, formic, and propionic acids; and long chain carboxylic acids such as oleic, palmitic, stearic and myristic acids. Other suitable organotin derivatives include dialkyltin phenoxides, dialkyltin mercaptides, and dialkyltin alkoxides.

[0030] In a particular embodiment of the present invention, the ratio of equivalents of organic acid arising from the hydrolysis of a carboxylic acid derivative of the organotin catalyst relative to the equivalents of organotin compound present in the electrodepositable composition is no more than 2.0, and typically no more than 1.0. It has been observed that while carboxylic acid derivatives of the organotin oxide catalyst provide advantages for ease of handling and ease of incorporation into the electrodepositable composition, such materials can be undesirable because the carboxylic acid generated upon hydrolysis of the organotin carboxylate can lower the composition pH, adversely affect throwpower of the composition and promote bacterial infestation of the bath.

[0031] It should be understood that for purposes of the present invention, the organotin catalyst can comprise one or more of the dialkyltin compounds having the structure (I) above, one or more derivatives thereof, and mixtures thereof, provided the composition is storage stable as discussed below, and provided that the catalyst is present in an amount sufficient to effect cure of the electrodepositable composition at a temperature at or below 340°F (171.1°C).

[0032] The organotin catalyst described in detail above can be present in the electrodepositable coating composition of the present invention in an amount of at least 0.1 percent by weight tin based on weight of total resin solids present in the electrodepositable coating composition. Also, the organotin catalyst can be present in the electrodepositable coating composition of the present invention in an amount less than or equal to 5.0 percent by weight tin, often less than or equal to 3.0 percent by weight tin, and typically less than or equal to 1.0 percent by weight tin based on weight of total resin solids present in the electrodepositable coating composition. The level of organotin catalyst present in the electrodepositable coating composition can range between any combination of these values, inclusive of the recited values, provided that the catalyst is present in an amount sufficient to effect cure (as determined by a method described in detail below) of the composition at a temperature at or below 340°F (171.1°C).

[0033] As used herein, the term "cure" as used in connection with a composition, e.g., "composition when cured" or a "cured composition", shall mean that any crosslinkable components of the composition are at least partially crosslinked. In certain embodiments of the present invention, the crosslink density of the crosslinkable components, i.e., the degree of crosslinking, ranges from 5% to 100% of complete crosslinking. In other embodiments, the crosslink density ranges from 35% to 85% of full crosslinking. In other embodiments, the crosslink density ranges from 50% to 85% of full crosslinking. One skilled in the art will understand that the presence and degree of crosslinking, i.e., the crosslink density, can be determined by a variety of methods, such as dynamic mechanical thermal analysis (DMTA) using a TA Instruments DMA 2980 DMTA analyzer conducted under nitrogen. This method determines the glass transition temperature and crosslink density of free films of coatings or polymers. These physical properties of a cured material are related to the structure of the crosslinked network. In an embodiment of the present invention, the sufficiency of cure is evaluated relative to the solvent resistance of the cured film. For example, solvent resistance can be measured by determining the number of double acetone rubs. For purposes of the present invention, a coating is deemed to be "cured" when the film

can withstand a minimum of 100 double acetone rubs without substantial softening of the film and no removal of the film.

[0034] As aforementioned, in addition to the organotin catalyst and/or derivatives thereof, the electrodepositable coating composition of the present invention comprises (a) an active hydrogen-containing, cationic salt group-containing resin, and (b) an at least partially blocked polyisocyanate curing agent.

[0035] The cationic resin (a) typically is derived from a polyepoxide and can be prepared by reacting together a polyepoxide and a polyhydroxyl group-containing material selected from alcoholic hydroxyl group-containing materials and phenolic hydroxyl group-containing materials to chain extend or build the molecular weight of the polyepoxide. The reaction product can then be reacted with a cationic salt group former to produce the cationic resin.

[0036] A chain extended polyepoxide typically is prepared as follows: the polyepoxide and polyhydroxyl group-containing material are reacted together neat or in the presence of an inert organic solvent such as a ketone, including methyl isobutyl ketone and methyl amyl ketone, aromatics such as toluene and xylene, and glycol ethers such as the dimethyl ether of diethylene glycol. The reaction typically is conducted at a temperature of 80°C to 160°C for 30 to 180 minutes until an epoxy group-containing resinous reaction product is obtained.

[0037] The equivalent ratio of reactants; i.e., epoxy:polyhydroxyl group-containing material is typically from 1.00:0.50 to 1.00:2.00.

[0038] The polyepoxide typically has at least two 1,2-epoxy groups. In general the epoxide equivalent weight of the polyepoxide will range from 100 to about 2000, typically from about 180 to 500. The epoxy compounds may be saturated or unsaturated, cyclic or acyclic, aliphatic, alicyclic, aromatic or heterocyclic. They may contain substituents such as halogen, hydroxyl, and ether groups.

[0039] Examples of polyepoxides are those having a 1,2-epoxy equivalency greater than one and preferably about two; that is, polyepoxides which have on average two epoxide groups per molecule. The preferred polyepoxides are polyglycidyl ethers of polyhydric alcohols such as cyclic polyols. Particularly preferred are polyglycidyl ethers of polyhydric phenols such as Bisphenol A. These polyepoxides can be produced by etherification of polyhydric phenols with an epihalohydrin or dihalohydrin such as epichlorohydrin or dichlorohydrin in the presence of alkali. Besides polyhydric phenols, other cyclic polyols can be used in preparing the polyglycidyl ethers of cyclic polyols. Examples of other cyclic polyols include alicyclic polyols, particularly cycloaliphatic polyols such as 1,2-cyclohexane diol and 1,2-bis(hydroxymethyl)cyclohexane. The preferred polyepoxides have epoxide equivalent weights ranging from about 180 to 2000, preferably from about 186 to 1200. Epoxy group-containing acrylic polymers can also be used. These polymers typically have an epoxy equivalent weight ranging from about 750 to 2000.

[0040] Examples of polyhydroxyl group-containing materials used to chain extend or increase the molecular weight of the polyepoxide (i.e., through hydroxyl-epoxy reaction) include alcoholic hydroxyl group-containing materials and phenolic hydroxyl group-containing materials. Examples of alcoholic hydroxyl group-containing materials are simple polyols such as neopentyl glycol; polyester polyols such as those described in U.S. Patent No. 4,148,772; polyether polyols such as those described in U.S. Patent No. 4,468,307; and urethane diols such as those described in U.S. Patent No. 4,931,157. Examples of phenolic hydroxyl group-containing materials are polyhydric phenols such as Bisphenol A, phloroglucinol, catechol, and resorcinol. Mixtures of alcoholic hydroxyl group-containing materials and phenolic hydroxyl group-containing materials may also be used. Bisphenol A is preferred.

[0041] The resin contains cationic salt groups, which can be incorporated into the resin molecule as follows: The resinous reaction product prepared as described above is further reacted with a cationic salt group former. By "cationic salt group former" is meant a material which is reactive with epoxy groups and which can be acidified before, during, or after reaction with the epoxy groups to form cationic salt groups. Examples of suitable materials include amines such as primary or secondary amines which can be acidified after reaction with the epoxy groups to form amine salt groups, or tertiary amines which can be acidified prior to reaction with the epoxy groups and which after reaction with the epoxy groups form quaternary ammonium salt groups. Examples of other cationic salt group formers are sulfides which can be mixed with acid prior to reaction with the epoxy groups and form ternary sulfonium salt groups upon subsequent reaction with the epoxy groups.

[0042] When amines are used as the cationic salt formers, monoamines typically are employed, and hydroxyl-containing amines are particularly preferred. Polyamines may be used but are not recommended because of a tendency to gel the resin.

[0043] Tertiary and secondary amines are preferred to primary amines because primary amines are polyfunctional with respect to epoxy groups and have a greater tendency to gel the reaction mixture. If polyamines or primary amines are used, they should be used in a substantial stoichiometric excess to the epoxy functionality in the polyepoxide so as to prevent gelation and the excess amine should be removed from the reaction mixture by vacuum stripping or other technique at the end of the reaction. The epoxy may be added to the amine to ensure excess amine.

[0044] Examples of hydroxyl-containing amines include alkanolamines, dialkanolamines, alkyl alkanolamines, and aralkyl alkanolamines containing from 1 to 18 carbon atoms, preferably 1 to 6 carbon atoms in each of the alkanol, alkyl and aryl groups. Specific examples include ethanolamine, N-methylethanolamine, diethanolamine, N-phenylethanolamine, N,N-dimethylethanolamine, N-methyldiethanolamine, 3-aminopropyldiethanolamine, and N-(2-hydroxy-

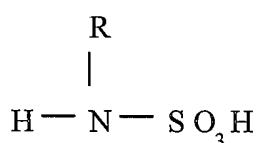
thyl)-piperazine.

[0045] Amines such as mono, di, and trialkylamines and mixed aryl-alkyl amines which do not contain hydroxyl groups or amines substituted with groups other than hydroxyl which do not negatively affect the reaction between the amine and the epoxy may also be used. Specific examples include ethylamine, methylethylamine, triethylamine, N-benzylidimethylamine, dicocoamine, 3-dimethylaminopropylamine, and N,N-dimethylcyclohexylamine.

[0046] Mixtures of the above mentioned amines may also be used.

[0047] The reaction of a primary and/or secondary amine with the polyepoxide takes place upon mixing of the amine and polyepoxide. The amine may be added to the polyepoxide or *vice versa*. The reaction can be conducted neat or in the presence of a suitable solvent such as methyl isobutyl ketone, xylene, or 1-methoxy-2-propanol. The reaction is generally exothermic and cooling may be desired. However, heating to a moderate temperature of about 50 to 150°C may be done to hasten the reaction.

[0048] The reaction product of the primary and/or secondary amine and the polyepoxide is made cationic and water dispersible by at least partial neutralization with an acid. Suitable acids include organic and inorganic acids. Nonlimiting examples of suitable organic acids include formic acid, acetic acid, and lactic acid. Nonlimiting examples of suitable inorganic acids include phosphoric acid and sulfamic acid. By "sulfamic acid" is meant sulfamic acid itself or derivatives thereof; i.e., an acid of the formula:



wherein R is hydrogen or an alkyl group having 1 to 4 carbon atoms. Sulfamic acid is preferred. Mixtures of the above mentioned acids may also be used.

[0049] The extent of neutralization of the cationic electrodepositable composition varies with the particular reaction product involved. However, sufficient acid should be used to disperse the electrodepositable composition in water. Typically, the amount of acid used provides at least 20 percent of all of the total neutralization. Excess acid may also be used beyond the amount required for 100 percent total neutralization.

[0050] In the reaction of a tertiary amine with a polyepoxide, the tertiary amine can be pre-reacted with the neutralizing acid to form the amine salt and then the amine salt reacted with the polyepoxide to form a quaternary salt group-containing resin. The reaction is conducted by mixing the amine salt with the polyepoxide in water. Typically, the water is present in an amount ranging from about 1.75 to about 20 percent by weight based on total reaction mixture solids.

[0051] In forming the quaternary ammonium salt group-containing resin, the reaction temperature can be varied from the lowest temperature at which the reaction will proceed, generally room temperature or slightly thereabove, to a maximum temperature of about 100 °C (at atmospheric pressure). At higher pressures, higher reaction temperatures may be used. Preferably, the reaction temperature is in the range of about 60 to 100°C. Solvents such as a sterically hindered ester, ether, or sterically hindered ketone may be used, but their use is not necessary.

[0052] In addition to the primary, secondary, and tertiary amines disclosed above, a portion of the amine that is reacted with the polyepoxide can be a ketimine of a polyamine, such as is described in U.S. Patent No. 4,104,147, column 6, line 23 to column 7, line 23. The ketimine groups decompose upon dispersing the amine-epoxy resin reaction product in water. In an embodiment of the present invention, at least a portion of the active hydrogens present in the resin (a) comprise primary amine groups derived from the reaction of a ketimine-containing compound and an epoxy group-containing material such as those described above.

[0053] In addition to resins containing amine salts and quaternary ammonium salt groups, cationic resins containing ternary sulfonium groups may be used in the composition of the present invention. Examples of these resins and their method of preparation are described in U.S. Patent Nos. 3,793,278 to DeBona and 3,959,106 to Bosso et al.

[0054] It should be understood that the active hydrogens associated with the cationic resin include any active hydrogens which are reactive with isocyanates at temperatures sufficient to cure the electrodepositable composition as previously discussed, i.e., at temperatures at or below 340°F (171.1°C). The active hydrogens typically are derived from reactive hydroxyl groups, and primary and secondary amino, including mixed groups such as hydroxyl and primary amino. In one embodiment of the present invention, at least a portion of the active hydrogens are derived from hydroxyl groups comprising phenolic hydroxyl groups. The cationic resin can have an active hydrogen content of 1 to 4 milliequivalents, typically 2 to 3 milliequivalents of active hydrogen per gram of resin solids.

[0055] The extent of cationic salt group formation should be such that when the resin is mixed with an aqueous medium and other ingredients, a stable dispersion of the electrodepositable composition will form. By "stable dispersion" is meant one that does not settle or is easily redispersible if some settling occurs. Moreover, the dispersion should be of sufficient cationic character that the dispersed resin particles will electrodeposit on a cathode when an electrical potential is set

up between an anode and a cathode immersed in the aqueous dispersion.

[0056] Generally, the cationic resin in the electrodepositable composition of the present invention contains from about 0.1 to 3.0, preferably from about 0.1 to 0.7 milliequivalents of cationic salt group per gram of resin solids. The cationic resin typically is non-gelled, having a number average molecular weight ranging from about 2000 to about 15,000, preferably from about 5000 to about 10,000. By "non-gelled" is meant that the resin is substantially free from crosslinking, and prior to cationic salt group formation, the resin has a measurable intrinsic viscosity when dissolved in a suitable solvent. In contrast, a gelled resin, having an essentially infinite molecular weight, would have an intrinsic viscosity too high to measure.

[0057] The active hydrogen-containing, cationic salt group-containing resin (a) can be present in the electrodepositable composition of the present invention in an amount ranging from 40 to 95 weight percent, typically from 50 to 75 weight percent based on weight of total resin solids present in the composition.

[0058] The electrodepositable composition of the present invention also contains an at least partially blocked polyisocyanate curing agent. The polyisocyanate curing agent may be a fully blocked polyisocyanate with substantially no free isocyanate groups, or it may be partially blocked and reacted with the resin backbone as described in U.S. Patent 3,984,299. The polyisocyanate can be an aliphatic or an aromatic polyisocyanate or a mixture of the two. Diisocyanates are preferred, although higher polyisocyanates can be used in place of or in combination with diisocyanates.

[0059] Examples of suitable aliphatic diisocyanates are straight chain aliphatic diisocyanates such as 1,4-tetramethylene diisocyanate, norbornane diisocyanate, and 1,6-hexamethylene diisocyanate. Also, cycloaliphatic diisocyanates can be employed. Examples include isophorone diisocyanate and 4,4'-methylene-bis-(cyclohexyl isocyanate). Examples of suitable aromatic diisocyanates are p-phenylene diisocyanate, diphenylmethane-4,4'-diisocyanate and 2,4- or 2,6-toluene diisocyanate. Examples of suitable higher polyisocyanates are triphenylmethane-4,4',4"-triisocyanate, 1,2,4-benzene triisocyanate and polymethylene polyphenyl isocyanate, and trimers of 1,6-hexamethylene diisocyanate.

[0060] Isocyanate prepolymers, for example, reaction products of polyisocyanates with polyols such as neopentyl glycol and trimethylol propane or with polymeric polyols such as polycaprolactone diols and triols (NCO/OH equivalent ratio greater than one) can also be used. A mixture of diphenylmethane-4,4'-diisocyanate and polymethylene polyphenyl isocyanate is preferred.

[0061] Any suitable alcohol or polyol can be used as a blocking agent for the polyisocyanate in the electrodepositable composition of the present invention provided that the agent will deblock at the curing temperature and provided a gelled product is not formed.

[0062] In the present invention, the blocking agent comprises one or more 1,2-glycols. In one embodiment of the present invention, the blocking agent comprises one or more 1,2-glycols, typically one or more C₃ to C₆ 1,2-glycols. For example, the blocking agent can be selected from at least one of 1,2-propanediol, 1,2-butanediol, 1,2-pentanediol and 1,2-hexanediol. It has been observed that the presence of such blocking agents facilitates dissolution or dispersion of the organotin catalyst in the resinous phase or components thereof.

[0063] Other suitable blocking agents include oximes such as methyl ethyl ketoxime, acetone oxime and cyclohexanone oxime and lactams such as epsilon-caprolactam.

[0064] The polyisocyanate curing agent (b) is usually present in the electrodepositable composition in an amount ranging from about 5 to 60 percent by weight, typically from about 25 to 50 percent by weight based on total weight of resin solids.

[0065] It should be understood that any of the previously described organotin catalysts, that is organotin catalysts having the structure (I) above, derivatives thereof, and mixtures thereof, can be incorporated into the electrodepositable composition of the present invention by any method or means provided that the stability of the composition is not compromised. For example, the organotin catalyst can be admixed with or dispersed in the reactants used to form the resin (a) during preparation of the resin (a). Also, the organotin catalyst can be admixed with or dispersed in one or more of the reactants used to form the resin (a) prior to resin preparation. In addition, the organotin catalyst can be admixed with or dispersed in the resin (a) either prior to or subsequent to neutralization with an acid. The organotin catalyst also can be admixed with or dispersed in the at least partially blocked polyisocyanate curing agent (b) prior to combining the resin (a) and the curing agent (b). Further, the organotin catalyst can be admixed with or dispersed in the admixture of the resin (a) and the curing agent (b). Alternatively, the organotin catalyst can be added to any of the optional additives, solvents, or adjuvant resinous materials as described below prior to addition of the optional ingredients to the composition. Also, the organotin catalyst can be directly admixed with or dispersed in the aqueous medium, prior to dispersion of the resinous phase in the aqueous medium. The organotin catalyst also can be added neat to the electrodepositable composition subsequent to dispersion in the aqueous medium. Additionally, if desired, the organotin catalyst can be added on-line to the electrodeposition bath in the form of an additive material. It should be understood that the catalyst can be incorporated into the electrodepositable composition by one or more of the above described methods.

[0066] The electrodepositable composition may optionally contain a coalescing solvent such as hydrocarbons, alcohols, esters, ethers and ketones. Examples of preferred coalescing solvents are alcohols, including polyols, such as isopropanol, butanol, 2-ethylhexanol, ethylene glycol and propylene glycol; ethers such as the monobutyl and monohexyl

ethers of ethylene glycol; and ketones such as methyl isobutyl ketone and isophorone. The coalescing solvent is usually present in an amount up to 40 percent by weight, typically ranging from about 0.05 to 25 percent by weight based on total weight of the electrodepositable composition.

[0067] The electrodepositable composition of the present invention may further contain pigments and various other optional additives such as plasticizers, surfactants, wetting agents, defoamers, and anti-cratering agents, as well as adjuvant resinous materials different from the resin (a) and the curing agent (b). These optional ingredients, when present, are usually used in an amount up to 30 percent by weight, typically about 1 to 20 percent by weight based on weight of resin solids.

[0068] Suitable pigments include, but are not limited to, iron oxides, lead oxides, carbon black, coal dust, titanium dioxide, talc, clay, silica, and barium sulfate, as well as color pigments such as cadmium yellow, cadmium red, chromium yellow, and the like. The pigment content of the aqueous dispersion, generally expressed as the pigment to resin (or pigment to binder) ratio (P/B) is usually 0.05:1 to 1:1. In a particular embodiment, the electrodepositable coating composition of the present invention is free of lead-containing compounds.

[0069] The electrodepositable coating composition of the present invention is used in an electrodeposition process in the form of an aqueous dispersion. By "dispersion" is meant a two-phase transparent, translucent, or opaque aqueous resinous system in which the resin, pigment, and water insoluble materials are in the dispersed phase while water and water-soluble materials comprise the continuous phase. The dispersed phase has an average particle size of less than 10 microns, and can be less than 5 microns. The aqueous dispersion can contain at least 0.05 and usually 0.05 to 50 percent by weight resin solids, depending on the particular end use of the dispersion.

[0070] The electrodepositable compositions of the present invention in the form of an aqueous dispersion have excellent storage stability, that is, upon storage at a temperature of 140°F (60°C) for a period of 14 days, the compositions are stable. By "stable dispersion" is meant herein that the resinous phase and the organotin catalyst remain uniformly dispersed throughout the aqueous phase of the composition. Upon storage under the conditions described above, the dispersions do not flocculate or form a hard sediment. If over time some sedimentation occurs, it can be easily redispersed with low shear stirring.

[0071] In the process of electrodeposition the electrodepositable composition of the present invention in the form of an aqueous dispersion is placed in contact with an electrically conductive anode and cathode, where the substrate serves as the cathode. Upon passage of an electric current between the anode and cathode while they are in contact with the aqueous dispersion, an adherent film of the electrodepositable composition will deposit in a substantially continuous manner on the cathode. The film will contain the active hydrogen-containing resin, the blocked polyisocyanate curing agent, the organotin catalyst, and the optional additives from the non-aqueous phase of the dispersion.

[0072] It should be noted herein that the organotin catalyst is characterized in that the catalyst is substantially non-volatile at the curing temperature, that is, at temperatures at or below 340°F (171.1 °C). By "substantially non-volatile" is meant that the catalyst does not volatilize from the film into the curing oven environment at these temperatures during the curing process.

[0073] Electrodeposition is usually carried out at a constant voltage in the range of from about 1 volt to several thousand volts, typically between 50 and 500 volts. Current density is usually between 1.0 ampere and 15 amperes per square foot (10.8 to 161.5 amperes per square meter) and tends to decrease quickly during the electrodeposition process, indicating formation of a continuous self-insulating film. Any electroconductive substrate known in the art, especially metal substrates such as steel, zinc, aluminum, copper, magnesium or the like can be coated with the electrodepositable composition of the present invention. Steel substrates are preferred. It is customary to pretreat the substrate with a phosphate conversion, usually a zinc phosphate conversion coating, followed by a rinse which seals the conversion coating.

[0074] After deposition, the coating is heated to cure the deposited composition. The heating or curing operation can be carried out at a temperature in the range of from 250 to 400°F (121.1 to 204.4°C), typically from 300 to 340°F (148.8 to 171.1°C) for a period of time ranging from 1 to 60 minutes. The thickness of the resultant film typically can range from 10 to 50 microns.

[0075] The invention will be further described by reference to the following examples. Unless otherwise indicated, all parts and percentages are by weight.

EXAMPLES

[0076] Example A describes the preparation of a crosslinker used to prepare the resinous binders of Examples D and G; Example B describes the preparation of a crosslinking used to prepare the resinous binder of Example E; Example C describes the preparation of an additive resin used in the preparation of the binders of Examples D and G. Examples D, E, and F describe the preparation of cationic resinous binders used in the electrodepositable coating compositions of the present invention. Example G describes the preparation of a catalyst-free cationic resin. Examples 1 through 4 describe the preparation of electrodepositable coating compositions of the present invention. Comparative Examples 5

EP 1 546 271 B1

and 6 describe the preparation of cationic electrodepositable coating composition comprising dibutyltin oxide and trioc-
tyltin oxide, respectively.

EXAMPLE A

[0077] This example describes the preparation of a crosslinker used in Examples D and G. The crosslinker was prepared as follows:

Ingredients	Parts by weight (in grams)
Ethanol	92.0
Propylene glycol	456.0
Polyol ¹	739.5
Methylisobutyl ketone	476.5
MAZON® 1651 ²	92.8
DESMODUR® LS 2096 ³	42.1
Methylisobutyl ketone	76.5

¹ Bisphenol A/6 ethylene oxide adduct available from BASF Corporation as MACOL® 98B.

² Plasticizer available from BASF Corporation.

³ Isocyanate available from Bayer Corporation.

[0078] The ethanol, propylene glycol, polyol, first charge of methylisobutyl ketone and MAZON 1651 were added to a reaction flask. The DESMODUR LS 2096 was added slowly beginning at approximately 25°C, allowing the reaction to exotherm to 105°C, while not exceeding 110°C. The reaction was held at this temperature until IR analysis showed that all isocyanate had been consumed.

EXAMPLE B

[0079] This example describes the preparation of a crosslinker used in the resin of Example E.

Ingredients	Parts by weight (in grams)
1,2-butanediol	3274.61
Methylisobutyl ketone	1170.65
Dibutyltin dilaurate	4.04
PAPI® 2940 ¹	4796.4
Methylisobutyl ketone	254.35

¹ Polymeric MDI available from Dow Chemicals.

[0080] The 1,2-butanediol, methylisobutyl ketone and dibutyltin dilaurate were charged to a reaction flask under a nitrogen atmosphere and heated to 30°C. To this solution was added PAPI 2940 slowly, keeping the reaction temperature below 80°C. Upon completion of the addition, the second charge of methylisobutyl ketone was added and the mixture held at 85°C until IR analysis indicated no unreacted NCO remained.

EXAMPLE C

[0081] This example describes the preparation of an additive resin, used in the resins of Examples D and G. The additive was prepared from the following ingredients:

Ingredients	Parts by weight (in grams)
MAZEEN 355 70 ¹	603.3
Acetic acid	5.9
Dibutyltin dilaurate	0.66
Toluene diisocyanate	87.17

EP 1 546 271 B1

(continued)

Ingredients	Parts by weight (in grams)
Sulfamic acid	38.79
Deionized water	1289

¹ Aminediol available from BASF Corporation.

[0082] The acetic acid was added to the MAZEEN 355 70 and mixed thoroughly for 10 minutes. The dibutyltin dilaurate was then added and the solution mixed. The toluene diisocyanate was added slowly, controlling the exotherm to 100°C maximum. When the diisocyanate addition was complete, the solution was held at 100°C until no isocyanate was present as determined by IR analysis. Sulfamic acid was added and the solution was mixed well. The deionized water was added slowly and the mixture was mixed well to yields a dispersion having a solids content of 36% after 1 hour at 110°C.

EXAMPLE D

[0083] An electrodepositable resin containing dioctyltin oxide was prepared from the following ingredients:

Ingredients	Parts by weight (in grams)
Crosslinker of Example A	988.3
MAZON 1651	57.1
EPON 828 ¹	528.7
Bisphenol A	203.9
TETRONIC® 150R1 ²	0.173
Diethanolamine	36.1
Aminopropyl diethanolamine	79.2
EPON 828	5.74
Dioctyltin oxide	25.71
Sulfamic acid	29.8
Deionized water	1001
Lactic acid, 88% in water	1.16
Additive of Example C	126.5
Gum rosin solution ³	14.1
Deionized water	1045

¹ Epoxy resin available from Resolution Performance Products.

² Surfactant available from BASF Corporation.

³ A solution of 30% by weight abietic acid in MAZON 1651.

[0084] The crosslinker, MAZON 1651, EPON 828, bisphenol A and TETRONIC 150R1 were charged to a 4-neck round bottom flask fitted with a Dean-Stark trap, under a nitrogen atmosphere. The mixture was heated to 75°C and the diethanolamine was added. The mixture was stirred for 30 minutes, during which time an exotherm to 80°C was observed. The aminopropyl diethanolamine was added and the temperature was raised to 132°C. The mixture was held at this temperature for 90 minutes while collecting 29.3g of solvent in the Dean-Stark trap. The second charge of EPON 828 was added and the mixture was held for an additional hour at 132°C. The mixture was cooled to 100°C, the dioctyltin oxide was added, and the mixture was held for 30 minutes. 1630g of this mixture was poured into a premixed solution of the sulfamic acid, the first charge of deionized water, the lactic acid and the additive of Example B under vigorous agitation. The gum rosin solution was added and the mixture stirred for 30 minutes. The final charge of deionized water was added and mixed in well. The mixture was distilled under vacuum to remove solvent and a portion of the water. The solids content of the resultant dispersion was adjusted to approximately 40% by addition of deionized water.

EXAMPLE E

[0085] An electrodepositable resin containing dioctyltin oxide was prepared from the following ingredients:

EP 1 546 271 B1

	Ingredients	Parts by weight (in grams)
	EPON 880 ¹	461.01
5	Polyol described in Example A	93.75
	Bisphenol A	199.07
	Methylisobutyl ketone	15.38
	Ethyltriphenyl phosphonium iodide	0.45
	Polyol described in Example A	93.75
10	Methylisobutyl ketone	28.00
	Crosslinker of Example B	862.53
	Diketimine ²	42.75
	N-methylethanolamine	36.51
15	Diocetyl tin oxide	21.18
	Sulfamic acid	29.14
	Deionized water	1024.58
	Gum rosin solution of Example D	14.24
20	Deionized water	592.88
	Deionized water	600.68

¹ An epoxy resin available from Resolution Performance Products.

² The reaction product of diethylenetriamine and methylisobutyl ketone, 73% solids in methylisobutyl ketone.

[0086] The EPON 828, initial charge of polyol, bisphenol A and the initial charge of methylisobutyl ketone were charged to a reaction vessel and heated under a nitrogen atmosphere to 125°C. Ethyltriphenyl phosphonium iodide then was added and the reaction mixture allowed to exotherm to approximately 145°C. The reaction was held at 145°C for 2 hrs and the second charge of polyol was added. The reaction was then cooled to 125°C and the second charge of methylisobutyl ketone, the crosslinker of Example B, the diketimine and N-methylethanolamine were added in succession. The mixture was allowed to exotherm and then a temperature of 122°C was established. The mixture was held at 122°C for 2 hours. The dioctyltin oxide then was added and the reaction mixture was stirred for 15 minutes at 122°C. The resin mixture (1600 parts) was dispersed in aqueous medium by adding it to a mixture the sulfamic acid and the first charge of deionized water. After 30 minutes, the gum rosin solution was added and the dispersion was further thinned with the last two charges of deionized water in stages. The dispersion was vacuum stripped to remove organic solvent to give a dispersion having a solids content of 43.58 percent after 1 hour at 110°C.

EXAMPLE F

[0087] An electrodepositable resin containing dioctyltin oxide was prepared from the following ingredients:

	Ingredients	Parts by weight (in grams)
	DER732 ¹	711
45	n-Butyl ether of ethylene glycol	12.1
	Bisphenol A	164.5
	Benzyl dimethyl amine	1.65
	n-Butyl ether of ethylene glycol	164.5
50	JEFFAMINE® D400 ²	184.7
	EPON 828	19.5
	n-Butyl ether of ethylene glycol	3.0
	Dioctyltin oxide	161.9
	Acetic acid	22.5
55	Deionized water	972.1
	Sulfamic acid	33.6

EP 1 546 271 B1

(continued)

Ingredients	Parts by weight (in grams)
Deionized water	1519

- ¹ Aliphatic epoxy resin available from Dow Chemical Company.
² A polyoxypropylene diamine available from Huntsman Corporation.

[0088] The DER732, n-butyl ether of ethylene glycol, and bisphenol A were charged to a flask. The mixture was heated to 130°C and the benzyldimethyl amine was added. The reaction mixture was held at 135°C until the epoxide equivalent weight of the mixture was 1232. The second charge of n-butyl ether of ethylene glycol was added and the mixture was cooled to 95°C. The JEFFAMINE D400 was added and the reaction held at 95°C until the Gardner-Holdt viscosity of a 50% solution of the resin diluted in methoxy propanol was "J". A mixture of the EPON 828 and third charge of n-butyl ether of ethylene glycol was added and the mixture held until the Gardner-Holdt viscosity of a 50% solution of the resin diluted in methoxy propanol was "P+". The dioctyltin oxide and acetic acid were added and the mixture was stirred for 20 minutes to dissolve the dioctyltin oxide. The resulting resin (1138 parts) was poured into a mixture of the first charge of deionized water and sulfamic acid under agitation and mixed for 30 minutes. The final charge of deionized water was added and the dispersion was mixed well. The final aqueous dispersion had a measured solids content of 29.7% after 1 hour at 110°C.

EXAMPLE G

[0089] A catalyst-free electrodepositable resin composition was prepared from the following ingredients:

Ingredients	Parts by weight (in grams)
Crosslinker of Example A	988.3
MAZON 1651	57.1
EPON 828	528.6
Bisphenol A	209.3
TETRONIC® 150R1	0.173
Diethanolamine	36.1
Aminopropyl diethanolamine	79.2
EPON 828	5.74
Sulfamic acid	29.8
Deionized water	1001
Lactic acid, 88% in water	1.16
Additive of Example C	126.5
Gum rosin solution	14.1
Deionized water	1045

[0090] The crosslinker, MAZON 1651, EPON 828, bisphenol A and TETRONIC 150R1 were charged to a 4-neck round bottom flask fitted with a Dean-Stark trap, under a nitrogen atmosphere. The mixture was heated to 75°C and the diethanolamine was added. The mixture was stirred for 30 minutes, during which time an exotherm to approximately 80°C was observed. The aminopropyl diethanolamine was added and the temperature was raised to 132°C. The mixture was held at this temperature for 90 minutes while collecting 29.3 parts of solvent in the Dean-Stark trap. The second charge of EPON 828 was added and the mixture was held for an additional hour at 132°C. 1630 parts of this mixture was poured into a mixture of the sulfamic acid, the first charge of deionized water, the lactic acid and the additive of Example B under vigorous agitation. The gum rosin solution was added and the mixture stirred for 30 minutes. The final charge of deionized water was added and mixed in well. The mixture was distilled under vacuum to remove solvent. The solids content of the resultant dispersion was adjusted to approximately 40% by addition of deionized water.

PAINT EXAMPLES

EXAMPLE 1

[0091] This example describes the preparation of a pigment paste suitable for use in the electrodeposition paint compositions for Examples 2, 3, 4, and Comparative Example 6. The pigment paste was prepared from the following ingredients:

Ingredients	Parts by weight (in grams)
Cationic resin ¹	9970.4
MAZON 1651	1153.2
Propylene glycol monobutyl ether	1027.7
SURFYNOL® GA ²	242.3
Titanium dioxide ³	12,000
Carbon black ⁴	113.1
Clay ⁵	4037.7
Deionized water	6758

¹ As prepared in US Pat. No. 6,190,525, Example C.

² A surfactant available from Air Products and Chemicals, Inc.

³ Available from Kerr-McGee Corp. as CR-800E.

⁴ Available from Degussa Corp. as PRINTEX® 200.

⁵ Available from Engelhard Corp. as ASP-200.

[0092] The above ingredients were added in the order shown under high shear agitation. After the ingredients were thoroughly blended, the pigment paste was transferred to a horizontal sand mill and ground to a Hegman value >7.0. The pigment paste was then collected. The measured solids were 59.5% following one hour @ 110°C.

EXAMPLE 2

[0093] A cationic electrodepositable coating composition was prepared from the following ingredients:

Ingredients	Parts by weight (in grams)
Resin of Example D	1635.6
Pigment paste of Example 1	246.5
MAZON 1651	51.4
4.5% Yttrium acetate ¹	96.6
Deionized water	1759.2

¹ A solution prepared by mixing 112.9g yttrium trioxide, 5568g water and 180.1g acetic acid at 97°C until homogeneous.

[0094] Under moderate agitation the MAZON 1651 was added to the pigment paste of Example 1. The yttrium acetate solution was then added after diluting it with 400g of deionized water. This mixture was added to the resin of Example D after reducing it with 200g of water under agitation. The remaining amount of water was then added. The composition was allowed to stir for at least 4 hours, then ultrafiltered 20%.

EXAMPLE 3

[0095] A cationic electrodepositable coating composition was prepared from the following ingredients:

Ingredients	Parts by weight (in grams)
Resin of Example E	936.7
Pigment paste of Example 1	155.7
MAZON 1651	32.5

EP 1 546 271 B1

(continued)

Ingredients	Parts by weight (in grams)
Propylene glycol monomethyl ether	24
4.5% Yttrium acetate of Example 2	61
Deionized water	1214.1

[0096] Under moderate agitation the MAZON 1651 and propylene glycol monomethyl ether were added to the pigment paste of Example 1. The yttrium acetate solution was then added after diluting it with 400g of water. This mixture was added to the resin of Example E after reducing it with 200g of water under agitation. The remaining amount of water was then added. The composition was allowed to stir for at least 4 hours, then ultrafiltered 20%.

EXAMPLE 4

[0097] A cationic electrodepositable coating composition was prepared from the following ingredients:

Ingredients	Parts by weight (in grams)
Resin of Example G	882.5
Resin of Example F	152.3
Pigment paste of Example 1	137.4
MAZON 1651	26.4
Ethylene glycol monohexyl ether	12
4.5% Yttrium acetate of Example 2	61
Deionized water	1128.4

[0098] The resin of Example F was reduced with 200g of water, then added to the resin of Example G. In a separate vessel under moderate agitation, the MAZON 1651 and ethylene glycol monohexyl ether were added to the pigment paste of Example 1, and the yttrium acetate solution was then added after diluting it with 400g of water. This mixture was then added to the blend of resins of Examples F and G under agitation, followed by the remaining amount of water. The composition was allowed to stir for at least 4 hours, then ultrafiltered 20%.

EXAMPLE 5-COMPARATIVE (DIBUTYLTIN OXIDE CONTROL)

[0099] A cationic electrodeposition coating composition was prepared from the following ingredients:

Ingredients	Parts by weight (in grams)
E6300 ¹	1957.6
E6301 ²	242.1
Deionized water	1808.3

¹ A resin blend available from PPG Industries.

² A pigment paste containing dibutyltin oxide catalyst, available from PPG Industries.

[0100] Under moderate agitation the pigment paste E6301 was diluted with 200g of water and added to the resin blend E6300 after reducing it with 400g of water. The remaining amount of water was then added. The paint was allowed to stir for at least 4 hours, then ultrafiltered 20%.

EXAMPLE 6 - COMPARATIVE (TRIOCTYLTIN OXIDE CONTROL)

[0101]

EP 1 546 271 B1

Ingredients	Parts by weight (in grams)
Resin of Example G	1020.5
Pigment paste of Example 1	155.7
Trioctyltin oxide	7.6
MAZON 1651	32.5
4.5% Yttrium acetate of Example 2	61
Deionized water	1122.7

[0102] Under moderate agitation the trioctyltin oxide and MAZON 1651 were added to the pigment paste of Example 1. The yttrium acetate solution was then added after diluting it with 400g of water. This mixture was added to the resin of Example G after reducing it with 200g of water under agitation. The remaining amount of water was then added. The composition was allowed to stir for at least 4 hours, then ultrafiltered 20%.

EXAMPLE 7 (COMPARATIVE)

[0103] A dibutyltin diacetate-containing resin solution was prepared by stirring the following ingredients together:

Ingredients	Parts by weight (in grams)
Resin of Example G	150
Dibutyltin diacetate	0.76
Deionized water	183

EXAMPLE 8 (COMPARATIVE)

[0104] A trioctyltin oxide-containing resin solution was prepared by stirring the following ingredients together:

Ingredients	Parts by weight (in grams)
Resin of Example G	150
Trioctyltin oxide	1.04

TEST PROCEDURES

[0105] The electrodepositable coating compositions were electrodeposited on phosphated cold rolled steel, commercially available from ACT Laboratories. The time of electrodeposition was 2 minutes for each composition. Additional conditions of electrodeposition are presented in Table 1. The resulting films were cured at 320°F for 20 minutes. The degree of cure was tested by double solvent rubs (DAR), in which a rag was soaked in acetone and rubbed over the film surface up to 200 times. These results are also reported in Table 1 as the number of double acetone rubs required to remove the cured paint.

Table 1

Paint	Temperature of paint bath	Voltage	Film Build (mils)	DAR
Example 2	35°C (95°F)	200	21 μm (0.84)	>100
Example 3	32°C (90°F)	140	21 μm (0.84)	>100
Example 4	32°C (90°F)	140	20 μm (0.80)	>100
Example 5*	35°C (95°F)	200	21 μm (0.84)	>100
Example 6*	32°C (90°F)	150	18μm (0.71)	<5
* comparative Examples				

RESIN STABILITY TESTING

[0106] Stability was tested by placing 4 ounces of each tin catalyst-containing resin listed below at 60°C (140°F) for two weeks. These were compared to the same resin without a tin catalyst, noting visual appearance immediately after introduction of the tin species and after exposure to heat. Results are presented in below Table 2.

Table 2

Resin	Catalyst	Appearance	
		Initial	2 weeks/60°C (140°F)
Example D	Diocetyl tin oxide	No change	Very slight settle
Example 7*	Dibutyltin oxide	Fine white settle	¼" fluffy white settle
Example 8*	Triocetyl tin oxide	No change	Yellow oil separation
Example G**	None	No change	No change
* comparative Examples			
** control			

[0107] The examples in Table 1 above demonstrate that electrodepositable coating compositions containing resins prepared with dioctyltin oxide (DOTO; Examples 2, 3 and 4) cure as well as a coating composition containing a tin catalyst that must be milled independently in order to be active. These compositions also exhibit cure response far superior a composition prepared by direct addition of the DOTO to the composition.

[0108] Additionally, it is demonstrated in Table 2 that resins made with DOTO (Example D) are more stable than resins containing liquid tin catalysts, which hydrolyze to inactive tin compounds.

Claims

1. An electrodepositable coating composition comprising a resinous phase dispersed in an aqueous medium, said resinous phase comprising:

- (a) an active hydrogen-containing, cationic salt group-containing resin; and
- (b) a polyisocyanate curing agent at least partially blocked with a blocking agent comprising one or more 1,2-glycols

whereby the electrodepositable coating composition comprises an organotin catalyst for effecting cure between the resin (a) and the curing agent (b), wherein said catalyst is a dialkyltin compound having the following structure (I):



where R_1 and R_2 are the same or different, and each independently represents a monovalent hydrocarbon group, wherein the sum of the carbon atoms of R_1 and R_2 is greater than 8, said catalyst being present in the electrodepositable coating composition in an amount sufficient to effect cure of the electrodepositable composition at a temperature at or below 340°F (171.1°C).

- 2. The electrodepositable coating composition of claim 1, wherein at least one of R_1 and R_2 represents a monovalent hydrocarbon group having at least 4 carbon atoms, provided that at least one of R_1 and R_2 represents a monovalent hydrocarbon group having greater than 4 carbon atoms.
- 3. The electrodepositable coating composition of claim 1, wherein at least a portion of the catalyst is dispersed in one or both of the resin (a) and the curing agent (b) prior to dispersing the resinous phase in the aqueous medium.
- 4. The electrodepositable coating composition of claim 1, wherein at least a portion of the catalyst is dispersed in the aqueous medium prior to dispersion of the resinous phase in the aqueous medium.

5. The electrodepositable coating composition of claim 1, wherein the catalyst is present in the coating composition in an amount sufficient to effect cure of the coating composition at or below a temperature of 320°F (160°C).
6. The electrodepositable coating composition of claim 1, wherein the resin (a) comprises active hydrogens derived from reactive hydroxyl groups and/or primary amine groups.
7. The electrodepositable coating composition of claim 6, wherein at least a portion of the hydroxyl groups comprise phenolic hydroxyl groups.
8. The electrodepositable coating composition of claim 6, wherein the resin (a) is the reaction product of a polyepoxide and a diglycidyl ether of a polyhydric phenol.
9. The electrodepositable coating composition of claim 1, wherein at least a portion of the active hydrogens present in the resin (a) comprise primary amine groups derived from the reaction of a ketimine-containing compound and an epoxy group-containing material.
10. The electrodepositable coating composition of claim 1, wherein the 1,2-glycol comprises a C₃ to C₆ 1,2-glycol.
11. The electrodepositable coating composition of claim 1, wherein the curing agent (b) comprises a blocking agent selected from at least one of 1,2-propanediol, 1,2-butanediol, 1,3-butanediol, 1,2-pentanediol and 1,2-hexanediol.
12. The electrodepositable coating composition of claim 1, wherein the resin (a) comprises reactive hydroxyl groups and/or primary amine groups,
13. The electrodepositable coating composition of claim 12, wherein at least a portion of the reactive hydroxyl groups comprise phenolic hydroxyl groups.
14. The electrodepositable coating composition of claim 1, wherein the catalyst is substantially non-volatile at a temperature at or below 340°F (171.1°C).
15. The electrodepositable coating composition of claim 1, wherein at least one of R₁ and R₂ represents a monovalent hydrocarbon group having 8 or more carbon atoms.
16. The electrodepositable coating composition of claim 1, wherein the catalyst comprises dioctyltin oxide.
17. The electrodepositable coating composition of claim 1, wherein the catalyst is present in the coating composition in an amount ranging from 0.1 to 5.0 percent by weight of tin based on weight of total resin solids present in the electrodepositable coating composition.
18. The electrodepositable coating composition of claim 1, which is free of lead-containing compounds.
19. The electrodepositable coating composition of claim 1, further comprising at least one of a bismuth compound, a zirconium compound, and a zinc compound.
20. A method for preparing an electrodepositable coating composition comprising a resinous phase dispersed in an aqueous medium, said resinous phase comprising:
 - (a) an active hydrogen-containing, cationic salt group-containing resin;
 - (b) a polyisocyanate curing agent at least partially blocked with a blocking agent comprising one or more 1,2-glycols; and
 - (c) an organotin catalyst for effecting the cure of the resin (a) and the curing agent (b),

said method comprising the steps of

- (1) preparing the resin (a) from a mixture of reactive components;
- (2) preparing the at least partially blocked polyisocyanate curing agent (b) separate from the resin (a) by reacting a polyisocyanate and a blocking agent;
- (3) admixing the resin (a) and the curing agent (b) to form a resinous admixture;

- (4) blending an organic and/or inorganic acid with the resinous admixture to form an acidified admixture; and
(5) dispersing the acidified admixture of (4) in an aqueous medium, wherein

the organotin catalyst (c) is incorporated into the mixture of reactive components during the preparation of the resin (a) in step (1),

wherein the catalyst (c) is a dialkyltin compound having the following structure (I):



where R_1 and R_2 are the same or different, and each independently represents a monovalent hydrocarbon group wherein the sum of the carbon atoms in R_1 and R_2 is greater than 8, said catalyst being present in the electrodepositable coating composition in an amount sufficient to effect cure of the electrodepositable composition at a temperature at or below 340°F (171.1°C).

21. The method of claim 20, wherein the catalyst (c) is defined as in any of claims 2, 16 and 17. .

22. The method of claim 20, wherein the resin (a) is prepared in step (1) by reacting a polyepoxide, a polyhydroxyl group-containing material at least a portion of which comprises phenolic hydroxyl groups, and a cationic salt group-former selected from the group consisting of amines and ketimines.

23. The method of claim 20, wherein the curing agent (b) is prepared in step (2) by reacting a polyisocyanate with a blocking agent comprising a C_3 to C_6 1,2-glycol.

24. The method of claim 22, wherein the active hydrogens present in the resin (a) are derived from reactive hydroxyl groups at least a portion of which comprise phenolic hydroxyl groups, and/or primary amine groups derived from the reaction of a ketimine-containing compound and an epoxy-group containing materials.

25. A method of electrocoating a conductive substrate serving as a cathode in an electrical circuit comprising said cathode and an anode, wherein said cathode and anode are immersed in an aqueous electrocoating composition according to any of claims 1-19, said method comprising passing electric current between said cathode and anode to cause deposition of the electrocoating composition onto the substrate as a substantially continuous film.

Patentansprüche

1. Elektrophoretisch abscheidbare Beschichtungszusammensetzung, enthaltend eine Harzphase, die in einem wässrigen Medium dispergiert ist, wobei diese Harzphase enthält:

- a) ein aktiven Wasserstoff enthaltendes, kationische Salzgruppen enthaltendes Harz und
b) ein Polyisocyanathärtungsmittel, das zumindest teilweise mit einem Blockierungsmittel blockiert ist, das ein oder mehrere 1,2-Glykole enthält,

wobei die elektrophoretisch abscheidbare Beschichtungszusammensetzung einen zinnorganischen Katalysator enthält, um Härtung zwischen dem Harz (a) und dem Härtungsmittel (b) zu bewirken, wobei dieser Katalysator eine Dialkylzinnverbindung mit der folgenden Struktur (I) ist:



worin R_1 und R_2 gleich oder unterschiedlich sind und jeweils unabhängig voneinander für eine einbindige Kohlenwasserstoffgruppe stehen, wobei die Summe der Kohlenstoffatome von R_1 und R_2 größer als 8 ist, und dieser Katalysator in der elektrophoretisch abscheidbaren Beschichtungszusammensetzung in einer Menge vorhanden ist, die ausreichend ist, um Härtung der elektrophoretisch abscheidbaren Beschichtungszusammensetzung zu bewirken.

EP 1 546 271 B1

zung bei einer Temperatur von oder unterhalb 340°F (171,1 °C) zu bewirken.

- 5 2. Elektrophoretisch abscheidbare Beschichtungszusammensetzung nach Anspruch 1, wobei wenigstens eines von R_1 und R_2 für eine einbindige Kohlenwasserstoffgruppe mit wenigstens 4 Kohlenstoffatomen steht, vorausgesetzt, dass wenigstens eines von R_1 und R_2 für eine einbindige Kohlenwasserstoffgruppe mit mehr als 4 Kohlenstoffatomen steht.
- 10 3. Elektrophoretisch abscheidbare Beschichtungszusammensetzung nach Anspruch 1, wobei wenigstens ein Teil des Katalysators in einem davon oder sowohl dem Harz (a) als auch dem Härtungsmittel (b) vor dem Dispergieren der Harzphase in dem wässrigen Medium dispergiert ist.
- 15 4. Elektrophoretisch abscheidbare Beschichtungszusammensetzung nach Anspruch 1, wobei wenigstens ein Teil des Katalysators in dem wässrigen Medium vor der Dispergierung der Harzphase in dem wässrigen Medium dispergiert ist.
- 5 5. Elektrophoretisch abscheidbare Beschichtungszusammensetzung nach Anspruch 1, wobei der Katalysator in der Beschichtungszusammensetzung in einer Menge vorhanden ist, die ausreichend ist, um Härtung der Beschichtungszusammensetzung bei oder unterhalb einer Temperatur von 320°F (160 °C) zu bewirken.
- 20 6. Elektrophoretisch abscheidbare Beschichtungszusammensetzung nach Anspruch 1, wobei das Harz (a) aktive Wasserstoffatome enthält, die sich von reaktiven Hydroxylgruppen und/oder primären Amingruppen ableiten.
- 25 7. Elektrophoretisch abscheidbare Beschichtungszusammensetzung nach Anspruch 6, wobei wenigstens ein Teil der Hydroxylgruppen phenolische Hydroxylgruppen umfasst.
8. Elektrophoretisch abscheidbare Beschichtungszusammensetzung nach Anspruch 6, wobei das Harz (a) das Reaktionsprodukt eines Polyepoxids und eines Diglycidylethers eines mehrwertigen Phenols ist.
- 30 9. Elektrophoretisch abscheidbare Beschichtungszusammensetzung nach Anspruch 1, wobei wenigstens ein Teil der aktiven Wasserstoffatome, die in dem Harz (a) vorhanden sind, primäre Amingruppen umfassen, die sich von der Reaktion einer ketiminhaltigen Verbindung und eines epoxyhaltigen Materials ableiten.
- 35 10. Elektrophoretisch abscheidbare Beschichtungszusammensetzung nach Anspruch 1, wobei das 1,2-Glykol ein C_3 -bis C_6 -1,2-Glykol umfasst.
11. Elektrophoretisch abscheidbare Beschichtungszusammensetzung nach Anspruch 1, wobei das Härtungsmittel (b) ein Blockierungsmittel, ausgewählt aus wenigstens einem von 1,2-Propandiol, 1,2-Butandiol, 1,3-Butandiol, 1,2,-Pentandiol und 1,2-Hexandiol, enthält.
- 40 12. Elektrophoretisch abscheidbare Beschichtungszusammensetzung nach Anspruch 1, wobei das Harz (a) reaktive Hydroxylgruppen und/oder primäre Amingruppen enthält.
13. Elektrophoretisch abscheidbare Beschichtungszusammensetzung nach Anspruch 12, wobei wenigstens ein Teil der reaktiven Hydroxylgruppen phenolische Hydroxylgruppen umfasst.
- 45 14. Elektrophoretisch abscheidbare Beschichtungszusammensetzung nach Anspruch 1, wobei der Katalysator bei Temperaturen von oder unterhalb 340°F (171,1 °C) im Wesentlichen nicht flüchtig ist.
- 50 15. Elektrophoretisch abscheidbare Beschichtungszusammensetzung nach Anspruch 1, wobei wenigstens eines von R_1 und R_2 für eine einbindige Kohlenwasserstoffgruppe mit 8 oder mehr Kohlenstoffatomen steht.
16. Elektrophoretisch abscheidbare Beschichtungszusammensetzung nach Anspruch 1, wobei der Katalysator Diocetylzinnoxid umfasst.
- 55 17. Elektrophoretisch abscheidbare Beschichtungszusammensetzung nach Anspruch 1, wobei der Katalysator in der Beschichtungszusammensetzung in einer Menge in einem Bereich von 0,1 bis 5,0 Gew.-% Zinn, bezogen auf das Gesamtgewicht der Harzfeststoffe, die in der elektrophoretisch abscheidbaren Beschichtungszusammensetzung vorhanden sind, vorhanden ist.

18. Elektrophoretisch abscheidbare Beschichtungszusammensetzung nach Anspruch 1, die frei von bleihaltigen Verbindungen ist.

19. Elektrophoretisch abscheidbare Beschichtungszusammensetzung nach Anspruch 1, die zusätzlich wenigstens eines von einer Wismutverbindung, einer Zirkoniumverbindung und einer Zinkverbindung enthält.

20. Verfahren zur Herstellung einer elektrophoretisch abscheidbaren Beschichtungszusammensetzung, enthaltend eine Harzphase, die in einem wässrigen Medium dispergiert ist, wobei diese Harzphase enthält:

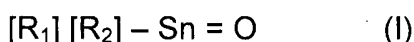
- (a) ein aktiven Wasserstoff enthaltendes, kationische Salzgruppen enthaltendes Harz,
- (b) ein Polyisocyanathärtungsmittel, das zumindest teilweise mit einem Blockierungsmittel blockiert ist, das ein oder mehrere 1,2-Glykole enthält, und
- (c) einen zinnorganischen Katalysator, um die Härtung des Harzes (a) und des Härtungsmittels (b) zu bewirken,

wobei das Verfahren die Schritte umfasst:

- (1) Herstellung des Harz (a) aus einer Mischung von reaktiven Komponenten,
- (2) Herstellung des wenigstens teilweise blockierten Polyisocyanathärtungsmittels (b), unabhängig von dem Harz (a), durch Umsetzen eines Polyisocyanats und eines Blockierungsmittels,
- (3) Mischen des Harzes (a) und des Härtungsmittels (b), um eine harzhaltige Mischung zu bilden,
- (4) Mischen einer organischen und/oder einer anorganischen Säure mit der Harzmischung, um eine angesäuerte Mischung zu bilden, und
- (5) Dispergieren der angesäuerten Mischung aus (4) in einem wässrigen Medium,

wobei der zinnorganische Katalysator (c) in die Mischung der reaktiven Komponenten während der Herstellung des Harzes (a) in Schritt (1) eingebracht wird,

wobei der Katalysator (c) eine Dialkylzinnverbindung mit der folgenden Struktur (I) ist:



worin R_1 und R_2 gleich oder unterschiedlich sind und jedes unabhängig voneinander für eine einbindige Kohlenwasserstoffgruppe steht, wobei die Summe der Kohlenstoffatome in R_1 und R_2 größer als 8 ist, und dieser Katalysator in der elektrophoretisch abscheidbaren Beschichtungszusammensetzung in einer Menge vorhanden ist, die ausreicht, um Härtung der elektrophoretisch abscheidbaren Beschichtungszusammensetzung bei einer Temperatur von oder unterhalb 340°F (171,1 °C) zu bewirken.

21. Verfahren nach Anspruch 20, wobei der Katalysator (c) wie in einem der Ansprüche 2, 16 und 17 definiert ist.

22. Verfahren nach Anspruch 20, wobei das Harz (a) in Schritt (1) durch Umsetzen eines Polyepoxids, eines polyhydroxylgruppenhaltigen Stoffs, bei dem wenigstens ein Teil phenolische Hydroxylgruppen enthält, und eines kationischen Salzgruppen Bildners, ausgewählt aus der Gruppe bestehend aus Aminen und Ketaminen, hergestellt wird.

23. Verfahren nach Anspruch 20, wobei das Härtungsmittel (b) in Schritt (2) durch Umsetzen eines Polyisocyanats mit einem Blockierungsmittel, enthaltend ein C_3 - bis C_6 - 1,2-Glykol, hergestellt wird.

24. Verfahren nach Anspruch 22, wobei die aktiven Wasserstoffe, die in Harz (a) vorhanden sind, aus reaktiven Hydroxylgruppen, von denen wenigstens ein Teil phenolische Hydroxylgruppen umfasst, und/oder primären Amingruppen, die sich von der Reaktion einer ketiminhaltigen Verbindung und einer epoxygruppenhaltigen Verbindung ableiten, stammen.

25. Verfahren zur elektrophoretischen Beschichtung eines leitfähigen Substrats, das als Kathode in einem elektrischen Schaltkreis, enthaltend diese Kathode und eine Anode, dient, wobei diese Kathode und Anode in eine wässrige elektrophoretisch abscheidbare Beschichtungszusammensetzung gemäß einem der Ansprüche 1 - 19 eingetaucht sind, und das Verfahren das Durchleiten von elektrischem Strom zwischen dieser Kathode und der Anode umfasst, um

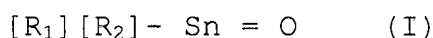
die Abscheidung der elektrophoretisch abscheidbaren Beschichtungszusammensetzung auf dem Substrat als einen im Wesentlichen kontinuierlichen Film zu bewirken.

5 Revendications

1. Composition de revêtement électrodéposable comprenant une phase résineuse dispersée dans un milieu aqueux, ladite phase résineuse comprenant :

- 10 (a) une résine contenant des groupes sels cationiques, contenant des atomes d'hydrogène actifs ; et
(b) un agent durcisseur polyisocyanate au moins partiellement bloqué par un agent de blocage comprenant un ou plusieurs 1,2-glycols

- 15 **caractérisée en ce que** ladite composition de revêtement électrodéposable comprend un catalyseur organostannique pour effectuer le durcissement entre la résine (a) et l'agent durcisseur (b), dans laquelle ledit catalyseur est un composé de dialkylétain ayant la structure (I) suivante :



- 20 où R_1 et R_2 sont identiques ou différents, et chacun représente indépendamment un groupe hydrocarbure monovalent, la somme des atomes de carbone de R_1 et R_2 étant supérieure à 8, ledit catalyseur étant présent dans la composition de revêtement électrodéposable en une quantité suffisante pour effectuer le durcissement de la composition électrodéposable à une température de 171,1°C (340°F) ou moins.

- 25 2. Composition de revêtement électrodéposable selon la revendication 1, dans laquelle un des R_1 et R_2 au moins représente un groupe hydrocarbure monovalent ayant au moins 4 atomes de carbone, à condition qu'au moins un des R_1 et R_2 représente un groupe hydrocarbure monovalent ayant plus de 4 atomes de carbone.

- 30 3. Composition de revêtement électrodéposable selon la revendication 1, dans laquelle une partie au moins du catalyseur est dispersée dans l'un ou l'autre de la résine (a) ou de l'agent durcisseur (b), ou les deux, avant dispersion de la phase résineuse dans le milieu aqueux.

- 35 4. Composition de revêtement électrodéposable selon la revendication 1, dans laquelle une partie au moins du catalyseur est dispersée dans le milieu aqueux avant dispersion de la phase résineuse dans le milieu aqueux.

- 40 5. Composition de revêtement électrodéposable selon la revendication 1, dans laquelle le catalyseur est présent dans la composition de revêtement en une quantité suffisante pour effectuer le durcissement de la composition de revêtement à une température de 160°C (320°F) ou moins.

6. Composition de revêtement électrodéposable selon la revendication 1, dans laquelle la résine (a) comprend des atomes d'hydrogène actifs dérivés de groupes hydroxyle réactifs et/ou de groupes amine primaire.

- 45 7. Composition de revêtement électrodéposable selon la revendication 6, dans laquelle une partie au moins des groupes hydroxyle comprend des groupes hydroxyle phénoliques.

8. Composition de revêtement électrodéposable selon la revendication 6, dans laquelle la résine (a) est le produit de réaction d'un polyépoxyde et d'un éther diglycidyle de phénol polyhydrique.

- 50 9. Composition de revêtement électrodéposable selon la revendication 1, dans laquelle une partie au moins des atomes d'hydrogène actifs présents dans la résine (a) comprend des groupes amine primaire dérivés de la réaction d'un composé contenant un cétimine et d'un matériau contenant des groupes époxy.

- 55 10. Composition de revêtement électrodéposable selon la revendication 1, dans laquelle le 1,2-glycol comprend un 1,2-glycol C_3 à C_6 .

11. Composition de revêtement électrodéposable selon la revendication 1, dans laquelle l'agent durcisseur (b) comprend

un agent de blocage choisi parmi au moins l'un des suivants : 1,2-propanediol, 1,2-butanediol, 1,3-butanediol, 1,2-pentanediol et 1,2-hexanediol.

12. Composition de revêtement électrodéposable selon la revendication 1, dans laquelle la résine (a) comprend des groupes hydroxyle réactifs et/ou des groupes amine primaire.

13. Composition de revêtement électrodéposable selon la revendication 12, dans laquelle une partie au moins des groupes hydroxyle réactifs comprennent des groupes hydroxyle phénoliques.

14. Composition de revêtement électrodéposable selon la revendication 1, dans laquelle le catalyseur est sensiblement non volatil à une température de 171,1°C (340°F) ou moins.

15. Composition de revêtement électrodéposable selon la revendication 1, dans laquelle un des R₁ et R₂ au moins représente un groupe hydrocarbure monovalent ayant 8 atomes de carbone ou plus.

16. Composition de revêtement électrodéposable selon la revendication 1, dans laquelle le catalyseur comprend un oxyde de dioctylétain.

17. Composition de revêtement électrodéposable selon la revendication 1, dans laquelle le catalyseur est présent dans la composition de revêtement en une quantité allant de 0,1 à 5,0 % en poids d'étain sur la base du poids des fractions solides totales de résine présentes dans la composition de revêtement électrodéposable.

18. Composition de revêtement électrodéposable selon la revendication 1, qui est exempte de composés contenant du plomb.

19. Composition de revêtement électrodéposable selon la revendication 1, comprenant en outre au moins un composé de bismuth et/ou un composé de zirconium et/ou un composé de zinc.

20. Procédé de préparation d'une composition de revêtement électrodéposable comprenant une phase résineuse dispersée dans un milieu aqueux, ladite phase résineuse comprenant :

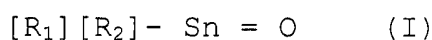
- (a) une résine contenant des groupes sels cationiques, contenant des atomes d'hydrogène actifs ;
- (b) un agent durcisseur polyisocyanate au moins partiellement bloqué par un agent de blocage comprenant un ou plusieurs 1,2-glycols ; et
- (c) un catalyseur organostannique pour effectuer le durcissement entre la résine (a) et l'agent durcisseur (b),

ledit procédé comprenant les étapes consistant à :

- (1) préparer la résine (a) à partir d'un mélange de composants réactifs ;
- (2) préparer l'agent durcisseur polyisocyanate (b) au moins partiellement bloqué séparément de la résine (a) en faisant réagir un polyisocyanate et un agent de blocage ;
- (3) mélanger la résine (a) et l'agent durcisseur (b) pour former un mélange résineux ;
- (4) incorporer par mélange un acide organique et/ou inorganique au mélange résineux pour former un mélange acidifié ; et
- (5) disperser le mélange acidifié obtenu en (4) dans un milieu aqueux, dans lequel

le catalyseur organostannique (c) est incorporé dans le mélange des composants réactifs pendant la préparation de la résine (a) à l'étape (1),

le catalyseur (c) étant un composé de dialkylétain ayant la structure (I) suivants :



où R₁ et R₂ sont identiques ou différents, et chacun représente indépendamment un groupe hydrocarbure monovalent, la somme des atomes de carbone dans R₁ et R₂ étant supérieure à 8, ledit catalyseur étant présent dans la composition de revêtement électrodéposable en une quantité suffisante pour effectuer le durcissement de la composition électrodéposable à une température de 171,1°C (340°F) ou moins.

21. Procédé selon la revendication 20, dans lequel le catalyseur (c) est tel que défini dans l'une quelconque des revendications 2, 16 et 17.

22. Procédé selon la revendication 20, dans lequel la résine (a) est préparée à l'étape (1) en faisant réagir
un polyépoxyde,
un matériau contenant des groupes polyhydroxyle dont une partie au moins comprend des groupes hydroxyle
phénoliques, et
un composé formant sel cationique choisi dans le groupe constitué par les amines et les cétimines.

23. Procédé selon la revendication 20, dans lequel l'agent durcisseur (b) est préparé à l'étape (2) en faisant réagir un
polyisocyanate avec un agent de blocage comprenant un 1,2-glycol C₃ à C₆.

24. Procédé selon la revendication 22, dans lequel les atomes d'hydrogène actifs présents dans la résine (a) sont
dérivés de groupes hydroxyle réactifs dont une partie au moins comprend des groupes hydroxyle phénoliques, et/ou
des groupes amine primaire dérivés de la réaction d'un composé contenant un cétimine et d'un matériau contenant
des groupes époxy.

25. Procédé de revêtement par électrodéposition d'un substrat conducteur servant de cathode dans un circuit électrique
comprenant ladite cathode et une anode, dans lequel lesdites cathode et anode sont immergées dans une compo-
sition aqueuse d'électrodéposition selon l'une quelconque des revendications 1 à 19,
ledit procédé consistant à faire passer un courant électrique entre ladite cathode et anode pour que la composition
d'électrodéposition se dépose sur le substrat sous la forme d'un film sensiblement continu.

REFERENCES CITED IN THE DESCRIPTION

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ELEKTROMOS ÚTON LEVÁLASZTHATÓ BEVONAT-ÖSSZETÉTEL ÉS AZ EHEZ KAPCSOLÓDÓ ELJÁRÁS

Szabadalmi igénypontok

1. Elektromos úton leválasztható bevonat-összetétel, amely vizes közegben diszpergált gyantafázist tartalmaz, ahol a gyantafázis a következőket tartalmazza:

- (a) aktív hidrogént tartalmazó és kationos sócsoportot tartalmazó gyanta; és
- (b) poliizocianát-kikeményítőanyag, amely egy gátlószerezrel legalább részben gátolt, és amely egy vagy több 1,2-glikolt tartalmaz,

ahol az elektromos úton leválasztható bevonat-összetétel szerves önkatalizátort tartalmaz, azért, hogy a gyanta (a) és a kikeményítőanyag (b) között kikeményítsen, ahol a katalizátor egy dialkil-ón vegyület, amelynek szerkezete (I) a következő:



ahol R_1 és R_2 jelentése azonos vagy különböző és mindegyik egymástól függetlenül egy vegyértékű szénhidrogén csoport, ahol R_1 és R_2 összes szénatomjainak száma nagyobb, mint 8,

a katalizátor az elektromos úton leválasztható bevonat összetételében elégséges mennyiségben van jelen ahhoz, hogy az elektromos úton leválasztható bevonat összetételét legfeljebb 340°F (171.1°C) hőmérsékleten kikeményítse.

2. Az 1. igénypont szerinti, elektromos úton leválasztható bevonat-összetétel, ahol R_1 és R_2 közül legalább az egyiknek legalább 4 szénatomos, egyvegyértékű szénhidrogén csoportja van, feltéve, hogy R_1 és R_2 közül legalább az egyiknek olyan egyvegyértékű szénhidrogén csoportja van, melynek több mint 4 szénatomja van.

3. Az 1. igénypont szerinti, elektromos úton leválasztható bevonat-összetétel, ahol legalább a katalizátor egy része a gyanta (a) és a kikeményítőanyag (b) közül legalább az egyikben diszpergálva lett a gyantafázis diszpergálása előtt a vizes közegben.

4. Az 1. igénypont szerinti, elektromos úton leválasztható bevonat-összetétel, ahol legalább a katalizátor egy része diszpergálva van a gyantafázis diszpergálása előtt a vizes közegben.

5. Az 1. igénypont szerinti, elektromos úton leválasztható bevonat-összetétel, ahol a katalizátor a bevonat összetételében elégséges mennyiségben van jelen ahhoz, hogy a bevonat összetételét legfeljebb 320°F (160°C) hőmérsékleten kikeményítse.

6. Az 1. igénypont szerinti, elektromos úton leválasztható bevonat-összetétel, ahol a gyanta (a) aktív hidrogéneket tartalmaz, amelyek reaktív hidroxilcsoportból és/vagy primer aminocsoportból származnak.

7. A 6. igénypont szerinti, elektromos úton leválasztható bevonat-összetétel, ahol legalább a hidroxilcsoportok egy része fenolos hidroxilcsoportot képez.

8. A 6. igénypont szerinti, elektromos úton leválasztható bevonat-összetétel, ahol a gyanta (a) egy poliepoxid és egy polihidroxi-fenol diglicidil-étere reakciójának a terméke.

9. Az 1. igénypont szerinti, elektromos úton leválasztható bevonat-összetétel, ahol legalább a gyantában (a) jelenlévő aktív hidrogének egy része primer aminocsoportokat képez, amely csoportok egy ketamin-tartalmú vegyület reakciójából vagy egy epoxi-csoportot tartalmazó anyag reakciójából származnak.

10. Az 1. igénypont szerinti, elektromos úton leválasztható bevonat-összetétel, ahol az 1,2-glikol C3-C6 1,2-glikolt tartalmaz.

11. Az 1. igénypont szerinti, elektromos úton leválasztható bevonat-összetétel, ahol a kikeményítőanyag (b) gátlószerrel tartalmaz, amely 1,2-propándiol, 1,2-butándiol, 1,3-butándiol, 1,2-pentándiol és 1,2-hexándiol legalább egyike közül van kiválasztva.

12. Az 1. igénypont szerinti, elektromos úton leválasztható bevonat-összetétel, ahol a gyanta (a) reaktív hidroxil-csoportokat és/vagy primer aminocsoportokat képez.

13. A 12. igénypont szerinti, elektromos úton leválasztható bevonat-összetétel, ahol legalább a reaktív hidroxilcsoportok egy része fenolos hidroxilcsoportokat képez.

14. Az 1. igénypont szerinti, elektromos úton leválasztható bevonat-összetétel, ahol a katalizátor legfeljebb 340 °F (171,1 °C) hőmérsékleten lényegében nem illékony.

15. Az 1. igénypont szerinti, elektromos úton leválasztható bevonat-összetétel, ahol R1 és R2 közül legalább az egyik egyvegyértékű szénhidrogén csoport, amelynek legalább 8 szénatomja van.

16. Az 1. igénypont szerinti, elektromos úton leválasztható bevonat-összetétel, ahol a katalizátor dioktil-ón-oxidot tartalmaz.

17. Az 1. igénypont szerinti, elektromos úton leválasztható bevonat-összetétel, ahol a katalizátor a bevonat-összetételben az ón tömegére számítva 0,1- 5,0 tömegszázalék közötti mennyiségben van jelen, a teljes gyanta-szilárdanyag tömege alapján, amely az elektromos úton leválasztható bevonat-összetételben van.

18. Az 1. igénypont szerinti, elektromos úton leválasztható bevonat-összetétel, amely ólomtartalmú vegyülettől mentes.

19. Az 1. igénypont szerinti, elektromos úton leválasztható bevonat-összetétel, amely továbbá egy bizmut vegyület, egy cirkónium vegyület és egy cink vegyület közül legalább az egyiket tartalmazza.

20. Eljárás egy elektromos úton leválasztható bevonat-összetétel előállítására, amely vízes közegben diszpergált gyantafázist tartalmaz, ahol a gyantafázis a következőket tartalmazza:

- (a) aktív hidrogént tartalmazó és kationos sócsoportot tartalmazó gyanta;
- (b) poliizocianát-kikeményítőanyag, amely gátlószerrel legalább részben gátolt, amely egy vagy több 1,2-glikolt tartalmaz; és

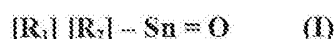
(c) egy szerves önkatalizátor a gyanta (a) és a kikeményítőanyag (b) kikeményítésére,

ahol az eljárás a következő lépéseket tartalmazza

- (1) a gyanta (a) előállítása egy reaktív vegyület keverékéből;
- (2) a gyantától (a) elkülönülő legalább részlegesen gátló polizocianát kikeményítőanyag (b) előállítása polizocianát és gátlószer reagáltatása révén;
- (3) a gyanta (a) és a kikeményítőanyag (b) összekeverése gyantakeverék képzéséhez;
- (4) egy szerves és/vagy nem szerves sav összekeverése a gyantakeverékkel, egy savasított keverék képzéséhez; és
- (5) a savasított keverék (4) vizes közegben való diszpergálása, ahol

a szerves önkatalizátor (c), beépül a reaktív komponens keverékébe a gyanta (a) előállításának első lépésében (1),

ahol a katalizátor (c) egy dialkil-ön vegyület, mely szerkezete (I) a következő:



ahol R_1 és R_2 jelentése azonos vagy különböző és egymástól független mindegyik, melynek egyvegyértékű szénhidrogén csoportja van, ahol R_1 és R_2 összes szénatomja nagyobb, mint 8,

a katalizátor az elektromos úton leválasztható bevonat összetételében egy elégséges mennyiségben van jelen ahhoz, hogy az elektromos úton leválasztható bevonat összetételét legfeljebb 340°F (171.1°C) hőmérsékleten kikeményítse.

21. A 20. igénypont szerinti eljárás, ahol a katalizátor (c) a 2., 16. és 17. igénypontok bármelyikében meghatározott katalizátor.

22. A 20. igénypont szerinti eljárás, ahol a gyantát (a) az első lépésben (1) állítjuk elő a következők reagáltatásával: poliepoxid, polihidroxil csoportot tartalmazó anyag, amelyek legalább egy része a fenolos hidroxil-csoportot képez és egy kationos sócsoportot képző szer, amely aminokból és ketonokból álló csoportból választott.

23. A 20. igénypont szerinti eljárás, ahol kikeményítőanyagot (b) a második lépésben (2) állítjuk elő egy polizocianát reagáltatása révén egy gátlószerrel, amely C3-C6 1,2-glikolt tartalmaz.

24. A 22. igénypont szerinti eljárás, ahol a gyantában (a) jelenlévő aktív hidrogének reaktív hidroxil-csoportokból származnak, amelyek legalább egy része fenolos hidroxilcsoportokat képez és/vagy olyan primer aminocsoportokat képez, amelyek egy ketamin-tartalmú vegyület és egy epoxi-csoportot tartalmazó anyag reakciójából származnak.

25. Eljárás katódot és anódot tartalmazó elektromos áramkörben katódként szolgáló vezetőképes szubsztrát elektromos bevonására, ahol az 1-19. igénypontok bármelyike szerinti vizes elektromos bevonat-összetételbe merítjük be a katódot és az anódot, és az eljárás az katód és anód közötti elektromos áram átjuttatását tartalmazza, azért, hogy az elektromos bevonat-összetétel lerakódása a szubsztráton lényegében egy folytonos filmet képezzen.