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(54) Title: ELECTROCOAT COATING WITH LOW GLOSS

(57) Abstract: An electrocoat coating composition that forms a matte or low gloss coating on an electrically conductive substrate comprises an aqueous emulsion or dispersion of a binder consisting essentially of (a) a polyester with a hydroxyl number of from about 15 to about 40 mg KOH/g, (b) an amine- or carboxylic acid-functional acrylic polymer with a hydroxyl number of from about 150 to about 200 mg KOH/g, (c) at least one crosslinker for the polyester and the acrylic polymer, and (d) optionally, up to about 20% by weight, based on total binder weight, of one or more additional resins or polymers, wherein the electrocoat coating composition comprises about 1.5 to about 4 parts by weight acrylic polymer per 1 part by weight polyester.

ELECTROCOAT COATING WITH LOW GLOSS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of United States Provisional Application No. 61/445,262, filed on February 22, 2011, the entire disclosure of which is incorporated herein by reference.

FIELD OF THE INVENTION

[0002] This invention is in the field of electrocoat (electrodeposition) coating compositions, methods of making and applying such coating compositions, and the coatings and coated substrates provided by applying such coating compositions to substrates.

BACKGROUND

[0003] The statements in this section provide background information related to this disclosure and may not constitute prior art.

[0004] Low gloss coatings have been used in some applications, for example for stylistic reasons or to make film irregularities less apparent. Pigment flatting agents have been used to reduce gloss of coatings. Chen et al., U.S. Patent No. 6,331,582 and Rennie et al., U.S. Patent No. 5,907,006 are examples of methods of producing low gloss coatings using matting agents. Many patents describe ways to prepare powder coating compositions that yield low gloss coatings, including Minesso et al., U.S. Patent Application Publication No. US 2010/0120978, describing using a carboxylic acid-functional branched polyester to prepare a low gloss powder coating composition; Fugier et al., U.S. Patent Application Publication No. US 2010/0010151, describing a powder coating composition obtainable by mixing two separately produced powder coating compositions; Rodriguez-Sanamarta et al., U.S. Patent Application Publication No. US 2009/0053539, describing powder coating aluminum substrate with a powder coating based on (meth)acrylate resin that may also include a polyester resin; Asami et al., U.S. Patent Application Publication No. US 2006/0173127, describing a matte powder coating composition comprising two powder coatings of different gelation times; Tullos

et al., U.S. Patent Application Publication No. US 2003/0134978, describing a powder coating including a matting agent; Nicholl et al., U.S. Patent No. 7,041,737, describing a powder coating composition that is a mixture of a high gloss system containing a glycidyl methacrylate resin and a low gloss system containing a carboxyl-terminated polyester; Torborg et al., U.S. Patent No. 7,034,075, describing a low gloss powder coating comprising a dry-blended combination of a mixture of a glycidyl group-containing acrylic resin and curing agent and comprising a carboxyl group-containing material incompatible with the mixture; Decker et al., U.S. Patent No. 6,852,765, describing a powder coating including a a crosslinkable base polymer, a crosslinkable acrylic polymer, and a free radical initiator further including spheroidal particles; Moens et al., U.S. Patent No. 6,844,072, describing a powder coating including an amorphous, carboxyl-containing polyester containing isophthalic acid, a semi-crystalline, carboxyl-containing polyester, a specific glycidyl group-containing acrylic copolymer, and curing agent for the polyesters; Norris et al., U.S. Patent No. 6,599,993, describing a powder including a branched carboxylic acid-functional polyester of a certain M_n and an epoxy-functional material; Dumain et al., U.S. Patent No. 6,472,071, describing a powder coating composition comprising a polyester having hydroxyl and carboxyl groups and a glycidyl-containing acrylic copolymer of a T_g less than about 55°C and M_n greater than about 8000; Chung et al., U.S. Patent No. 6,410,147, describing a crosslinkable composition including at least two partially compatible crosslinkable components that are a polar polymer and a non-polar polymer; Reichert et al., U.S. Patent No. 6,369,145, describing a low gloss coating derived from a polyester/triglycidyl isocyanurate powder coating that includes an ethylene/acrylic acid copolymer and zinc salt of a fatty acid or β-diketone; Muthiah et al., U.S. Patent No. 5,684,067, describing a polyester/triglycidyl isocyanurate powder coating that includes an ethylene/acrylic acid copolymer, 2-mercapto benzothiazole or its metal salt, and polyolefin wax; Alford, U.S. Patent No. 6,350821, describing a matte powder coating composition including two carboxyl-functional polyester resins having a difference in acid values and an epoxide-functional crosslinking agent; Dumain et al., U.S. Patent No. 6,093,774, describing a low gloss powder coating composition comprising a glycidyl-containing acrylic polymer, a copolymer of an ethylenically unsaturated compound and an anhydride, and a dicarboxylic acid of 4-20 carbons; Rennie et al., U.S. Patent No. 5,907,006, describing

powder compositions incorporating matting agents in the form of terephthalic acid dianilide or a substituted derivative; Meier-Westhues et al., U.S. Patent No. 5,786,419, describing powder coatings for matte coatings containing a hydroxyl group-containing component, an addition polymerization compound based on (cyclo)aliphatic diisocyanates that contains uretdione groups, a component containing carboxyl and/or carboxylic acid anhydride groups, and a component having groups reactive with carboxyl and/or carboxylic acid anhydride groups, the components being used in defined amounts; Prucnal et al., U.S. Patent No. 5,744,522, describing a low gloss coating composition including a glycidyl group-containing acrylic copolymer, an aromatic polyester, and an isocyanurate curing agent of a particular structure; Hoebeke et al., U.S. Patent Nos. 5,525,370 and 5,436,311, describing a powder composition with a mixture of a linear carboxyl group-containing polyester and a glycidyl group-containing acrylic copolymer; Umehara et al., U.S. Patent No. 5,491,202, describing three thermosetting polyester resins having certain moduli of elasticity when cured with the hardener; Nozaki et al., U.S. Patent No. 5,229,470, describing a matte powder coating composition comprising two polyesters of certain hydroxyl values in particular weight ratio and differences in gel time and acid value; and Yallourakis, U.S. Patent No. 4,242,253, disclosing a low gloss powder coating having a blend of polyester, epoxy resin, triglycidyl isocyanurate, calcium carbonate, and polypropylene particles.

[0005] Electrocoat coating compositions and methods are used to coat conductive articles, for example steel automotive bodies, wheels, or parts. The aqueous electrocoat coating compositions, or “baths,” typically are pigmented, aqueous dispersions or emulsions of a binder including a principal, film-forming resin ("polymer" and "resin" are used interchangeably in this disclosure) that is ionically stabilized in the aqueous medium. In automotive or industrial applications, for which durable coatings are desired, the electrocoat compositions are formulated to be curable (thermosetting) compositions. This is usually accomplished by emulsifying along with the principal, film-forming resin a crosslinking agent or crosslinker that can react with functional groups on the principal resin under appropriate curing conditions, such as with the application of heat, and so cure the coating. The ionically-charged binder and its associated coating components are electrodeposited onto a conductive substrate, for example a steel car body, by submerging the substrate in the electrocoat bath and then applying an electrical potential between the substrate and a submerged electrode of

opposite charge, for example a stainless steel bar. The charged coating material migrates to and deposits on the conductive substrate. The deposited coating is then cured, for example (as mentioned) by heating the coated substrate to cause a crosslinking agent to react with the resin.

SUMMARY OF THE DISCLOSURE

[0006] Electrocoat coatings are expected to provide excellent durability and protection against corrosion. Electrocoat coating compositions should also be stable against having pigments or other particulate matter settle out of the dispersion, which would cause defects in the coating. Particulate flatting agents cannot be incorporated in large amounts that would produce instability or settling. The electrocoat coating compositions now disclosed are stable and the disclosed methods produce durable coatings that protect against corrosion, but also provide a matte appearance with little or no flatting agent being incorporated.

[0007] As now disclosed, an electrocoat coating composition that forms a matte or low gloss coating on an electrically conductive substrate comprises an aqueous emulsion or dispersion of a binder consisting essentially of (a) a polyester with a hydroxyl number of from about 15 to about 40 mg KOH/g, (b) an amine- or carboxylic acid-functional acrylic polymer with a hydroxyl number of from about 150 to about 200 mg KOH/g, (c) at least one crosslinker for the polyester and the acrylic polymer, and (d) optionally, up to about 20% by weight, based on total binder weight, of one or more additional resins or polymers. "Total binder weight" refers to the combined weight of all film-forming components of the coating composition. The acrylic polymer may have an amine or carboxylic acid equivalent weight of from about 150 to about 5000; in certain embodiments, the acrylic polymer has an amine or carboxylic acid equivalent weight of from about 500 to about 2000. Hydroxyl number is measured according to ASTM D4214. Amine equivalent weight is measured according to ASTM D4370, and carboxylic acid equivalent weight is measured according to ASTM D1639 or D4370; or both amine equivalent weight and carboxylic acid equivalent weight may be calculated from the monomer composition of the acrylic polymer. The acrylic polymer (b) and the polyester (a) are present in the coating composition in a weight ratio of from about 4 parts by weight acrylic polymer : 1 part by weight polyester (about 4:1 by weight) to

about 1.5 parts by weight acrylic polymer : 1 part by weight polyester (about 1.5:1 by weight). Stated in another way, the binder of the electrocoat coating composition includes about 1.5 to about 4 parts by weight of the acrylic polymer (b) per 1 part by weight of the polyester (a).

[0008] A cathodic electrocoat coating composition that forms a matte or low gloss coating on an electrically conductive substrate is prepared by combining a hydroxyl-functional polyester with a hydroxyl- and amine- or epoxide-functional acrylic polymer to form a polymer mixture. The mixture may be free of organic solvent (i.e., it may be a nonvolatile, molten mixture). When the acrylic polymer is epoxide-functional, a secondary amine is then reacted with the epoxide groups of the acrylic polymer in the mixture to provide tertiary amine groups. The polyester (a) has a hydroxyl number of from about 15 to about 40 mg KOH/g. The acrylic polymer (b) has a hydroxyl number of from about 150 to about 200 mg KOH/g and an amine equivalent weight of from about 150 to about 5000 or, if the acrylic polymer is epoxide-functional, the reaction with the secondary amine produces an acrylic polymer (b) with an amine equivalent weight of from about 150 to about 5000. The acrylic polymer and the polyester are present in the polymer mixture in a weight ratio of from about 4 parts by weight acrylic polymer : 1 part by weight polyester (about 4:1 by weight) to about 1.5 parts by weight acrylic polymer : 1 part by weight polyester (about 1.5:1 by weight). That is, the polymer mixture includes about 1.5 to about 4 parts by weight acrylic polymer per 1 part by weight polyester. At least one crosslinker (c) for the polyester and the acrylic polymer and, optionally, other materials are combined with the polymer mixture to form a binder mixture. The binder optionally has up to about 20% by weight, based on total binder weight, of one or more resins or polymers (d) in addition to the polyester (a), the acrylic polymer (b), and the at least one crosslinker (c). The amine-functional acrylic polymer (b) is then at least partially neutralized with an organic acid, and the binder mixture is dispersed in an aqueous medium to form a binder dispersion or emulsion. One or more pigments are added to the binder dispersion or emulsion to produce the electrocoat coating composition, optionally along with more water, cosolvent, neutralizing acid, and one or more further conventional additives. Part or all of the optional 20% by weight, based on total binder weight, of the one or more resins or polymers (d) in addition to the polyester (a), the acrylic polymer (b), and the at least one crosslinker (c) may serve as pigment dispersant and be added at this point as part of a

pigment paste in which the pigments are dispersed. A matting agent may be added to the binder dispersion or emulsion in preparing the electrocoat coating composition, either as part of a pigment paste or separately from it.

[0009] An electrically conductive substrate, such as a metal automotive vehicle body, wheel, or part, is coated by placing the electrically conductive substrate in the cathodic aqueous electrocoat coating composition containing the amine-functional acrylic polymer, with the substrate as cathode and a second electrode in the aqueous electrocoat coating composition serving as anode, and passing a current through the aqueous electrocoat coating composition to deposit a coating layer comprising the binder onto the electrically conductive substrate. The deposited coating layer may then be cured to a cured coating layer on the substrate. The at least one crosslinker (c) reacts with the polyester (a) and acrylic polymer (b), and, optionally, one or more resins (d) under curing conditions, e.g., at an elevated temperature. The cured coating has a 60° gloss of less than about 25, as measured according to ASTM D523. Subsequent coating layers may be applied on a portion, but less than the whole, of the electrodeposited coating layer. For example, other layers such as one or more of a spray-applied primer surfacer and a topcoat layer or topcoat layers (e.g., a colored basecoat layer and a clearcoat layer) may be applied over a portion but less than all of the electrodeposited coating layer's surface. AT least a part of the electrodeposited coating layer remains uncoated with any further coating layer. All coating layers may be cured.

[0010] Alternatively, an anodic electrocoat coating composition that forms a matte or low gloss coating on an electrically conductive substrate is prepared by combining a hydroxyl-functional polyester (a) with a hydroxyl- and carboxylic acid-functional acrylic polymer (b) to form a polymer mixture. The mixture may be free of organic solvent (i.e., the polyester and acrylic may be combined as a nonvolatile, molten mixture). The polyester (a) has a hydroxyl number of from about 15 to about 40 mg KOH/g. The acrylic polymer (b) has a hydroxyl number of from about 150 to about 200 mg KOH/g and a carboxylic acid equivalent weight of from about 150 to about 5000. The acrylic polymer and the polyester are present in the polymer mixture in a weight ratio of from about 4 parts by weight acrylic polymer : 1 part by weight polyester (about 4:1 by weight) to about 1.5 parts by weight acrylic polymer : 1 part by weight polyester (about 1.5:1 by weight). That is, the polymer mixture includes about 1.5 to about 4 parts by weight acrylic polymer per 1 part by weight polyester. At least one crosslinker (c) for

the polyester and the acrylic polymer and, optionally, other materials are combined with the polymer mixture to form a binder mixture. The binder optionally has up to about 20% by weight, based on total binder weight, of one or more resins or polymers (d) in addition to the polyester (a), the acrylic polymer (b), and the at least one crosslinker (c). The carboxylic acid-functional acrylic polymer (b) is then at least partially neutralized with ammonia and/or an amine, and the binder mixture is dispersed in an aqueous medium to form a binder dispersion or emulsion. One or more pigments and optionally one or more coating additives are added to the binder dispersion or emulsion to produce the electrocoat coating composition, , optionally along with more water, cosolvent, neutralizing base, and one or more further conventional additives. Part or all of the optional 20% by weight, based on total binder weight, of the one or more resins or polymers (d) in addition to the polyester (a), the acrylic polymer (b), and the at least one crosslinker (c) may serve as pigment dispersant and be added at this point as part of a pigment paste in which the pigments are dispersed. A matting agent may be added to the binder dispersion or emulsion in preparing the electrocoat coating composition, either as part of a pigment paste or separately from it.

[0011] An electrically conductive substrate, such as a metal automotive wheel or part or metal appliance body, is coated by placing the electrically conductive substrate in the anodic aqueous electrocoat coating composition containing the carboxylic acid-functional acrylic polymer, with the substrate as anode and a second electrode in the aqueous electrocoat coating composition serving as cathode, and passing a current through the aqueous electrocoat coating composition to deposit a coating layer comprising the binder onto the electrically conductive substrate. The deposited coating layer may then be cured to a cured coating layer. The at least one crosslinker (c) reacts with the polyester (a) and acrylic polymer (b), and, optionally, one or more resins (d) under curing conditions, e.g., at an elevated temperature. The cured coating has a 60° gloss of less than about 25, as measured according to ASTM D523. Subsequent coating layers may be applied on a portion, but less than the whole, of the electrodeposited coating layer. For example, other layers such as one or more of a spray-applied primer surfacer and a topcoat layer or topcoat layers (e.g., a colored basecoat layer and a clearcoat layer) may be applied over a portion but less than all of the electrodeposited coating layer's surface. At least a part of the electrodeposited coating layer remains uncoated with any further coating layer. All coating layers may be cured.

[0012] A coated substrate comprises a coating layer on the substrate, the coating layer comprising a cured coating formed from the electrocoat coatings already described by the methods already described.

[0013] In describing the invention, a "matte" or "low gloss" coating refers to a coating having a 60° gloss of not more than about 25, as determined according to ASTM D523. For convenience, "polymer" and "resin" are used interchangeably to encompass resins, oligomers, and polymers. "Binder" refers to the film-forming components of the coating composition. An acrylic polymer is a vinyl polymer prepared by addition polymerization of one or more acrylate and methacrylate monomers, optionally also with other vinyl monomers. For convenience, "acrylic" and "vinyl" are used interchangeably to refer to polymers of vinyl monomers (such as acrylate and methacylate monomers), as typically at least one acrylate or methacrylate monomer is copolymerized in the polymers (b).

[0014] "A" and "an" as used herein indicate "at least one" of the item is present; a plurality of such items may be present, when possible or desirable. In this disclosure, the numerical values represent approximate measures or limits to ranges to encompass minor deviations from the given values and embodiments having about the value mentioned as well as those having exactly the value mentioned. Other than in the working examples provides at the end of the detailed description, all numerical values of parameters (e.g., of quantities or conditions) in this specification, including the appended claims, are to be understood as being modified in all instances by the term "about" whether or not "about" actually appears before the numerical value. "About" indicates that the stated numerical value allows some slight imprecision (with some approach to exactness in the value; approximately or reasonably close to the value; nearly). If the imprecision provided by "about" is not otherwise understood in the art with this ordinary meaning, then "about" as used herein indicates at least variations that may arise from ordinary methods of measuring and using such parameters. In addition, disclosures of numerical ranges include disclosure of all possible values and subdivided ranges within the entire range, whether or not exemplary included values or subdivided ranges are also given.

DETAILED DESCRIPTION OF EMBODIMENTS

[0015] The polyester resin (a) having a hydroxyl-functional polyester with a hydroxyl number of from about 15 to about 40 mg KOH/g may be prepared generally by the condensation polymerization of polycarboxylic acid or anhydride compounds and polyol compounds. Preferably, the polycarboxylic acid or anhydride compounds and polyol compounds are entirely or mainly di-functional, so that dicarboxylic acid compounds, anhydrides of dicarboxylic acid compounds, and diols are used to prepare substantially linear polyester diols, although minor amounts of mono-functional, tri-functional, and higher functionality materials (perhaps up to about 5 mole percent) can be included, such as for endcapping (reacting a final polyfunctional compound with a polyester prepolymer). Suitable, nonlimiting examples of dicarboxylic acids and anydrides include glutaric acid, succinic acid, malonic acid, oxalic acid, phthalic acid, hexahydrophthalic acid, adipic acid, maleic acid, anhydrides of these, and the like, singly or in combination. Suitable, nonlimiting examples of higher functionality acids and/or anhydrides include trimellitic anhydride and the acid-functional half-esters of higher functionality polyols reacted with cyclic anhydrides, e.g. the reaction product of three moles of maleic anhydride and one mole of trimethylolpropane. Suitable, nonlimiting examples of monocarboxylic acids include pelargonic acid, stearic acid, and glycolic acid. Suitable, nonlimiting examples of diols include ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, tetrapropylene glycol, cyclohexanedimethanol, 2-ethyl-1,6-hexanediol, 1,4-butanediol, 1,5-pentanediol, 1,3-propanediol, butylene glycol, neopentyl glycol, diethanolamine, and the like, singly or in combination. Suitable, nonlimiting examples of triols or other higher functionality polyols, include trimethylolpropane and pentaerythritol. Suitable, nonlimiting examples of monoalcohols include butanol, hexanol, and ethanolamine.

[0016] The polyester is typically prepared by heating the acid and alcohol reactants together in the presence of an esterification catalyst. Typical catalysts for polymerization of a polyester resin are protonic acids, Lewis acids, titanium alkoxides, and dialkyltin oxides; others are known and may be used. The synthesis may be carried out without solvent present or with solvent, such as a solvent like toluene that forms an

azeotrope with water to aid in removing by-product water to drive the reaction to completion.

[0017] The reactants are selected and apportioned to provide a polyester with hydroxyl number of from about 15 to about 40 mg KOH/g. In certain embodiments, the polyester is solid at room temperature. In various embodiments, the polyester may have have a glass transition temperature from about 30°C to about 90°C. Glass transition temperatures are determined by gel permeation chromatography using polystyrene standards.

[0018] The electrocoat coating composition also includes an acrylic polymer (b) having hydroxyl and either amine groups or carboxylic acid groups. The amine or carboxylic acid groups are present in an amount and neutralized to an extent (from at least partial neutralization to overneutralization) to stabilize the binder dispersion. The acrylic polymer has one or more kinds of hydroxyl group-containing monomer units (a1) and one or more kinds of amine or carboxylic acid group-containing monomer units (a2). In various embodiments, amine group-containing monomer units (a2) may be provided by polymerization of a monomer to provide a monomer unit having a first functionality that is derivatized after polymerization to produce monomer units (a2) having amine or latent amine functionality. The acrylic polymer includes an amount of the hydroxyl group-containing monomer units (a1) to provide a hydroxyl number of from about 150 to about 200 mg KOH/g and an amount of the amine or carboxylic acid group-containing monomer units (a2) to stabilize the salted acrylic polymer electrocoat coating composition. In various embodiments, the acrylic polymer may have a hydroxyl number of from about 160 to about 200 mg KOH/g, or from about 150 to about 190 mg KOH/g, or from about 170 to about 200 mg KOH/g, or from about 160 to about 180 mg KOH/g. The acrylic polymer has an amine or carboxylic acid equivalent weight of from about 150 to about 5000; in various embodiments, the acrylic polymer has an amine or carboxylic acid equivalent weight of from about 500 to about 2000.

[0019] The monomer units (a1) may be provided by polymerizing a hydroxyl-containing, additional-polymerizable monomer or by polymerizing an additional-polymerizable monomer having functionality that is derivatized after polymerization to provide the hydroxyl group, or by a combination of these methods. It is possible to use all customary and known, hydroxyl-containing, olefinically unsaturated monomers in polymerization of the acrylic polymer to provide monomer units (a1).

Examples of suitable monomers that may be polymerized to provide monomer units (a1) in the acrylic polymer are hydroxyalkyl esters of acrylic acid, methacrylic acid or another α,β-olefinically unsaturated carboxylic acid, which derive from an alkylene glycol esterified with the acid or that may be obtained by reacting the α,β-olefinically unsaturated carboxylic acid with an alkylene oxide, especially hydroxyalkyl esters of acrylic acid, methacrylic acid, ethacrylic acid, crotonic acid, maleic acid, fumaric acid or itaconic acid in which the hydroxyalkyl group preferably contains up to 20 carbon atoms, such as 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, 3-hydroxybutyl, 4-hydroxybutyl acrylate, methacrylate, ethacrylate, crotonate, maleate, fumarate or itaconate; or hydroxycycloalkyl esters such as 1,4-bis-(hydroxymethyl)cyclohexane, octahydro-4,7-methano-1H-indenedimethanol or methylpropanediol monoacrylate, monomethacrylate, monoethacrylate, monocrotonate, monomaleate, monofumarate or monoitaconate; or reaction products of cyclic esters, such as epsilon-caprolactone, for example, and any of these hydroxyalkyl or hydroxycycloalkyl esters; or olefinically unsaturated alcohols such as allyl alcohol. The monomer units (a1) may also or alternatively be provided in the acrylic polymer by polymerizing a monomer that is derivatized or adducted after polymerization to provide a hydroxyl group. Among nonlimiting examples of suitable such monomers and their derivizations are (1) any of the hydroxyl-functional monomers already mentioned that, after polymerization, are further reacted with cyclic esters, such as epsilon-caprolactone; and (2) glydicyl-functional monomers such as glydicyl acrylate, glycidyl methacrylate, and allyl glycidyl ether that, after polymerization, are further reacted with a monocarboxylic acid such as acetic acid, propionic acid, or hexanoic acid or monoamines such as dibutylamine, methylethanolamine, and diethanolamine.

[0020] Likewise, the monomer units (a2) may be provided by polymerizing an amine- or carboxylic acid-containing, additional-polymerizable monomer or by polymerizing an additional-polymerizable monomer having functionality that is derivatized after polymerization to provide the amine or carboxylic acid group, or by both. The acrylic polymer has monomer units (a2) with amine groups in a cathodically electrodepositable electrocoat coating composition or has monomer units (a2) with carboxylic acid groups in an anodically electrodepositable electrocoat coating composition Examples of suitable monomers that may be polymerized to provide

monomer units (a2) in the acrylic polymer are N,N'-dimethylaminoethyl methacrylate, tert-butylaminoethyl methacrylate, N,N'-dimethylaminoethyl acrylate, tert-butylaminoethyl acrylate, or other such amino monomers for cathodically electrodepositable electrocoat coating compositions; and acrylic acid, methacrylic acid, ethacrylic acid, crotonic acid, maleic acid, maleic anhydride, fumaric acid or itaconic acid, itaconic anhydride, monoesters of ethylenically unsaturated dicarboxylic acids or anhydrides such as monomaleates like methyl maleate, monofumarates like methyl fumarate, and monoitaconates like methyl itaconate, and other such carboxyl monomers for anodically electrodepositable coating compositions. The monomer units (a2) may also or alternatively be provided in the acrylic polymer by polymerizing a monomer that is derivatized after polymerization to provide an amine or carboxylic acid group. In one method, an acrylic polymer formed from epoxide group-containing, addition-polymerizable monomer is, after polymerization, reacted with a compound having one secondary amine group to produce a tertiary amine group. Suitable examples of compounds having one secondary amine group include alkanolamines such as diethanolamine, dipropanolamine, diisopropanolamine, dibutanolamine, diisobutanolamine, diglycolamine, methylethanolamine, dimethylamine, dibutylamine, dipropylamine, and methylbutylamine. In one method, an acrylic polymer formed from hydroxyl group-containing, addition-polymerizable monomer, such as any of those already mentioned, is, after polymerization, reacted with a cyclic carboxylic acid anhydride to produce a carboxylic acid group. Suitable cyclic carboxylic anhydrides include maleic anhydride, succinic anhydride, trimellitic anhydride, hexahydrophthalic, phthalic anhydride, tetrahydrophthallic anhydride, isophthalic anhydride, methyl hexahydrophthalic anhydride, glutaric anhydride, 2-dodecen-1-ylsuccinic anhydride, dodecenylsuccinic anhydride, and combinations of these. In these embodiments, only a part of the hydroxyl groups of the acrylic polymer is reacted with the cyclic carboxylic acid anhydride so that, after this reaction, the acrylic polymer has a hydroxyl number of from about 150 to about 200 mg KOH/g in addition to having carboxylic acid functionality.

[0021] When the acrylic polymer has epoxide group-containing monomer units and is reacted with a compound having a single secondary amine group, both a tertiary amine and a hydroxyl group are provided. In this case, the resulting monomer unit having both a tertiary amine and a hydroxyl group is both the (a1) and the (a2)

monomer unit. When the secondary amine reactant includes one or more hydroxyl groups, the resulting monomer unit has both a tertiary amine group and a plurality of hydroxyl groups. The acrylic polymer may further include additional, different (a1) or (a2) monomer units. The reaction of the epoxide groups with the compound having a single secondary amine group may be conducted after the acrylic polymer, still having the epoxide groups, is combined with the polyester resin.

[0022] A sufficient amount of (a2) monomer units are included to form a stable and electrodepositable electrocoat coating composition when neutralized or salted. In general, the acrylic polymer has an amine or carboxylic acid equivalent weight of from about 200 to about 5000.

[0023] Examples of suitable comonomers that may be copolymerized in preparing the acrylic polymer having (a1) and (a2) monomer units include, without limitation, ethylenically unsatured esters, nitriles, or amides of α,β-ethylenically unsaturated monocarboxylic acids containing 3 to 5 carbon atoms and ethylenically unsaturated dicarboxylic acid and anhydrides; vinyl esters, vinyl ethers, vinyl ketones, vinyl amides, and vinyl compounds of aromatics and heterocycles. Representative examples include acrylic and methacrylic amides, and aminoalkyl amides; acrylonitrile and methacrylonitriles; esters of acrylic and methacrylic acid, including those of saturated aliphatic and cycloaliphatic alcohols containing 1 to 20 carbon atoms such as methyl methacrylate, ethyl acrylate, ethyl methacrylate, propyl acrylate, propyl methacrylate, isopropyl acrylate, isopropyl methacrylate, butyl acrylate, butyl methacrylate, isobutyl acrylate, isobutyl methacrylate, t-butyl acrylate, t-butyl methacrylate, amyl acrylate, amyl methacrylate, isoamyl acrylate, isoamyl methacrylate, hexyl acrylate, hexyl methacrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, decyl acrylate, decyl methacrylate, isodecyl acrylate, isodecyl methacrylate, dodecyl acrylate, dodecyl methacrylate, cyclohexyl acrylate, cyclohexyl methacrylate, substituted cyclohexyl acrylates and methacrylates, 3,5,5-trimethylhexyl acrylate, 3,5,5-trimethylhexyl methacrylate; dimethylaminoethyl, tert-butyl amino, tetrahydrofurfuryl, and isobornyl acrylates and methacrylates; the corresponding esters of maleic, fumaric, crotonic, isocrotonic, vinylacetic, and itaconic acids, and the like, such as maleic acid dimethyl ester and maleic acid monohexyl ester; vinyl monomers such as vinyl acetate, vinyl propionate, vinyl ethyl ether, and vinyl ethyl ketone, styrene, α-methyl styrene,

vinyl toluene, 2-vinyl pyrrolidone, t-butyl styrene, and the like. Other useful polymerizable co-monomers include, for example, alkoxyethyl acrylates and methacrylates, acryloxy acrylates and methacrylates, and compounds such as acrylonitrile, methacrylonitrile, acrolein, and methacrolein. Combinations of these are usually employed.

[0024] In various embodiments, the monomers used to make the acrylic polymer (b) may be chosen and used in such amounts to provide a theoretical glass transition temperature of from about 38°C to about 45°C, as determined using the Fox equation (T.G. Fox, Bull. Am. Physics Soc., Vol. 1, Issue No. 3, p. 123 (1956)).

[0025] Acrylic polymers may be prepared by using conventional techniques, such as free radical polymerization, cationic polymerization, or anionic polymerization, in, for example, a batch, semi-batch, or continuous feed process. For instance, the polymerization may be carried out by heating the ethylenically unsaturated monomers in bulk or in solution in the presence of a free radical source, such as an organic peroxide or azo compound and, optionally, a chain transfer agent, in a batch or continuous feed reactor. Alternatively, the monomers and initiator(s) may be fed into the heated reactor at a controlled rate in a semi-batch process.

[0026] Typical free radical sources are organic peroxides such as dialkyl peroxides, peroxyesters, peroxydicarbonates, diacyl peroxides, hydroperoxides, and peroxyketals; and azo compounds such as 2,2'-azobis(2-methylbutanenitrile) and 1,1'-azobis(cycohexanecarbonitrile). Typical chain transfer agents are mercaptans such as octyl mercaptan, n- or tert-dodecyl mercaptan, thiosalicyclic acid, mercaptoacetic acid, and mercaptoethanol; halogenated compounds, and dimeric alpha-methyl styrene. The free radical polymerization is usually carried out at temperatures from about 20°C to about 250°C, for example from 90°C to 170°C.

[0027] Nonlimiting examples of suitable reaction solvents that may be present include, without limitation, inert organic solvents such as ketones, including methyl isobutyl ketone and methyl amyl ketone, aromatic solvents such as toluene, xylene, Aromatic 100, and Aromatic 150, and esters, such as butyl acetate, n-propyl acetate, hexyl acetate, glycol ethers such as ethylene glycol monobutyl ether, propylene glycol monobutyl ether, and propylene glycol monopropyl ether and their esters such as propylene glycol monomethyl ether acetate.

[0028] The polyester and acrylic polymer may be combined to form a polymer mixture. When the acrylic polymer is epoxide-functional, a secondary amine is then reacted with the epoxide groups of the acrylic polymer to give tertiary amine groups. The acrylic polymer and the polyester are used in a ratio of from about 4 parts by weight acrylic polymer : 1 part by weight polyester (about 4:1 by weight) to about 1.5 parts by weight acrylic polymer : 1 part by weight polyester (about 1.5:1 by weight) so that electrocoat coating composition will include about 1.5 to about 4 parts by weight acrylic polymer per 1 part by weight polyester.

[0029] A crosslinker and optionally other materials are combined with the polymer mixture to form a binder mixture. Other orders of combining polyester, acrylic, crosslinker, and other materials may be used. Nonlimiting, suitable examples of crosslinking agents are blocked polyisocyanates and aminoplast resins. Suitable examples of blocked polyisocyanates crosslinkers that may be used are blocked aromatic, aliphatic or cycloaliphatic polyisocyanates such as blocked polyisocyanates selected from diphenylmethane-4,4'-diisocyanate (MDI), 2,4- or 2,6-toluene diisocyanate (TDI), p-phenylene diisocyanate, tetramethylene diisocyanate, hexamethylene diisocyanate, dicyclohexylmethane-4,4'-diisocyanate, isophorone diisocyanate, mixtures of phenylmethane-4,4'-diisocyanate, polymethylene polyphenylisocyanate, , 2-isocyanatopropylcyclohexyl isocyanate, dicyclohexylmethane 2,4'-diisocyanate, 1,3-bis(iso-cyanatomethyl)cyclohexane, diisocyanates derived from dimer fatty acids, as sold under the commercial designation DDI 1410 by Henkel, 1,8-diisocyanato-4-isocyanatomethyloctane, 1,7-diisocyanato-4-isocyanato-methylheptane or 1-isocyanato-2-(3-isocyanatopropyl)-cyclohexane, and higher polyisocyanates such as triphenylmethane-4,4',4"-triisocyanate, mixtures of these polyisocyanates, and polyisocyanates derived from these that contain isocyanurate, biuret, allophanate, iminooxadiazinedione, urethane, urea, or uretdione groups. Polyisocyanates containing urethane groups, for example, are obtained by reacting some of the isocyanate groups with polyols, such as trimethylolpropane, neopentyl glycol, and glycerol, hydroxyl-functional polyesters, or hydroxyl-functional polyethers, for example, with the reactants being in a ratio to yield an isocyanate-functional product. The isocyanate groups are reacted with a blocking agent that prevents premature reaction of the isocyanate groups in the aqueous electrocoat coating composition but that deblocks after the coating is electrodeposited and exposed to curing conditions at the curing temperature to allow

reaction with binder resin. Examples of suitable blocking agents include phenol, cresol, xylenol, epsilon-caprolactam, delta-valerolactam, gamma-butyrolactam, diethyl malonate, dimethyl malonate, ethyl acetoacetate, methyl acetoacetate, alcohols such as methanol, ethanol, isopropanol, propanol, isobutanol, tert-butanol, butanol, glycol monoethers such as ethylene or propylene glycol monoethers, acid amides (e.g. acetoanilide), imides (e.g. succinimide), amines (e.g. diphenylamine), imidazole, urea, ethylene urea, 2-oxazolidone, ethylene imine, oximes (e.g. methylethyl ketoxime), and the like. The blocked polyisocyanate crosslinkers may be used singly or in combinations of two or more blocked polyisocyanate crosslinkers. Suitable polyisocyanates and blocked polyisocyanate crosslinkers are available from BASF SE, Evonik Industries, and Bayer Material Science LLC. When the acrylic polymer is epoxide-functional, the reaction of the secondary amine with the epoxide groups of the acrylic polymer to give tertiary amine groups may be carried out after the crosslinker and optional other materials are combined with the polymer mixture.

[0030] Depending upon the application and performance standards, and genererally only in anodic electrocoat coating compositions, the crosslinker may be or include an aminoplast or phenolplast resin. As understood by those skilled in the art, an aminoplast resin is formed by the reaction product of formaldehyde and amine where the preferred amine is a urea or a melamine; a phenolplast resin is formed analogously. Although urea and melamine are the preferred amines, other amines such as triazines, triazoles, diazines, guanidines, or guanamines may also be used to prepare the aminoplast resins. Furthermore, although formaldehyde is preferred for forming the aminoplasts or phenolplast resin, other aldehydes, such as acetaldehyde, crotonaldehyde, and benzaldehyde, may also be used. Nonlimiting examples of suitable aminoplast resins include monomeric and polymeric melamine-formaldehyde resins, including melamine resins that are partially or fully alkylated using alcohols that preferably have one to six, more preferably one to four carbon atoms, such as hexamethoxy methylated melamine; urea-formaldehyde resins including methylol ureas and siloxy ureas such as butylated urea formaldehyde resin, alkylated benzoguanimines, guanyl ureas, guanidines, biguanidines, polyguanidines, and the like. Illustrative but non-limiting examples of useful aminoplast resins are those available under the trademark CYMEL from Cytec Industries and RESIMENE from Solutia Inc. Specific examples are CYMEL 1130 and 1156 and RESIMENE 750 and 753.

[0031] Optionally, plasticizers, flexibilizing resins, hydrophilic solvents, or both can be included in the binder mixture. Nonlimiting examples of plasticizers include ethylene or propylene oxide adducts of nonyl phenols, bisphenol A, cresol, or other such materials, or polyglycols based on ethylene oxide and/or propylene oxide. Plasticizers can be used at levels of up to 15 percent by weight of the total binder weight, for example from about 5 to about 10% by weight of the total binder weight. Modified epoxy flexibilizing resins can also be used at levels of up to 15 percent by weight of the total binder weight, for example from about 5 to about 10% by weight of the total binder weight. Nonlimiting examples of coalescing solvents include alcohols, glycol ethers, polyols, and ketones. Specific examples of suitable coalescing solvents include monobutyl and monohexyl ethers of ethylene glycol, phenyl ether of propylene glycol, monoalkyl ethers of ethylene glycol such as the monomethyl, monoethyl, monopropyl, and monobutyl ethers of ethylene glycol or propylene glycol; dialkyl ethers of ethylene glycol or propylene glycol such as ethylene glycol dimethyl ether and propylene glycol dimethyl ether; butyl carbitol; diacetone alcohol. The amount of coalescing solvent is not critical and is generally between about 0 to 15 percent by weight, preferably about 0.5 to 5 percent by weight based on total weight of the binder solids.

[0032] Other resins or polymers besides the plasticizer just described may be included, so long as the amount of resin or polymer (d) (resin or polymer other than the polyester, the acrylic polymer, and the crosslinker) is only up to about 20% by weight, based on total binder weight.

[0033] An amine-functional binder mixture is emulsified in water in the presence of an acid or a carboxylic acid- or anhydride-functional binder mixture is emulsified in water in the presence of a base. Nonlimiting examples of suitable acids include phosphoric acid, phosphonic acid, propionic acid, formic acid, acetic acid, lactic acid, or citric acid. Nonlimiting examples of suitable bases include ammonia, monoalkylamines, dialkylamines, or trialkylamines such as ethylamine, propylamine, dimethylamine, dibutylamine and cyclohexylamine; monoalkanolamine, dialkanolamine or trialkanolamine such as ethanolamine, diethanolamine, triethanolamine, propanolamine, isopropanolamine, diisopropanolamine, dimethylethanolamine and diethylethanolamine; morpholine, e.g., N-methylmorpholine or N-ethylmorpholine. The salting acid or base may be blended with the binder, mixed with the water, or both, before the binder is added to the water. The acid or base is used in an amount sufficient

to neutralize enough of the amine or acid groups to impart water-dispersibility to the binder and to make the binder electrophoretic. The amine or acid groups may be fully neutralized or even overneutralized; however, partial neutralization is usually sufficient to impart the required water-dispersibility and electrophoretic character. Saying that the resin is at least partially neutralized means that at least part of the neutralizable groups of the binder is neutralized, and up to all of such groups may be neutralized or even overneutralized. Typically, the binder is from about 40 to 150 percent neutralized and in some embodiments the binder is from about 60 to 120 percent neutralized.

[0034] The binder emulsion is then used to prepare an electrocoat coating composition (or bath). The electrocoat bath usually includes one or more pigments, generally added as part of a pigment paste or dispersion, and may contain any further desired materials such as coalescing aids, antifoaming aids, and other additives that may be added before or after emulsifying the binder. The pigments used may be inorganic pigments, including metal oxides, chromates, molybdates, phosphates, and silicates. Examples of inorganic pigments and fillers that could be employed are titanium dioxide, barium sulfate, carbon black, ocher, sienna, umber, hematite, limonite, red iron oxide, transparent red iron oxide, black iron oxide, brown iron oxide, chromium oxide green, strontium chromate, zinc phosphate, silica, calcium carbonate, talc, barytes, ferric ammonium ferrocyanide (Prussian blue), ultramarine, lead chromate, lead molybdate, aluminum silicate, precipitated barium sulfate, aluminum phosphomolybdate, and mica flake pigments. Organic pigments may also be used. Examples of useful organic pigments are metallized and non-metallized azo reds, quinacridone reds and violets, perylene reds, copper phthalocyanine blues and greens, carbazole violet, monoarylide and diarylide yellows, benzimidazolone yellows, tolyl orange, naphthol orange, and the like. A flatting agent may be included in the pigment paste or dispersion in an amount of up to about

[0035] The pigments may be dispersed using a grind resin or a pigment dispersant. The binder of the electrocoat coating composition may include optionally, up to about 20% by weight, based on total binder weight, of one or more resins or polymers other than the polyester, acrylic polymer, and crosslinker, such as any plasticizer or grind resin or other film-forming dispersant. Suitable examples of grind resin or pigment dispersant are those disclosed in EP 0 505 445 (Example 1.3); Ott et al., US 6,274,649; Carpenter et al., U.S. Pats. No. 5,231,134, 5,527,614, and 5,536,776; December, U.S.

Pates. No. 6,376,616, 6,881,779, and 6,919,402. Grind resins or dispersants typically may be used at levels of up to 15 percent by weight of the total binder weight, for example from about 5 to about 10% by weight of the total binder weight. The pigment-to-resin weight ratio in the electrocoat bath can be important and should be preferably less than 50:100, more preferably less than 40:100, and usually about 10 to 30:100. Higher pigment-to-resin solids weight ratios have been found to adversely affect coalescence and flow. Usually, the pigment is 10-40 percent by weight of the nonvolatile material in the bath. Preferably, the pigment is 15 to 30 percent by weight of the nonvolatile material in the bath. Any of the pigments and fillers generally used in electrocoat coating compositions may be included. A particulate flatting (or matting) agent (e.g. precipitated silica flatting agent, may be included and dispersed with the pigments in the pigment paste or pigment dispersion. If used, the flatting agent may be included in an amount of up to 15% of the total amount of pigments and fillers, and in some embodiments up to 10% or up to 8% of the total amount of pigments and fillers. Suitable flatting agents are available from Evonik Degussa Corporation under the trademark Acematt® and from W.R. Grace under the trademark Syloid®.

[0036] The electrocoat coating compositions can contain optional ingredients such as dyes, flow control agents, plasticizers, catalysts, wetting agents, surfactants, UV absorbers, HALS compounds, antioxidants, defoamers and so forth. Examples of surfactants and wetting agents include alkyl imidazolines such as those available from Ciba-Geigy Industrial Chemicals as AMINE C® acetylenic alcohols such as those available from Air Products and Chemicals under the tradename SURFYNOL®. Surfactants and wetting agents, when present, typically amount to up to 2 percent by weight binder solids.

[0037] Curing catalysts such as tin catalysts can be used in the coating composition. Typical examples are without limitation, tin and bismuth compounds including dibutyltin dilaurate, dibutyltin oxide, and bismuth octoate. When used, catalysts are typically present in amounts of about 0.05 to 2 percent by weight tin based on weight of total binder solids.

[0038] In general, the electrocoat coating compositions have a solids content of from about 5 to about 25 percent by weight and in certain embodiments from about 15 to 20 percent by weight. In general, the electrocoat coating bath has a conductivity

within 200 to 3000 micromhos per centimeter and preferably within the range of 500 to 1500 micromhos per centimeter.

[0039] The electrocoat coating composition is electrodeposited onto a metallic substrate and then cured to form a coated article. The electrodeposition may be carried out by processes known to those skilled in the art. The electrocoat coating composition may be applied on any conductive substrate, such as steel, copper, aluminum, or other metals or metal alloys, in some embodiments typically at a dry film thickness of 10 to 35 μm. The article coated with the electrodeposited electrocoat coating layer may be a metallic automotive part or body, a metal automotive wheel, a household appliance part or body, a metal container or enclosure, metal furniture, or another kind of metal article or metal part of an article. A method of coating an electrically conductive substrate, such as a metal automotive vehicle body or part, comprises placing an electrically conductive substrate into the electrocoat coating composition and, using the electrically conductive substrate as the one electrode of an electric cell that also includes a second electroconductive electrode, passing a current through the electrocoat coating composition causing a coating layer to deposit onto the electrically conductive substrate. For the aqueous electrocoat coating composition containing the amine-functional acrylic polymer, the substrate is attached as the cathode and the second electrode as the anode of the electric cell; for the aqueous electrocoat coating composition containing the carboxylic acid-functional acrylic polymer, the substrate is attached as the anode and the second electrode serves as cathode in the electric cell. The substrate is coated in the bath typically for from about 90 to 120 seconds. After the coating layer has been electrodeposited on the substrate to make a coated article, the coated article is removed from the bath and rinsed with deionized water. The coating may be cured under appropriate conditions, for example by baking at from about 180° F to about 380° F for between about 15 and about 60 minutes. The cured coating has a 60° gloss of up to about 25, preferably of less than about 20, particularly preferably of less than about 10.

[0040] Subsequent coating layers may be applied on a portion, but less than the whole, of the electrodeposited coating layer. For example, other layers such as one or more of a spray-applied primer surfacer and a topcoat layer or topcoat layers (e.g., a colored basecoat layer and a clearcoat layer) may be applied over a portion but less than

all of the electrodeposited coating layer's surface. A single layer topcoat is also referred to as a topcoat enamel. In the automotive industry, the topcoat is typically a basecoat that is overcoated with a clearcoat layer. A primer surfacer and the topcoat enamel or basecoat and clearcoat composite topcoat may be waterborne, solventborne, or a powder coating, which may be a dry powder or an aqueous powder slurry. Such further coating compositions may be purchased from BASF or prepared and applied as, for example, in on or more of U.S. Patents No. 7,338,989; 7,297,742; 6,916,877; 6,887,526; 6,727,316; 6,437,036; 6,413,642; 6,210,758; 6,099,899; 5,888,655; 5,866,259; 5,552,487; 5,536,785; 4,882,003; 4,190,569; 7,375,174; 7,342,071; 7,297,749; 7,261,926; 7,226,971; 7,160,973; 7,151,133; 7,060,357; 7,045,588; 7,041,729; 6,995,208; 6,927,271; 6,914,096; 6,900,270; 6,818,303; 6,812,300; 6,780,909; 6,737,468; 6,652,919; 6,583,212; 6,462,144; 6,337,139; 6,165,618; 6,129,989; 6,001,424; 5,981,080;5,855,964; 5,629,374; 5,601,879; 5,508,349; 5,502,101; 5,494,970; and 5,281,443, each assigned to BASF and each incorporated herein by reference.

[0041] Example

[0042] 4585 Grams acrylic polymer (polymerized from 25 wt.% hydroxymethyl methacrylate, 27 wt.% styrene, 15 wt.% methyl methacrylate, 10% wt.% glycidyl methacrylate, 23 wt.% butyl acrylate; 65 wt.% nonvolatile content, 27% toluene, 8% ethylene glycol monobutyl ether) are charged to a reactor and heated under nitrogen to 105-115°C. Solvent is distilled under vacuum, adding 891 grams of ethylene glycol monobutyl ether after a part of the distillate has been collected. After a total of 1524 grams of distillate is removed, the vacuum is removed. Maintaining the temperature at 105-115°C, 1539 grams of caprolactam-blocked isophorone diisocyanate and 1539 grams of RUCOTE® 123 (a polyester powder resin manufactured by Bayer, hydroxyl number 23 mg KOH/g, acid value 2 mgKOH/g, T_g 60°C, viscosity 7500 cPs (ICI cone and plate at 200°C)) are added and mixed until melted and blended. An additional 200 grams of ethylene glycol monobutyl ether are added, followed by 144 grams methylethanol amine and 20 grams of ethylene glycol monobutyl ether. The reaction mixture is allowed to exotherm and the contents of the reactor are stirred for 45 to 60 minutes. Next, a mixture of 196 grams of 88% lactic acid and 72 grams water is added and mixed in for 10-15 minutes. The contents of the reactor are then stirred into 7242 grams of water to produce an emulsion. The reactor is rinsed with 3693 grams of water, which is then added with stirring to the emulsion.

[0043] A pigment paste is prepared by combining 600 grams of an epoxy resin prepared according to EP 0 505 445 (Example 1.3), 66 grams of water, 28 grams of dibutyl tin oxide, 24 grams of a bismuth salt, 9 grams of carbon black, 77 grams of a yellow pigment, 6 grams of a green pigment, 10 grams of a red pigment, 40 grams of a white pigment, 373 grams of a clay, 38 grams of Acematt® OK412 from Evonik Degussa Corporation, and about 50 grams of water. The mixture is milled to a pigment fineness of about 15 micrometers to produce the pigment paste.

[0044] An electrodepostion coating compositon is prepared by combining 2382 grams of the emulsion, 583 grams of the pigment paste, 257 grams (90 grams nonvolatile) of an epoxy flexibilizing resin in water, and 3357 grams of water. A test panel (phosphated steel, 4x12 inches) is submerged in the bath and attached as the cathode of an electric cell. A current is passed between the cathode and an anode for about two minutes to deposit a coating layer on the test panel. The test panel is then removed, rinsed with water, and placed in a forced air oven heated to 360°F for 25 minutes to cure the deposited coating layer. The 60° gloss of the cured coating is about 8.

CLAIMS

What is claimed is:

1. An electrocoat coating composition comprising an aqueous emulsion or dispersion of a binder consisting essentially of

(a) a polyester with a hydroxyl number of from about 15 to about 40 mg KOH/g,

(b) an at least partially neutralized amine- or carboxylic acid-functional acrylic polymer with a hydroxyl number of from about 150 to about 200 mg KOH/g,

(c) at least one crosslinker for the polyester and the acrylic polymer, and

(d) optionally, up to about 20% by weight, based on total binder weight, of one or more additional resins or polymers,

wherein the electrocoat coating composition comprises about 1.5 to about 4 parts by weight acrylic polymer (b) per 1 part by weight polyester (a) and

wherein the electrocoat coating composition produces a matte coating when electrodeposited on a substrate and cured.

2. An electrocoat coating composition according to claim 1, wherein the acrylic polymer has an amine or carboxylic acid equivalent weight of from about 150 to about 5000.

3. An electrocoat coating composition according to claim 1 or claim 2, further including a matting agent.

4. A method of coating an electroconductive substrate, comprising placing the substrate in an electrocoat coating composition according to any one of claims 1 to 3, wherein the substrate is connected as an electrode; passing current between the substrate electrode and a second electrode in the electrocoat coating composition to electrodeposit a coating layer onto the substrate; and curing the coating layer to produce a coated substrate.

5. A coated substrate prepared according to claim 4, wherein the coated substrate has a 60° gloss of less than about 20.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2011/059333

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D5/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

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

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00/75242 A2 (PPG IND OHIO INC [US]) 14 December 2000 (2000-12-14) claims 1-5, 15, 18,24,26,49,51; example 1	1-5
X	US 2010/129659 A1 (NEMOTO YUKIHIRO [JP] ET AL) 27 May 2010 (2010-05-27) claims 1,8; examples 1-13	1-5
X	WO 03/040244 A1 (PPG IND OHIO INC [US]) 15 May 2003 (2003-05-15) claims 1-3,5,7,8,17,23,94; examples 1-5	1-5
X	DE 33 28 455 A1 (WIRTH THADDAEUS DR) 7 March 1985 (1985-03-07) claim 11; examples 26-45	1-5

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

[X] See patent family annex.

* Special categories of cited documents :

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 January 2012	18/01/2012

Name and mailing address of the ISA/	Authorized officer
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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2011/059333

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 032 570 A2 (DU PONT [US]) 29 July 1981 (1981-07-29) claims 1-5,9,10; examples I-XIV -----	1-5
X	US 4 094 843 A (MCGINNISS VINCENT DANIEL) 13 June 1978 (1978-06-13) claims 1-5,7,8,12; examples 1-6 -----	1-5

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2011/059333

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 0075242 A2	14-12-2000	AU 5278900 A	28-12-2000
		WO 0075242 A2	14-12-2000
US 2010129659 A1	27-05-2010	CN 101733243 A	16-06-2010
		JP 2010149106 A	08-07-2010
		US 2010129659 A1	27-05-2010
WO 03040244 A1	15-05-2003	US 2003098238 A1	29-05-2003
		US 2005092607 A1	05-05-2005
		WO 03040244 A1	15-05-2003
DE 3328455 A1	07-03-1985	NONE	
EP 0032570 A2	29-07-1981	BR 8008248 A	21-07-1981
		EP 0032570 A2	29-07-1981
US 4094843 A	13-06-1978	NONE	