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(54) Title: MODIFIED EPOXY RESIN COMPOSITIONS, REDUCED GLOSS COATING COMPOSITIONS

(57) Abstract

Epoxy resin compositions containing carboxyl-containing polymers as a low gloss additive are rendered more storage stable by the addition of a stabilizing amount of at least one stabilizer compound which is (a) at least one Group IA, IIA, IIB, IIIA, VIB or VIII of the periodic table of the elements metal salt of an organic carboxylic acid; (b) at least one of zinc carbonate, zinc oxide, sodium carbonate or potassium carbonate; or (c) any combination of (a) and (b). These compositions are particularly useful in powder coating applications.

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MODIFIED EPOXY RESIN COMPOSITIONS, REDUCED GLOSS COATING COMPOSITIONS

The present invention concerns modified epoxy resin compositions, curable compositions thereof and reduced gloss coating compositions.

Epoxy resin based powder coatings generally have a high gloss. In some applications, it is desirable to have coatings with reduced gloss. It is important that formulations which provide coatings with reduced gloss also provide coatings with a stable level of gloss over a period of time that the coating formulation might need to be stored.

Davis in US 4,419,495 discloses coating compositions containing an epoxy resin and as at least a part of the curing agent a polymer containing a group reactive with an epoxy resin. These coating compositions are said to have low gloss. While such coatings do indeed have low gloss, the coating compositions have a relatively short storage life. By that it is meant that the longer the coating composition is stored, the higher the gloss of the resulting coating. The gloss reduction pertains to comparison of the gloss of the coating prepared from like epoxy-containing substituents but not containing any copolymer having a group reactive with an epoxy group.

It would therefore be desirable to have available a modified epoxy resin composition containing a polymer with polymer groups reactive with an epoxy group which when formulated into a coating composition the coating composition would have improved storage stability with respect to the gloss value of the resultant coating.

One aspect of the present invention pertains to an improvement in a modified epoxy resin composition comprising

(A) at least one epoxy resin containing an average of more than one vicinal epoxy group per molecule and at least one aromatic ring in its backbone; and

(B) at least one polymer prepared from one or more ethylenically unsaturated monomers wherein at least one of such monomers contains a carboxylic acid group;

wherein the improvement resides in incorporating into said composition

(C) a stabilizing amount of at least one stabilizer compound which is

(a) at least one Group IA, IIA, IIB, IIIA, VIB or VIII of the periodic table of the elements metal salt of an organic carboxylic acid;
(b) at least one of zinc carbonate, zinc oxide, sodium carbonate or potassium carbonate; or
(c) any combination of (a) and (b).

Another aspect of the present invention pertains to an improvement in a composition suitable as a curing agent for epoxy resins which comprises

(1) at least one polymer prepared from one or more ethylenically unsaturated monomers wherein at least one of such monomers contains a carboxylic acid group; and

(2) at least one curing agent for said epoxy resin which curing agent is different from component (1);

wherein said improvement resides in incorporating into said curing agent composition

(3) a stabilizing amount of at least one stabilizer compound which is
(a) at least one Group IA, IIA, IIB, IIIA, VIB or VIII of the periodic table of the elements metal salt of an organic carboxylic acid;
(b) at least one of zinc carbonate, zinc oxide, sodium carbonate or potassium carbonate; or
(c) any combination of (a) and (b).

Another aspect of the present invention pertains to an improvement in a curable composition comprising

(A) at least one epoxy resin containing an average of more than one vicinal epoxy group per molecule and at least one aromatic ring in its backbone; and
(B) at least one polymer prepared from one or more ethylenically unsaturated monomers wherein at least one of such monomers contains a carboxylic acid group;
(D) at least one curing agent for component (A) which is different from either component (B) or the prereaction product of components (B) and (C);

wherein said improvement resides in incorporating into said composition;

(C) a stabilizing amount of at least one stabilizer compound which is
(a) at least one Group IA, IIA, IIB, IIIA, VIB or VIII of the periodic table of the elements metal salt of an organic carboxylic acid;
(b) at least one of zinc carbonate, zinc oxide, sodium carbonate or potassium carbonate; or
(c) any combination of (a) and (b).

A further aspect of the present invention pertains to an improvement in a powder coating composition which contains substantial quantities of pigment(s) or filler(s) comprising

(A) at least one epoxy resin containing an average of more than one vicinal epoxy group per molecule and at least one aromatic ring in its backbone;

(B) at least one polymer prepared from one or more ethylenically unsaturated monomers wherein at least one of such monomers contains a carboxylic acid group;

(D) at least one curing agent for component (A) which is different from either component (B) or the prereaction product of components (B) and (C); and

(E) at least one or more additional component(s) including pigment, filler, flow control agent, leveling aid or other additive;

wherein said improvement resides in incorporating into said composition;

(C) a stabilizing amount of at least one stabilizer compound which is

(a) at least one Group IA, IIA, IIB, IIIA, VIB or VIII of the periodic table of the elements metal salt of an organic carboxylic acid;

(b) at least one of zinc carbonate, zinc oxide, sodium carbonate or potassium carbonate; or

(c) any combination of (a) and (b).

A further aspect of the present invention pertains to an improvement in a powder coating composition which is essentially free of pigment(s) and filler(s) comprising

(A) at least one epoxy resin containing an average of more than one vicinal epoxy group per molecule and at least one aromatic ring in its backbone;

(B) at least one polymer prepared from one or more ethylenically unsaturated monomers wherein at least one of such monomers contains a carboxylic acid group;

(D) at least one curing agent for component (A) which is different from either component (B) or the prereaction product of components (B) and (C); and

(E) at least one or more additional component(s) selected from the group consisting of flow control agent, leveling aid, and promoter or catalyst;

wherein said improvement resides in incorporating into said composition;

(C) a stabilizing amount of at least one stabilizer compound which is

(a) at least one Group IA, IIA, IIB, IIIA, VIB or VIII of the periodic table of the elements metal salt of an organic carboxylic acid;

(b) at least one of zinc carbonate, zinc oxide, sodium carbonate or potassium carbonate; or

(c) any combination of (a) and (b).

A further aspect of the present invention pertains to the product resulting from curing the aforementioned curable composition.

A further aspect of the present invention pertains to articles which have been coated with the aforementioned coating composition.

The present invention may suitably comprise, consist of, or consist essentially of, the aforementioned components.

The invention illustratively disclosed herein suitably may be practiced in the absence of any component which is not specifically disclosed or enumerated herein and any of the compounds may contain or be free of any substituent not specifically named herein.

References herein to the Periodic Table of the Elements refer to that distributed by the Sargent-Welch Scientific Company as catalog no. S-18806.

The term "essentially free of pigment(s) and/or filler(s)" means that the composition is entirely free of or contains only inconsequential quantities of pigment(s) and/or filler(s), usually zero or less than 3, preferably less than 2, more preferably less than 1 percent by weight based upon total composition weight.

The term "contains substantial quantities of pigment(s) or filler(s)" means that the compositions contains more than inconsequential quantities of pigment(s) and/or filler(s), usually at least 3 percent by weight based upon total composition weight.

In the compositions of the present invention, all of the components can be simultaneously blended or mixed together by any suitable means.

Alternatively, the compositions of the present invention can be prepared by blending any one of the components: epoxy resin, carboxyl-containing polymer or stabilizer with a preblend of the remaining two components.

Also alternatively, the compositions of the present invention can be prepared by blending the epoxy resin with a prereaction product of the carboxyl-containing polymer and the stabilizer.

The blending can be accomplished by any suitable means such as dry blending, melt extrusion, 2-roll mill or other means of melt compounding, or any combination thereof.

When the compositions are prepared by melt extrusion, the temperature should be at a temperature such that no reaction takes place between the epoxy groups of the epoxy resin and the carboxyl groups of carboxyl-containing polymer. Preferably, the melt extrusion blending is conducted at a temperature of from 30°C to 120°C, more preferably from 40°C to 100°C, most preferably from 50°C to 70°C.

In any of the aforementioned methods of blending, the blending is conducted for a time sufficient to cause the resultant blend to be substantially homogeneous. By substantially homogeneous, it is meant a fine, uniform suspension with no individual particles large enough to be seen.

The preferred method of blending the carboxyl-containing polymer or the ionomer form of the carboxyl-containing polymer, the reaction product of the carboxyl-containing polymer with the stabilizer, is to blend the carboxyl-containing polymer or the ionomer form of the carboxyl-containing polymer with the epoxy resin in a separate step to form an epoxy resin modified with the carboxyl-containing polymer. The advantage of blending in this manner is that the carboxyl-containing polymer is more uniformly dispersed in the epoxy resin than if it is blended directly into a powder coating formulation. Also, it is preferable to blend the epoxy resin and the carboxyl-containing polymer or the ionomer form of the carboxyl-containing polymer at conditions which do not result in reaction between the epoxy groups and the acid groups. Such conditions are preferably at a temperature of from 30°C to 120°C, more preferably from 40°C to 100°C, most preferably from 50°C to 70°C.

In all of the compositions of the present invention, it is preferable to employ the ionomer form of the carboxyl-containing polymer. This is accomplished by prereacting the carboxyl-contining polymer with the stabilizer compound.

In the preparation of the curable compositions and the powder coating compositions, all of the components can be added separately and then blended or melt extruded or otherwise mixed or blended or any combination of mixing and blending. However, it is preferred to prepare a preblend of epoxy resin, carboxyl-containing polymer and stabilizer with the carboxyl-containing polymer and stabilizer being preblended or prereacted prior to blending with the epoxy resin prior to blending this preblend with the remaining components of the composition.

In the modified epoxy resin compositions and the curable compositions of the present invention, the stabilizer, component (C), is employed in an amount sufficient to provide a ratio of equivalents of metal per carboxyl equivalent of at least 0.04:1, preferably from 0.08:1 to 6:1, more preferably from 0.15:1 to 1:1.

In the compositions of the present invention which are suitable as curing agents for epoxy resins, the stabilizer, component (3), is employed in an amount sufficient to provide a ratio of equivalents of metal per carboxyl equivalent of at least 0.04:1, preferably from 0.08:1 to 6:1, more preferably from 0.15:1 to 1:1.

In the coating compositions of the present invention which contain substantial quantities of filler and/or pigment, the stabilizer, component (C), is employed in an amount sufficient to provide a ratio of equivalents of metal per carboxyl equivalent of at least 0.04:1, preferably from 0.08:1 to 6:1, more preferably from 0.15:1 to 1:1.

In the coating compositions of the present invention which are substantially free of filler and/or pigment, the stabilizer, component (C), is employed in an amount sufficient to provide a ratio of equivalents of metal per carboxyl equivalent of at least 0.5:1, preferably from 0.6:1 to 6:1, more preferably from 0.7:1 to 1:1.

In the curable compositions of the present invention, the epoxy resin component (A) is employed in an amount of from 66 to 99, preferably from 80 to 96, more preferably from 80 to 92 percent by weight based upon the combined weight of epoxy resin (A) and carboxyl-containing polymer (B).

In the curable compositions of the present invention, the carboxyl-containing polymer component (B) is employed in an amount of from 1 to 33, preferably from 4 to 20, more preferably from 8 to 20 percent by weight based upon the combined weight of epoxy resin component (A) and carboxyl-containing polymer component (B).

In the curable compositions of the present invention, the amount of the other curing agent, component (D), depends upon the particular curing agent being employed. Usually the other curing agent is employed in amounts which provide a ratio of equivalents of this curing agent, component (D), plus the polymer containing carboxylic acid groups or ionomers thereof, component (B), per epoxide equivalent contained in component (A) of from 0.8:1 to 3:1, preferably from 0.9:1 to 2.5:1, more preferably from 1:1 to 2:1.

In the curing agent compositions of the present invention the carboxyl-containing polymer, component (1), is employed in an amount of from 1 to 99, preferably from 3 to 96, more preferably from 25 to 90 percent by weight based upon the combined weight of components (1) and (2).

In the curing agent compositions of the present invention the other or different curing agent, component (2), is employed in an amount of from 99 to 1, preferably from 97 to 4, more preferably from 75 to 10 percent by weight based upon the combined weight of components (1) and (2).

In the curing agent compositions of the present invention, a promoter or catalyst component, can, if it is desirable to employ such promoter or catalyst, be employed in an amount of from 0.01 to 2, preferably from 0.1 to 1.5, more preferably from 0.2 to 0.8 percent by weight based upon the combined weight of all of the curing agents, the stabilizer component and the promoter or catalyst.

The curing agent compositions of the present invention can be prepared by simple blending or melt extruding all of the components.

The curable compositions can be prepared by blending, mixing, melt extruding or a combination thereof all of the components thereof.

The preparation of the curing agent compositions are usually prepared at temperatures of from 20°C to 200°C, preferably from 50°C to 150°C, more preferably from 70°C to 130°C for a time sufficient to produce a homogeneous product, usually within a time of from 15 seconds to 2 hours, depending upon how the components are blended together. If an extruder is employed in the preparation of the composition, shorter times of from 15 seconds up to 2 minutes is suitably employed. If a batch reactor or blender is employed, longer times are employed to prepare the composition such as from 5 minutes up to 2 hours.

It is not necessary to remove the byproduct(s) from the reaction between the carboxyl-containing polymer component and the stabilizer component prior to or after blending with the epoxy resin component. However, if desired, they can be readily removed by subjecting the composition to a vacuum and if desired heating while subjecting the composition to a vacuum at a temperature which is not detrimental to the composition, usually from room or ambient temperature to a temperature not above 120°C, preferably not above 100°C, more preferably not above 70°C. The pressure can be from zero to 760, preferably from zero to 200, more preferably from zero to 60 mm Hg absolute.

EPOXY RESINS

Suitable epoxy resins which can be employed herein as component (A) include, for example, any epoxy resin which contains at least one aromatic ring in its backbone.

Particularly suitable epoxy resins include, for example, the glycidyl ethers of: dihydric phenols, bisphenols, phenol- or substituted phenol-aldehyde novolac resins, adducts of dihydric phenols or bisphenols with an alkylene oxide having from 2 to 4 carbon atoms per molecule, phenol or substituted phenol-unsaturated hydrocarbon resins, or any combination of any two or more of such compounds; wherein said epoxy resin contains an average of more than one glycidyl ether group per molecule. These compounds can also contain substituent groups such as saturated aliphatic hydrocarbon, unsaturated aliphatic hydrocarbon, halogens including chlorine, bromine, fluorine, iodine, nitro, or nitrile. Likewise, the hydrocarbon substituent groups can also be substituted with such halogens including chlorine, bromine, fluorine, iodine, nitro, or nitrile. Also, these compounds can be specifically free of any one or more of such substituent groups and likewise the substituted hydrocarbons can be specifically free of any one or more of such substituent groups. Further, such compounds and substituted hydrocarbons can contain any substituent group not specifically enumerated herein. Likewise, the compounds and substituted hydrocarbons can be free of any substituent group not specifically enumerated herein.

The preferred epoxy resins include, for example, the glycidyl ethers of: resorcinol, catechol, hydroquinone, bisphenol A (4,4'-isopropylidenediphenol), bisphenol F (2,2'-methylenediphenol), bisphenol K (4,4'-dihydroxydiphenyl ketone), bisphenol S (4,4'-sulfonyldiphenol), fluorene, phenol-formaldehyde novolac resins, cresol-formaldehyde novolac resins, phenol-dicyclopentadiene resins, phenol-higher oligomers of dicyclopentadiene resins, cresol-dicyclopentadiene resins, cresol-higher oligomers of dicyclopentadiene resins; adducts of: either resorcinol, catechol, hydroquinone, bisphenol A, bisphenol F, bisphenol K, bisphenol S, or fluorene with ethylene oxide, propylene oxide or butylene oxide or any combination of such alkylene oxides; or any combination of any two or more of such glycidyl ethers. Also suitable are any of the aforementioned glycidyl ethers which contain from 1 to 2 halogen atoms, preferably bromine, per aromatic ring.

The epoxy resins of the present invention preferably have equivalent weights of from 200 to 2000, more preferably from 500 to 955, most preferably from 575 to 820. The equivalent weight being calculated on the basis of there being no substituent groups on the aromatic rings of the epoxy resin even if they in fact do contain substituent groups.

POLYMERS CONTAINING CARBOXYLIC ACID GROUP

Suitable polymers prepared from one or more ethylenically unsaturated monomers wherein at least one of such monomers contains a carboxylic acid group which can be employed herein as component (B) or (1) include, for example, those copolymers or interpolymers of one or more alpha-olefins having from 2 to 10 carbon atoms and one or more ethylenically unsaturated carboxylic acids or half esters of dibasic ethylenically unsaturated carboxylic acids.

Particularly suitable alpha-olefins include, for example, ethylene, propylene, butene, pentene, hexene, heptene, octene, nonene, decene or any combination of any two or more alpha-olefins. Ethylene is preferred.

Particularly suitable ethylenically unsaturated carboxylic acids include, for example, acrylic, methacrylic, maleic, fumaric, itaconic. Preferred are acrylic acid and methacrylic acid with acrylic acid being most preferred.

Particularly suitable half esters include the C_1 to C_{10}, preferably C_1 to C_6, more preferably C_1-C_4 hydrocarbon half esters of maleic, fumaric or itaconic acids. More particularly suitable are the methyl, ethyl, propyl, butyl, pentyl and hexyl half esters of such acids.

STABILIZER COMPONENT

Suitable stabilizers which can be employed herein include, for example, Group IA, IIA, IIB, IIIA, VIB or VIII of the periodic table of the elements metal salts of an organic carboxylic acid; zinc carbonate, zinc oxide, sodium carbonate or potassium carbonate; or any combination of any such stabilizers.

Particularly suitable stabilizers include, for example, zinc oxide, sodium carbonate, zinc carbonate, potassium carbonate, or sodium, lithium, potassium, zinc, calcium, magnesium, nickel, aluminum or chromium salt of a saturated or unsaturated aliphatic or cycloaliphatic or aromatic organic carboxylic acid having from 1 to 30, preferably from 1 to 18, more preferably from 1 to 2 carbon atoms per molecule, or a combination of any two or more of such compounds. Preferably such carboxylic acid salts include, for example zinc carbonate, zinc acetate, zinc propionate, zinc stearate, sodium acetate, calcium propionate, or any combination of any two or more of such compounds.

OTHER CURING AGENTS

Suitable curing agents which can be employed herein in addition to the polymers containing a carboxylic acid group or an ionomer thereof in the curing agent compositions or the curable compositions or powder coating compositions include, for example, guanidines, biguanides, aliphatic amines, aromatic amines, compounds containing an average of more than one phenolic hydroxyl group per molecule, aliphatic, cycloaliphatic or aromatic di- or poly-carboxylic acids or anhydrides, or any combination of two or more of such curing agents.

Particularly suitable curing agents which can be employed herein as component (D) or (2) include, for example, dicyandiamide, o-tolubiguanide, acid functional polyesters, compounds containing more than one phenolic group per molecule, or any combination of any two or more of such curing agents. The preferred curing agent is dicyandiamide.

The actual amount of curing agent employed depends upon the particular curing agent being employed. Usually the curing agent is employed in amounts which provide a ratio of equivalents of this curing agent plus the polymer containing carboxylic acid groups or ionomers thereof per epoxide equivalent of from 0.8:1 to 3:1, preferably from 0.9:1 to 2.5:1, more preferably from 1:1 to 2:1.

PROMOTER OR CATALYST

Suitable promoters or catalysts for promoting the.reaction between the curing agent component(s) with the epoxy resin, include, for example, primary, secondary or tertiary aliphatic or cycloaliphatic or aromatic amines, Lewis acids, Lewis bases, or any combination of any two or more of such promoters or catalysts.

Particularly suitable promoters or catalysts include, for example, imidazoles, substituted imidazoles, imidazoles adducted with an epoxide-containing compound such as mono-, di-or polyglycidyl ether compounds, substituted imidazoles adducted with an epoxide-containing compound such as mono-, di- or polyglycidyl ether compounds, or any combination of any two or more of such promoters or catalysts. The preferred promoters or catalysts are 2-methyl imidazole, 2-methyl imidazole adducted with a diglycidyl ether of bisphenol A, or any combination of any two or more of such promoters or catalysts.

The amount of promoter will depend upon the particular promoter and curing agent being employed. Usually, the amount of promoter employed is from 0.01 to 2, preferably from 0.1 to 1.5, more preferably from 0.2 to 0.8 percent by weight based upon the combined weight of all of the curing agents, the stabilizer component and the promoter or catalyst.

FILLERS

Suitable fillers which can be employed herein include, for example, mineral fillers such as, for example, inorganic oxides, carbonates, sulfates or silicates of a metal of Groups IA, IIA, IIIA, IIB, VIB, or VIII of the periodic table of the elements, or any combination of any two or more of such fillers. The preferred fillers are titanium oxide, calcium carbonate, barium sulfate, magnesium silicate strontium silicate, or any combination of any two or more of such fillers.

PIGMENTS

Suitable pigments which can be employed herein include, for example, any inorganic or organic pigment which will provide the composition with the desired color or any combination of any two or more of such pigments.

FLOW MODIFIERS OR FLOW CONTROL AGENTS

Suitable flow modifiers or flow control agents which can be employed herein include, for example, acrylate copolymers, silicones, fluorocarbons, or any combination of any two or more of such flow modifiers or flow control agents. The preferred modifiers or flow control agents are acrylate copolymers.

LEVELING AGENTS

Suitable leveling agents which can be employed herein include, for example, benzoin.

The optional fillers, pigments, flow modifiers or flow control agents, leveling agents, which can be employed herein are employed in functional amounts, i.e. those amounts which provide the coating with the desired properties which the particular additive imparts to the coating. These amounts will vary with the particular epoxy resin, curing agent and additive employed.

The filler(s) is (are) usually employed in amounts of from zero to 60, preferably from zero to 50, more preferably from 2 to 35 percent by weight based upon the total weight of the composition.

The pigment(s) is (are) usually employed in amounts of from zero to 50, preferably from zero to 40, more preferably from 2 to 35 percent by weight based upon the total weight of the composition.

The flow modifier(s) or flow control agent(s) is (are) usually employed in amounts of from zero to 5, preferably from zero to 3, more preferably from zero to 2 percent by weight based upon the total weight of the composition.

The leveling agent(s) is (are) employed in amounts of from zero to 2, preferably from zero to 1.5, more preferably from zero to 0.5 percent by weight based upon the total weight of the composition.

The following examples are illustrative of the present invention, but are not to be construed as to limiting the scope thereof in any manner.

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FLOW MODIFIER(S)

Flow Modifier A is Moderez™ MFP commercially available from Synthron Chemicals.

FILLER(S)

BS-1 is barium sulfate commercially available from Mountain Minerals as Sparwite W-10.

BS-2 is barium sulfate commercially available from Pfizer as Barytes #1.

PIGMENT(S)

Pigment A is carbon black commercially available from Columbia Chemicals as Raven 2000.

COMPARATIVE EXPERIMENT A

1. Preparation of an Epoxy resin modified with 8.0% by weight of a Carboxyl-Containing Polymer.

A modified epoxy resin is prepared by extruder melt mixing at a temperature of 90°C-110°C Carboxyl-Containing Polymer A and Epoxy Resin A at a weight ratio of 0.087:1 in a 100-mm Baker-Perkins twin-screw extruder. The product is extruded as a thin sheet onto a chilled belt and then crushed.

2. Preparation of powder coating.

A powder coating formulation is prepared by melt mixing 2,000 g of the modified epoxy resin from 1 above, 80 g of Curing Agent B, and 26 g of Flow Modifier A. A dry blend of these components, prepared by shaking the components together in a plastic bag, is melt mixed in a Buss Condux PLK 46 extruder having two zones with zone 1 at 70°C, zone 2 at 90°C, and the screw at 70°C and 200 rpm. The extrudate is pressed with chilled rollers to a thin sheet, air cooled, ground to a fine powder with a Brinkmann ZM-1 grinder and sieved through 150 mesh brass sieves (105-micron opening). A portion of the powder is coated within two days following the melt-mixing. A portion of the powder is coated after aging for 43 days at ambient temperature. The powder is sprayed with a Gema Type 710 electrostatic spray gun, 60 kv applied, onto grounded cold rolled steel panels. The powder coated panels are baked for 15 minutes at 180°C and air cooled.

EXAMPLE 1

A powder coating formulation is prepared by melt mixing 2,000 g of the modified epoxy resin from Comparative Experiment A-1, 80 g of Curing Agent B, 26 g of Flow Modifier A, and 80 g of $CaPr_2$ stabilizer. The composition is prepared and tested in the same way and at the same time as Comparative Experiment A-2.

EXAMPLE 2

A powder coating formulation is prepared by melt mixing 2000 g of the modified epoxy resin from Comparative Experiment A-1, 80 g of Curing Agent B, 26 g of Flow Modifier A, and 240 g of $CaPr_2$ stabilizer. The composition is prepared and tested in the same way and at the same time as Comparative Experiment A-2.

COMPARATIVE EXPERIMENT B

1. Preparation of an Epoxy resin modified with 20% by weight of a Carboxyl-Containing Polymer.

A modified epoxy resin is prepared by melt mixing 2,000 g of Carboxyl-Containing Polymer A and 8,000 g of Epoxy Resin B. A dry blend of these components, prepared by shaking the components together in a plastic bag, is melt mixed in a Buss Condux PLK 46 extruder having two zones with zone 1 at 70°C, zone 2 at 80°C, and the screw at 70°C and 200 rpm. The modified epoxy resin extrudate is pressed with chilled rollers to a thin sheet, air cooled, and crushed.

2. Preparation of powder coating.

A powder coating formulation is prepared by melt mixing 600 g of the modified epoxy resin from 1 above, 600 g of additional Epoxy Resin B, 48 g of Curing Agent A, and 10.06 g of Flow Modifier A. A dry blend of these components, prepared by shaking the components together in a plastic bag, is melt mixed in a Buss Condux PLK 46 extruder having two zones with zone 1 at 70°C, zone 2 at 90°C, and the screw at 70°C and 200 rpm. The extrudate is pressed with chilled rollers to a thin sheet, air cooled, ground to a fine powder with a Brinkmann ZM-1 grinder and sieved through 150 mesh brass sieves (105-micron opening). A portion of the powder is coated within two days following the melt mixing. Another portion of the powder is coated after aging for 23 hours at 36°C. The powder is electrostatically sprayed with a Gema gun onto grounded cold rolled steel panels. The powder coated panels are baked for 15 minutes at 180°C and air cooled.

COMPARATIVE EXPERIMENT C

A powder coating formulation is prepared by melt mixing 600 g of the modified epoxy resin from Comparative Experiment B-1, 600 g of additional Epoxy Resin B, 48 g of Curing Agent A, 10.06 g of Flow Modifier A, and 12 g of $CaPr_2$ stabilizer. The composition is prepared and tested in the same way and at the same time as Comparative Experiment B-2.

EXAMPLE 3

A powder coating formulation is prepared by melt mixing 600 g of the modified epoxy resin from Comparative Experiment B-1, 600 g of additional Epoxy Resin B, 48 g of Curing Agent A, 10.06 g of Flow Modifier A, and 24 g of $CaPr_2$ stabilizer. The composition is prepared and tested in the same way and at the same time as Comparative Experiment B-2.

EXAMPLE 4

A powder coating formulation is prepared by melt mixing 600 g of the modified epoxy resin from Comparative Experiment B-1, 600 g of additional Epoxy Resin B, 48 g of Curing Agent A, 10.06 g of Flow Modifier A, and 48 g of $CaPr_2$ stabilizer. The composition is prepared and tested in the same way and at the same time as Comparative Experiment B-2.

COMPARATIVE EXPERIMENT D

1. Preparation of an Epoxy resin modified with 20% by weight of a Carboxyl-Containing Polymer.

Same as Comparative Experiment B-1.

2. Preparation of powder coating.

A powder coating formulation is prepared by melt mixing 600 g of the modified epoxy resin described in 1 above, 600 g of additional Epoxy Resin B, 48 g of Curing Agent A, 245 g of BS-2 filler, 22.97 g of Pigment A, and 15.31 g of Flow Modifier A. A dry blend, prepared by shaking the components together in a plastic bag, is melt mixed in a Buss Condux PLK 46 extruder having two zones with zone 1 at 70°C, zone 2 at 90°C, and the screw at 70°C and 200 rpm. The extrudate is pressed with chilled rollers to a thin sheet, air cooled, ground to a fine powder with a Brinkmann ZM-1 grinder and sieved through 150-mesh brass sieves. A portion of the powder is coated within one day following the melt mixing. A portion of the powder is coated after aging for 20 hours at 40°C. The powder is electrostatically sprayed with a Gema gun onto grounded cold rolled steel panels. The powder coated panels are baked for 15 minutes at 180°C and air cooled.

EXAMPLE 5

A powder coating formulation is prepared by melt mixing 600 g of the modified epoxy resin from Comparative Experiment D-1, 600 g of additional Epoxy Resin B, 48 g of Curing Agent A, 247 g of BS-2 filler, 23.19 g of Pigment A, and 15.46 g of Flow Modifier A, and 12 g of $CaPr_2$ stabilizer. The composition is prepared and tested in the same way and at the same time as Comparative Experiment D-2.

EXAMPLE 6

A powder coating formulation is prepared by melt mixing 600 g of the modified epoxy resin from Comparative Experiment D-1, 600 g of additional Epoxy Resin B, 48 g of Curing Agent A, 250 g of BS-2 filler, 23.41 g of Pigment A, and 15.61 g of Flow Modifier A, and 24 g of $CaPr_2$ stabilizer. The composition is prepared and tested in the same way and at the same time as Comparative Experiment D-2.

EXAMPLE 7

A powder coating formulation is prepared by melt mixing 600 g of the modified epoxy resin from Comparative Experiment D-1, 600 g of additional Epoxy Resin B, 48 g of Curing Agent A, 254 g of BS-2 filler, 23.85 g of Pigment A, and 15.90 g of Flow Modifier A, and 48 g of $CaPr_2$ stabilizer. The composition is prepared and tested in the same way and at the same time as Comparative Experiment D-2.

COMPARATIVE EXPERIMENT E

1. Preparation of an Epoxy resin modified with 15% by weight of a Carboxyl-Containing Polymer.

A modified epoxy resin is prepared by melt mixing 1,800 g of Carboxyl-Containing Polymer A and 10,200 g of Epoxy Resin B. A dry blend, prepared by shaking these components together in a plastic bag, is melt mixed in a Buss Condux PLK 46 extruder having two zones with zone 1 at 70°C, zone 2 at 80°C, and the screw at 70°C and 212 rpm. The modified epoxy resin extrudate is pressed with chilled rollers to a thin sheet, air cooled, and crushed.

2. Preparation of powder coating.

A powder coating formulation is prepared by melt mixing 1,200 g of the modified epoxy resin prepared in 1 above, 600 g of additional Epoxy Resin B, 72 g of Curing Agent A, and 18.9 g of Flow Modifier A. A dry blend, prepared by shaking the components together in a plastic bag, is melt mixed in a Buss Condux PLK 46 extruder having two zones with zone 1 at 70°C, zone 2 at 90°C, and the screw at 70°C and 200 rpm. The extrudate is pressed with chilled rollers to a thin sheet, air cooled, ground to a fine powder with a Brinkmann ZM-1 grinder and sieved through 150 mesh brass sieves. A portion of the powder is coated within two days following the melt mixing. A portion of the powder is coated after aging for 24 hours at 40°C. A portion of the powder is coated after aging for 27 days at ambient temperature. The powder is electrostatically sprayed with a Gema gun onto grounded cold rolled steel panels. The powder coated panels are baked for 15 minutes at 180°C and air cooled.

EXAMPLE 8

A powder coating formulation is prepared by melt mixing 1,200 g of the modified epoxy resin from Comparative Experiment E-1, 600 g of additional Epoxy Resin B, 72 g of Curing Agent A, 19.2 g of Flow Modifier A, and 31.2 g of $CaPr_2$ stabilizer. The composition is prepared and tested in the same way and at the same time as Comparative Experiment E-2.

EXAMPLE 9

A powder coating formulation is prepared by melt mixing 1,200 g of the modified epoxy resin from Comparative Experiment E-1, 600 g of additional Epoxy Resin B, 72 g of Curing Agent A, 19.3 g of Flow Modifier A, and 37.2 g of $ZnAc_2$ stabilizer. The composition is prepared and tested in the same way and at the same time as Comparative Experiment E-2.

EXAMPLE 10

A powder coating formulation is prepared by melt mixing 1,200 g of the modified epoxy resin from Comparative Experiment E-1, 600 g of additional Epoxy Resin B, 72 g of Curing Agent A, 20.0 g of Flow Modifier A, and 105.6 g of $ZnSt_2$ stabilizer. The composition is prepared and tested in the same way and at the same time as Comparative Experiment E-2.

COMPARATIVE EXPERIMENT F

1. Preparation of an Epoxy resin modified with 15% by weight of a Carboxyl-Containing Polymer.

A modified epoxy resin is prepared by melt mixing 900 g of Carboxyl-Containing Polymer A and 5,100 g of Epoxy Resin B. A dry blend, prepared by shaking the components together in a plastic bag, is melt mixed in a Buss Condux PLK 46 extruder with zone 1 at 70°C, zone 2 at 80°C, and the screw at 70°C and 212 rpm. The modified epoxy resin extrudate is pressed with chilled rollers to a thin sheet, air cooled, and crushed.

2. Preparation of powder coating.

A powder coating formulation is prepared by melt mixing 1,500 g of the modified epoxy resin prepared in 1 above, 60 g of Curing Agent A, 300 g of BS-1 filler, 28.6 g of Pigment A, and 19.1 g of Flow Modifier A. A dry blend, prepared by shaking the components together in a plastic bag, is melt mixed in a Buss Condux PLK 46 extruder having two zones with zone 1 at 70°C, zone 2 at 80°C, and the screw at 70°C and 200 rpm. The extrudate is pressed with chilled rollers to a thin sheet, air cooled, ground to a fine powder with a Brinkmann ZM-1 grinder and sieved through 150-mesh brass sieves. A portion of the powder is coated within one day following the melt mixing. Another portion of the powder is coated after aging for 24 hours at 40°C. Another portion of the powder is coated after aging for 33 days at ambient temperature. The powder is sprayed with a Wagner G100 EPB electrostatic spray gun onto grounded cold rolled steel panels. The powder coated panels are baked for 15 minutes at 180°C and air cooled.

EXAMPLE 11

A. Preparation of prereaction product of Carboxyl-Containing Polymer and metal salt.

A prereaction product (ionomer) of Carboxyl-Containing Polymer A is prepared by melt mixing 11.7 g/min of $CaPr_2$ stabilizer and 270 g/min of Carboxyl-Containing Polymer A in a Werner and Pfleiderer (WP) 30-mm twin-screw extruder. The barrel temperatures are: zone 1 at 52°C and zones 2 - 5 at 113°C - 121°C. The product is extruded through a 3-strand die, water cooled, and chopped to 1/4 in (6.35 mm) pellets.

B. Preparation of an Epoxy resin modified with 15% by weight of a Carboxyl-Containing Polymer.

A modified epoxy resin is prepared by melt mixing 900 g of the calcium ionomer of Carboxyl-Containing Polymer A prepared in A above and 5,100 g of Epoxy Resin B. The composition is prepared in the same way as the modified resin from Comparative Experiment F-1.

C. Preparation of powder coating.

A powder coating formulation is prepared by melt mixing 1500 g of the modified epoxy resin from B above, 60 g of Curing Agent A, 300 g of BS-1 filler, 28.6 g of Pigment A, and 19.1 g of Flow Modifier A. The composition is prepared and tested in the same way and at the same time as Comparative Experiment F-2.

EXAMPLE 12

A. Preparation of prereaction product of Carboxyl-Containing Polymer and metal salt.

A prereaction product (ionomer) of Carboxyl-Containing Polymer A is prepared by melt mixing 13.2 g/min of $ZnAc_2$ stabilizer and 270 g/min of Carboxyl-Containing Polymer A in a Werner and Pfleiderer (WP) 30-mm twin-screw extruder. The barrel temperatures are: zone 1 at 52°C and zones 2 - 5 at 113°C - 121°C. The product is extruded through a 3-strand die, water cooled, and chopped to 1/4 in (6.35 mm) pellets.

B. Preparation of an Epoxy resin modified with 15% by weight of a Carboxyl-Containing Polymer.

A modified epoxy resin is prepared by melt mixing 900 g of the zinc ionomer of Carboxyl-Containing Polymer A and 5,100 g of Epoxy Resin B. The composition is prepared in the same way as the modified resin from Comparative Experiment F-1.

C. Preparation of powder coating.

A powder coating formulation is prepared by melt mixing 1,500 g of the modified epoxy resin from B above, 60 g of Curing Agent A, 300 g of BS-1 filler, 28.6 g of Pigment A, and 19.1 g of Flow Modifier A. The composition is prepared and tested in the same way and at the same time as Comparative Experiment F-2.

COMPARATIVE EXPERIMENT G

1. Preparation of an Epoxy resin modified with 15% by weight of a Carboxyl-Containing Polymer.

A modified epoxy resin is prepared by melt mixing 600 g of Carboxyl-Containing Polymer A and 3,400 g of Epoxy Resin B. A dry blend, prepared by shaking the components together in a plastic bag, is melt mixed in a Buss Condux PLK 46 extruder having two zones with zone 1 at 70°C, zone 2 at 80°C, and the screw at 70°C and 200 rpm. The modified epoxy resin extrudate is pressed with chilled rollers to a thin sheet, air cooled, and crushed.

2. Preparation of powder coating.

A powder coating formulation is prepared by melt mixing 1,500 g of the modified epoxy resin prepared in 1 above, 60 g of Curing Agent A, 300 g of BS-1 filler, 28.6 g of Pigment A, and 19.1 g of Flow Modifier A. A dry blend, prepared by shaking the components together in a plastic bag, is melt mixed in a Buss Condux PLK 46 extruder having two zones with zone 1 at 70°C, zone 2 at 80°C, and the screw at 70°C and 200 rpm. The extrudate is pressed with chilled rollers to a thin sheet, air cooled, ground to a fine powder with a Brinkmann ZM-1 grinder and sieved through 150-mesh brass sieves. A portion of the powder is coated within one day following the melt mixing. A portion of the powder is coated after aging for 24 hours at 40°C. The powder is electrostatically sprayed with a Wagner gun onto grounded cold rolled steel panels. The powder coated panels are baked for 15 minutes at 180°C and air cooled.

EXAMPLE 13

A. Preparation of prereaction product of Carboxyl-Containing Polymer and metal salt.

A prereaction product (ionomer) of Carboxyl-Containing Polymer A is prepared by melt mixing 8.8 g/min of $ZnAc_2$ stabilizer and 355 g/min of Carboxyl-Containing Polymer A in a WP 30-mm twin-screw extruder. The barrel temperatures are zone 1 at 53°C and zones 2 - 5 at 109 - 117°C. The product is extruded through a 3-strand die, water cooled, and chopped to 1/4 in (6.35 mm) pellets.

B. Preparation of an Epoxy resin modified with 15% by weight of a Carboxyl-Containing Polymer.

A modified epoxy resin is prepared by melt mixing 600 g of the zinc ionomer of Carboxyl-Containing Polymer A prepared in A above and 3,400 g of Epoxy Resin B. The composition is prepared in the same way as the modified resin from Comparative Experiment G-1.

C. Preparation of powder coating.

A powder coating formulation is prepared by melt mixing 1,500 g of the modified epoxy resin from B above, 60 g of Curing Agent A, 300 g of BS-1 filler, 28.6 g of Pigment A, and 19.1 g of Flow Modifier A. The composition is prepared and tested in the same way and at the same time as Comparative Experiment G-2.

EXAMPLE 14

A. Preparation of prereaction product of Carboxyl-Containing Polymer and metal salt.

A prereaction product (ionomer) of Carboxyl-Containing Polymer A is prepared by melt mixing 17.1 g/min of $ZnAc_2$ stabilizer and 355 g/min of Carboxyl-Containing Polymer A in a WP 30-mm twin-screw extruder. The barrel temperatures are: zone 1 at 51°C and zones 2 - 5 at 105 - 116°C. The product is extruded through a 3-strand die, water cooled, and chopped to 1/4 in (6.35 mm) pellets.

B. Preparation of an Epoxy resin modified with 15% by weight of a Carboxyl-Containing Polymer.

A modified epoxy resin is prepared by melt mixing 600 g of the zinc ionomer of Carboxyl-Containing Polymer A and 3,400 g of Epoxy Resin B. The composition is prepared in the same way as the modified resin from Comparative Experiment G-1.

C. Preparation of powder coating.

A powder coating formulation is prepared by melt mixing 1500 g of the modified epoxy resin from B above, 60 g of Curing Agent A, 300 g of BS-1 filler, 28.6 g of Pigment A, and 19.1 g of Flow Modifier A. The composition is prepared and tested in the same way and at the same time as Comparative Experiment G-2.

EXAMPLE 15

A. Preparation of powder coating.

A powder coating formulation is prepared by melt mixing 1,500 g of the modified epoxy resin from Comparative Experiment G-1, 60 g of Curing Agent A, 300 g of BS-1 filler, 28.6 g of Pigment A, 19.1 g of Flow Modifier A, and 11.25 g of ZnAc2 stabilizer. The composition is prepared and tested in the same way and at the same time as Comparative Experiment G-2.

COMPARATIVE EXPERIMENT H

1. Preparation of an Epoxy resin modified with 15% by weight of a Carboxyl-Containing Polymer.

A modified epoxy resin is prepared by extruder melt mixing at a temperature of 90°C-110°C Carboxyl-Containing Polymer A and Epoxy Resin B at a weight ratio of 0.85:1 in a 100 mm Baker-Perkins twin-screw extruder. The product is extruded as a thin sheet onto a chilled belt and then crushed.

2. Preparation of powder coating.

A powder coating formulation is prepared by melt mixing 1,500 g of the modified epoxy resin from 1 above, 60 g of Curing Agent A, 300 g of BS-1 filler, 28.6 g of Pigment A, and 19.1 g of Flow Modifier A. A dry blend, prepared by shaking the components together in a plastic bag, is melt mixed in a Buss Condux PLK 46 extruder having two zones with zone 1 at 70°C, zone 2 at 80°C, and the screw at 70°C and 200 rpm. The extrudate is pressed with chilled rollers to a thin sheet, air cooled, ground to a fine powder with a Brinkmann ZM-1 grinder and sieved through 150-mesh brass sieves. A portion of the powder is coated within one day following the melt mixing. Another portion of the powder is coated after aging for 24 hours at 40°C. The powder is electrostatically sprayed with a Wagner gun onto grounded cold rolled steel panels. The powder coated panels are baked for 15 minutes at 180°C and air cooled.

EXAMPLE 16

A. Preparation of prereaction product of Carboxyl-Containing Polymer and metal salt.

A prereaction product (ionomer) of Carboxyl-Containing Polymer A is prepared by melt mixing 22.5 g/min of NaAc stabilizer and 355 g/min of Carboxyl-Containing Polymer A in a WP 30-mm twin-screw extruder. The barrel temperatures are zone 1 at 50°C and zones 2 - 5 at 104°C -

107°C. The product is extruded through a 3-strand die, water cooled, and chopped to 1/4 in (6.35 mm) pellets.

B. Preparation of an Epoxy resin modified with 15% by weight of a Carboxyl-Containing Polymer.

A modified epoxy resin is prepared by melt mixing 600 g of the zinc ionomer of Carboxyl-Containing Polymer A and 3,400 g of Epoxy Resin B. The composition is prepared in the same way as the modified resin from Comparative Experiment G-1.

C. Preparation of powder coating.

A powder coating formulation is prepared by melt mixing 1,500 g of the modified epoxy resin from B above, 60 g of Curing Agent A, 300 g of BS-1 filler, 28.6 g of Pigment A, and 19.1 g of Flow Modifier A. The composition is prepared and tested in the same way and at the same time as Comparative Experiment H-2.

EXAMPLE 17

A. Preparation of prereaction product of Carboxyl-Containing Polymer and metal salt.

A prereaction product (ionomer) of Carboxyl-Containing Polymer A is prepared by melt mixing 47.3 g/min of $ZnAc_2$ stabilizer and 355 g/min of Carboxyl-Containing Polymer A in a WP 30-mm twin-screw extruder. The barrel temperatures are zone 1 at 48°C and zones 2 - 5 at 105 - 113°C. The product is extruded through a 3-strand die, water cooled, and chopped to 1/4 in (6.35 mm) pellets.

B. Preparation of an Epoxy resin modified with 15% by weight of a Carboxyl-Containing Polymer.

A modified epoxy resin is prepared by melt mixing 600 g of the zinc ionomer of Carboxyl-Containing Polymer A and 3400 g of Epoxy Resin B. The composition is prepared in the same way as the modified resin from Comparative Experiment G-1.

C. Preparation of powder coating.

A powder coating formulation is prepared by melt mixing 1,500 g of the modified epoxy resin from B above, 60 g of Curing Agent A, 300 g of BS-1 filler, 28.6 g of Pigment A, and 19.1 g of Flow Modifier A. The composition is prepared and tested in the same way and at the same time as Comparative Experiment H-2.

EXAMPLE 18

A. Preparation of powder coating.

A powder coating formulation is prepared by melt mixing 1,500 g of the modified epoxy resin from Comparative Experiment G-1, 60 g of Curing Agent A, 300 g of BS-1 filler, 28.6 g of Pigment A, 19.1 g of Flow Modifier A, and 11.25 g of $ZnAc_2$ stabilizer. The composition is prepared and tested in the same way and at the same time as Comparative Experiment H-2.

EXAMPLE 19

A. Preparation of prereaction product of Carboxyl-Containing Polymer and metal salt.

A prereaction product (ionomer) of Carboxyl-Containing Polymer A is prepared by melt mixing 48.2 g/min of $ZnSt_2$ stabilizer and 355 g/min of Carboxyl-Containing Polymer A in a WP 30-mm twin-screw extruder. The barrel temperatures are zone 1 at 56°C and zones 2 - 5 at 128°C - 139°C. The product is extruded through a 3-strand die, water cooled, and chopped to 1/4 in (6.35 mm) pellets.

B. Preparation of an Epoxy resin modified with 15% by weight of a Carboxyl-Containing Polymer.

A modified epoxy resin is prepared by melt mixing 600 g of the zinc ionomer of Carboxyl-Containing Polymer A and 3400 g of Epoxy Resin B. The composition is prepared in the same way as the modified resin from Comparative Experiment G-1.

C. Preparation of powder coating.

A powder coating formulation is prepared by melt mixing 1,500 g of the modified epoxy resin, 60 g of Curing Agent A, 300 g of BS-1 filler, 28.6 g of Pigment A, and 19.1 g of Flow Modifier A. The composition is prepared and tested in the same way and at the same time as Comparative Experiment H-2.

EXAMPLE 20

A. Preparation of prereaction product of carboxyl-containing polymer and metal salt.

A prereaction product (ionomer) of Carboxyl-Containing Polymer A is prepared by melt mixing a dry-blended mixture of approximately 4,000 g of a 0.0488:1 weight ratio of $ZnAc_2$ stabilizer and the ion product (ionomer) of Carboxyl-Containing Polymer A in a WP 30-mm twin screw extruder. The barrel temperatures are: zone 1 at 44°C and zones 2-5 at 103°C - 111°C. A vacuum port set at 20 mm Hg absolute removed byproduct acetic acid. The product is extruded through a 3-strand die, water cooled, and chopped to 1/4 inch (6.35 mm) pellets.

B. Preparation of an epoxy resin modified with 15% by weight of a carboxyl-containing polymer.

A modified epoxy resin is prepared by melt mixing 450 g of the zinc ionomer of Carboxyl-Containing Polymer A prepared in A above and 2,550 g of Epoxy Resin B. A dry blend, prepared by shaking the components together in a plastic bag, is melt mixed in a Buss Condux PLK 46 extruder having two zones with zone 1 at 20°C, zone 2 at 70°C, and the screw at 20°C and 200 rpm. The modified epoxy resin extrudate is pressed with chilled rollers to a thin sheet, air cooled, and crushed.

C. Preparation of powder coating.

A powder coating formulation is prepared by melt mixing 1,570 g of modified epoxy resin from B above, 62.9 g of Curing Agent A, 315 g of BS-1 filler, 30 g of Pigment A, and 20 g of Flow Modifier A. A dry blend, prepared by shaking the components together in a plastic bag, is melt mixed in a Buss Condux PLK 46 extruder having two zones with zone 1 at 50°C, zone 2 at 80°C, and the screw at 50°C and 200 rpm. The extrudate is pressed with chilled rollers to a thin sheet, air cooled, ground to a fine powder with a Brinkmann ZM-1 grinder and sieved through 150 mesh brass sieves. A portion of the powder is coated within one day following the melt mixing. Another portion of the powder is coated after aging for 24 hours at 40°C. The powder is electrostatically sprayed with a Wagner gun onto cold rolled steel panels. The powder coated panels are baked for 15 minutes at 180°C and air cooled.

EXAMPLE 21

A. Preparation of prereaction product of carboxyl-containing polymer and metal salt.

A prereaction product (ionomer) of Carboxyl-Containing Polymer A is prepared by melt mixing a dry-blended mixture of 120.6 g of $ZnCO_3$ stabilizer and 4,324 g of Carboxyl-Containing Polymer A in a WP 30-mm twin screw extruder. The barrel temperatures are: zone 1 at 46°C and zones 2-5 at 105°C - 111°C. A vacuum port set at 20 mm Hg absolute removed byproduct water. The product is extruded through a 3-strand die, water cooled, and chopped to 1/4 inch (6.35 mm) pellets.

B. Preparation of an epoxy resin modified with 15% by weight of a carboxyl-containing polymer.

A modified epoxy resin is prepared by melt mixing 450 g of the zinc ionomer of Carboxyl-Containing Polymer A prepared in A above and 2,550 g of Epoxy Resin B. The composition is prepared in the same manner as in Example 20-B.

C. Preparation of powder coating.

A powder coating formulation is prepared by melt mixing 1,570 g of modified epoxy resin from B above, 62.9 g of Curing Agent A, 315 g of BS-1 filler, 30 g of Pigment A, and 20 g of Flow Modifier A. The composition is prepared in the same manner as in Example 20-C.

The following Table I provides a summary description of the examples and comparative experiments grouped in sets of concurrently obtained examples and comparative experiments.

Table I
Summary description of examples
Grouped in sets of concurrent examples

	Description
Concurrent Set I	Clear, unfilled formulation using epoxy resin modified with 8% by weight Carboxyl-Containing Polymer A. Calcium propionate was tested at two levels as an additive to the formulation.
Comp. Expt. A*	Control (Unstabilized)
Example 1	3.66 wt% calcium propionate included in formulation
Example 2	10.23 wt% calcium propionate included in formulation.
Concurrent Set II	Clear, unfilled formulation using Curing Agent A. The combined epoxy resins consisted of 0.1:0.9 weight ratio of Carboxyl-Containing Polymer A and Epoxy Resin B. Calcium propionate was tested at three levels as an additive to the formulation.
Comp. Expt. B*	Control (Unstabilized)
Comp. Expt. C*	0.94 wt% calcium propionate included in formulation.
Example 3	1.87 wt% calcium propionate included in formulation.
Example 4	3.67 wt% calcium propionate included in formulation.

* Not an example of the present invention.

Table I (contd.)
Summary description of example
Grouped in sets of concurrent examples

	Description
Concurrent Set III	Black, 16% filled formulation using Curing Agent A. The combined epoxy resins consisted of 0.1:0.9 weight ratio of Carboxyl-containing Copolymer A and Epoxy Resin B. Weight ratios of calcium propionate to epoxy resin were the same as concurrent set II.
Comp. Expt. D*	Control (Unstabilized)
Example 5	0.78 wt% calcium propionate
Example 6	1.54 wt% calcium propionate included in formulation.
Example 7	3.02 wt% calcium propionate included in formulation.
Concurrent Set IV	Clear, unfilled formulations using Epoxy Resin B modified with 15% by weight Carboxyl-Containing Polymer A and Curing Agent A. Calcium propionate, zinc acetate, and zinc stearate are compared at equal equivalents of the metal ion.
Comp. Expt. E*	Control (Unstabilized)
Example 8	1.62 wt% calcium propionate included in formulation.
Example 9	1.93 wt% zinc acetate included in formulation.
Example 10	5.29 wt% zinc stearate included in formulation.

* Not an example of the present invention.

Table I (contd.)
Summary description of examples
Grouped in sets of concurrent examples

	Description
Concurrent Set V	Black, 16 wt% filled formulations using Curing Agent A. The epoxy resin consisted of 0.15:0.85 weight ratio of Carboxyl-Containing Polymer A or Carboxyl-Containing Polymer A ionomer to Epoxy Resin B.
Comp. Expt. F*	Control (Unstabilized)
Example 11	Carboxyl-Containing Polymer A ionomer produced with calcium propionate at 0.16:1 equivalent ratio of metal ion to acid groups.
Example 12	Carboxyl-Containing Polymer A ionomer produced with zinc acetate at 0.16:1 equivalent ratio of ion to acid groups.

* Not an example of the present invention.

Table I (Contd.)
Summary description of examples
Grouped in sets of concurrent example

	Description
Concurrent Set VI	Similar to concurrent Set V.
Comp. Expt. G*	Control, Unstabilized
Example 13	Carboxyl-Containing Polymer A ionomer produced with zinc acetate at 0.08:1 equivalent ratio of ion to acid groups.
Example 14	Carboxyl-Containing Polymer A ionomer produced with zinc acetate at 0.16:1 equivalent ratio of ion to acid group.
Example 15	Based on Epoxy Resin B modified with 15% by weight Carboxyl-Containing Polymer A with 0.59 wt% zinc acetate added to formulation, giving 0.16:1 equivalent ratio of ion to acid groups.
Concurrent Set VII	Similar to concurrent set V.
Comp. Expt. H*	Control, Unstabilized
Example 16	Carboxyl-Containing Polymer A ionomer produced with sodium acetate at 0.16:1 equivalent ratio of ion to acid groups.
Example 17	Car boxyl-Containing Polymer A ionomer produced with zinc acetate at 0.48:1 equivalent ratio of ion to acid groups.
Example 18	Based on Epoxy Resin B modified with 15% by weight Carboxyl-Containing Polymer A with 1.55 wt% zinc acetate added to formulation, giving 0.48:1 equivalent ratio of ion to acid groups.
Example 19	Carboxyl-Containing Polymer A ionomer produced with zinc stearate at 0.16:1 equivalent ratio of ion to acid groups.

* Not an example of the present invention.

Table I (contd.)
Summary description of examples
Grouped in sets of concurrent examples

	Description
Concurrent Set VIII	Similar to concurrent Set V.
Example 20	Ionomer of carboxyl-containing polymer produced with zinc acetate at 0.16:1 equivalent ratio of ion to acid groups.
Example 21	Ionomer of carboxyl-containing polymer produced with zinc carbonate at 0.16:1 equivalent ratio of ion to acid groups.

The following Table II provides a summary of process conditions for the preparation of carboxyl-containing polymer ionomers.

Table II
Summary table of Carboxyl-Containing Polymer Ionomer
Preparation Melt Mixed on Werner and Pfleiderer 30-mm extruder

Ex.	Metal Salt[1]	Metal Salt Rate g/min	EAA Rate g/min	Equiv. Ratio[2]	Conv. %[3]	Zone 1 °C	Zones 2-5 °C
11	$CaPr_2$	11.7	270	0.16	ND[5]	52	113-121
12	$ZnAc_2$	13.2	270	0.16	100	52	113-121
13	$ZnAc_2$	8.8	355	0.08	75	53	109-117
14	$ZnAc_2$	17.1	355	0.16	100	51	105-116
16	NaAc	22.5	355	0.16	100	50	104-107
17	$ZnAc_2$	47.3	355	0.48	100	48	105-113
19	$ZnSt_2$	48.2	355	0.16	44	56	128-139
20	$ZnAc_2$	N/A[4]	140	0.16	100	44	103-111
21	$ZnCO_3$	N/A[4]	140	0.16	100	46	104-111

[1] $CaPr_2$, calcium propionate, $ZnAc_2$, zinc acetate; NaAc, sodium acetate; $ZnSt_2$, zinc stearate.

[2] Equivalent ratio of metal ion to acid groups.

[3] Percent conversion of the metal ion to carboxyl-containing polymer ionomer.

[4] Not applicable. The metal salt was premixed with the carboxyl-containing polymer ionomer. The feed rate indicated was for the mixture.

[5] Not determined.

Note: Screw speed was 400 rpm for all examples, except Example 19 which was 477 rpm.

The following Table III provides a summary of the preparation of the modified epoxy resins.

Table III
Summary table of modified epoxy resin preparation
Melt Mixed on an extruder (except as noted)

Example or Comp. Expt. No.	Epoxy Resin Type	EAA Copolymer Ionomer Type	EAA Polymer Wt.%
C. E. A*	ERA[1]	C-CPA[2]	8
C. E. B*	ERB[3]	C-CPA[2]	20
C. E. E*	ERB[3]	C-CPA[2]	15
C. E. F*	ERB[3]	C-CPA[2]	15
C. E. G*	ERB[3]	C-CPA[2]	15
C. E. H*	ERB[3]	C-CPA[2]	15
Ex. 11	ERB[3]	C-CPA[2] Ionomer $CaPr_2$[4] (0.16:1 Eq. ratio)	15
Ex. 12	ERB[3]	C-CPA[2] Ionomer $ZnAc_2$[4] (0.16:1 Eq. ratio)	15

* Not an example of the present invention.

[1] Epoxy Resin A.

[2] Carboxyl-containing copolymer A.

[3] Epoxy Resin B.

[4] $CaPr_2$ = Calcium propionate, $ZnAc_2$ = zinc acetate, NaAc = sodium acetate, $ZnSt_2$ = zinc stearate, $ZnCO_3$ = zinc carbonate.

Table III (contd.)
Summary table of modified epoxy resin preparation
Melt Mixed on an extruder (except as noted)

Example or Comp. Expt. No.	Epoxy Resin Type	EAA Copolymer Ionomer Type	EAA Polymer Wt.%
Ex. 13	ERB[1]	C-CPA[2] Ionomer $ZnAc_2$[3] (0.08:1 Eq. ratio)	15
Ex. 14	ERB[1]	C-CPA[2] Ionomer $ZnAc_2$[3] (0.16:1 Eq. ratio)	15
Ex. 16	ERB[1]	C-CPA[2] Ionomer NaAc[3] (0.16:1 Eq. ratio)	15
Ex. 17	ERB[1]	C-CPA[2] Ionomer $ZnAc_2$[3] (0.16:1 Eq. ratio)	15
Ex. 19	ERB[1]	C-CPA[2] Ionomer $ZnSt_2$[3] (0.16:1 Eq. ratio)	15
Ex. 20	ERB[1]	C-CPA[2] Ionomer $ZnAc_2$[3] (0.16:1 Eq. ratio)	15
Ex. 21	ERB[1]	C-CPA[2] Ionomer $ZnCO_3$[3] (0.16:1 Eq. ratio)	15

[1] Epoxy Resin B.

[2] Carboxyl-containing copolymer A.

[3] $CaPr_2$ = Calcium propionate, $ZnAc_2$ = zinc acetate, NaAc = sodium acetate, $ZnSt_2$ = zinc stearate, $ZnCO_3$ = zinc carbonate.

The following Table IV provides a summary of the formulation components for each of the comparative experiments and examples.

Table IV
Summary Table of Formulations in Weight Percent

	Modified Epoxy Resin	ERB[1]	Curing Agent	Flow modified	Pigment	Filler	Formulation Additive
CONCURRENT SET I							
Comp. Expt. A*	94.97	—	3,80	1.23	—	—	—
Example 1	91.49	—	3.66	1.19	—	—	3.66
Example 2	85.25	—	3.41	1.11	—	—	10.23
CONCURRENT SET II							
Comp. Expt. B*	47.69	47.69	3.82	0.80	—	—	—
Comp. Expt. C*	47.24	47.24	3.78	0.80	—	—	0.94
Example 3	46.79	46.79	3.74	0.80	—	—	1.87
Example 4	45.93	45.93	3.67	0.80	—	—	3.67

* Not an example of the present invention.

[1] Epoxy Resin B.

Table IV (contd.)
Summary Table of Formulations in Weight Percent

	Modified Epoxy Resin	ERB[1]	Curing Agent	Flow Modifier	Pigment	Filler	Formulation Additive
CONCURRENT SET III							
Comp. Expt. D*	39.18	39.18	3.13	1.00	1.50	16.00	—
Example 5	38.81	38.81	3.10	1.00	1.50	16.00	0.78
Example 6	38.44	38.44	3.08	1.00	1.50	16.00	1.54
Example 7	37.73	37.73	3.02	1.00	1.50	16.00	3.02

* Not an example of the present invention.

[1] Epoxy Resin B.

Table IV (contd.)
Summary Table of Formulations in Weight Percent

	Modified Epoxy Resin	ERB[1]	Curing Agent	Flow Modifier	Pigment	Filler	Formu-lation Additive
CONCURRENT SET IV							
Comp. Expt. E*	63.46	31.73	3.81	1.00	—	—	—
Example 8	62.42	31.21	3.75	1.00	—	—	1.62
Example 9	62.22	31.11	3.73	1.00	—	—	1.93
Example 10	60.07	30.04	3.60	1.00	—	—	5.29
CONCURRENT SET V							
Comp. Expt. F*	78.63	—	3.15	1.00	1.50	15.73	—
Example 11	78.63	—	3.15	1.00	1.50	15.73	—
Example 12	78.63	—	3.15	1.00	1.50	15.73	—

* Not an example of the present invention.

[1] Epoxy Resin B.

Table IV (contd.)
Summary Table of Formulations in Weight Percent

	Modified Epoxy Resin	ERB[1]	Curing Agent	Flow Modifier	Pigment	Filler	Formu-lation Additive
CONCURRENT SET VI							
Comp. Expt. G*	78.63	—	3.15	1.00	1.50	15.73	—
Example 13	78.63	—	3.15	1.00	1.50	15.73	—
Example 14	78.63	—	3.15	1.00	1.50	15.73	—
Example 15	78.17	—	3.13	1.00	1.49	15.63	0.59

* Not an example of the present invention.

[1] Epoxy Resin B.

Table IV (contd.)
Summary Table of Formulations in Weight Percent

	Modified Epoxy Resin	ERB[1]	Curing Agent	Flow Modifier	Pigment	Filler	Formulation Additive
CONCURRENT SET VII							
Comp. Expt. H*	78.63	—	3.15	1.00	1.50	15.73	—
Example 16	78.63	—	3.15	1.00	1.50	15.73	—
Example 17	78.63	—	3.15	1.00	1.50	15.73	—
Example 18	77.41	—	3.10	0.99	1.48	15.48	1.55
Example 19	78.63	—	3.15	1.00	1.50	15.73	-
CONCURRENT SET VIII							
Example 20	78.58	—	3.15	1.00	1.50	15.77	—
Example 21	78.58	—	3.15	1.00	1.50	15.77	—

* Not an example of the present invention.

[1] Epoxy Resin B.

The following Table V provides a summary of the coating thickness, coating gloss values, and the relative change in the gloss values comparing the coating from the aged powder to the coating from the fresh powder.

Table V
Summary Table of Coating Properties

	Number of panels averaged	Average Gloss % reflectance at 60°	% Relative change in gloss with age at 60°
CONCURRENT SET II			
Comp. Expt. B* Fresh	4	20.5	—
Comp. Expt. B* Aged 23 hrs. @ 36°C	3	41.0	100.0
Comp. Expt. C* Fresh	3	21.7	—
Comp. Expt. C* Aged 23 hrs @ 36°C	3	50.3	132.3
Example 3 Fresh	5	38.2	—
Example 3 Aged 23 hrs. @ 36°C	3	66.0	72.8
Example 4 Fresh	5	53.8	—
Example 4 Aged 23 hrs. @ 36°C	3	63.7	18.3

* Not an example of the present invention.

Table V (contd.)
Summary Table of Coating Properties

	Number of panels averaged	Average Gloss % reflectance at 60°	% Relative change in gloss with age at 60°
CONCURRENT SET III			
Comp. Expt. D* Fresh	4	8.5	—
Comp. Expt. D* Aged 20 hrs. @ 40°C	2	31.5	269.5
Example 5 Fresh	4	15.0	—
Example 5 Aged 20 hrs @ 40°C	3	34.0	126.7
Example 6 Fresh	4	26.0	—
Example 6 Aged 20 hrs. @ 40°C	3	37.7	44.9
Example 7 Fresh	4	36.5	—
Example 7 Aged 20 hrs. @ 40°C	2	47.5	30.1

* Not an example of the present invention.

Table V (contd.)
Summary Table of Coating Properties

	Number of panels averaged	Average Gloss % reflectance at 60°	% Relative change in gloss with age at 60°
CONCURRENT SET IV			
Comp. Expt. E* Fresh	4	13.5	—
Comp. Expt. E* Aged 24 hrs. @ 40°C	2	53.5	296.3
Comp. Expt. E* Aged 27 days @ ambient temperature	3	56.7	319.8
Example 8 Fresh	4	22.0	—
Example 8 Aged 24 hrs @ 40°C	3	54.3	147.0
Example 8 Aged 27 days @ ambient temperature	3	60.3	174.2
Example 9 Fresh	4	22.5	—
Example 9 Aged 24 hs. @ 40°C	3	8.5	-62.2
Example 9 Aged 27 days @ ambient temperature	2	13.5	-40.0
Example 10 Fresh	4	3.4	—
Example 10 Aged 24 hrs. @ 40°C	3	2.1	-38.9
Example 10 Aged 27 days @ ambient temperature	5	2.2	-37.2

* Not an example of the present invention.

Table V (contd.)
Summary Table of Coating Properties

	Number of panels averaged	Average Gloss % reflectance at 60°	% Relative change in gloss with age at 60°
CONCURRENT SET V			
Comp. Expt. F* Fresh	3	1.9	—
Comp. Expt. F* Aged 24 hrs. @ 40°C	2	14.0	636.8
Comp. Expt. F* Aged 33 days @ ambient temperature	1	12.5	557.9
Example 11 Fresh	3	7.5	—
Example 11 Aged 24 hrs @ 40°C	3	23.7	215.6
Example 11 Aged 33 days @ ambient temperature	1	23.0	206.7
Example 12 Fresh	3	6.6	—
Example 12 Aged 24 hrs @ 40°C	5	5.9	-11.4
Example 12 Aged 33 days @ ambient temperature	2	5.8	-13.3

* Not an example of the present invention.

Table V (contd.)
Summary Table of Coating Properties

CONCURRENT SET VI	Number of panels averaged	Average Gloss % reflectance at 60°	% Relative change in gloss with age at 60°
Comp. Expt. G* Fresh	5	3.4	—
Comp. Ept. G* Aged 24 hrs @ 40°C	2	17.5	408.7
Example 13 Fresh	4	4.6	—
Example 13 Aged 24 hrs @ 40°C	2	8.0	74.7
Example 14 Fresh	3	6.3	—
Example 14 Aged 24 hrs @ 40°C	2	6.3	0.0
Example 15 Fresh	4	3.3	—
Example 15 Aged 24 hrs @ 40°C	3	5.3	60.8

* Not an example of the present invention.

Table V (contd.)
Summary Table of Coating Properties

CONCURRENT SET VII	Number of panels averaged	Average Gloss % reflectance at 60°	% Relative change in gloss with age at 60°
Comp. Expt. H* Fresh	3	3.1	—
Comp. Expt. H* Aged 24 hrs @ 40°C	3	16.3	421.3
Example 16 Fresh	3	31.0	—
Example 16 Aged 24 hrs @ 40°C	3	35.0	12.9
Example 17 Fresh	3	4.0	—
Example 17 Aged 24 hrs @ 40°C	3	4.8	21.8
Example 18 Fresh	3	3.5	—
Example 18 Aged 24 hrs @ 40°C	3	3.5	1.9
Example 19 Fresh	3	33.3	—
Example 19 Aged 24 hrs @ 40°C	3	23.3	-30.0

* Not an example of the present invention.

Table V (contd.)
Summary Table of Coating Properties

CONCURRENT SET VIII	Number of panels averaged	Average Gloss % reflectance at 60°	% Relative change in gloss with age at 60°
Example 20 Fresh	4	6.4	—
Example 20 Aged 24 hrs @ 40°C	4	5.7	-11.4
Example 21 Fresh	4	6.5	—
Example 21 Aged 24 hrs @ 40°C	4	6.1	-6.1

CLAIMS

1. A modified epoxy resin composition comprising

(A) at least one epoxy resin containing an average of more than one vicinal epoxy group per molecule and at least one aromatic ring in its backbone; and

(B) at least one polymer prepared from one or more ethylenically unsaturated monomers wherein at least one of such monomers contains a carboxylic acid group;

characterized by incorporating into said composition

(C) a stabilizing amount of at least one stabilizer compound which is

(a) at least one Group IA, IIA, IIB, IIIA, VIB or VIII of the periodic table of the elements metal salt of an organic carboxylic acid;

(b) at least one of zinc carbonate, zinc oxide, sodium carbonate or potassium carbonate; or

(c) any combination of (a) and (b).

2. A curable composition comprising

(A) at least one epoxy resin containing an average of more than one vicinal epoxy group per molecule and at least one aromatic ring in its backbone;

(B) at least one polymer prepared from one or more ethylenically unsaturated monomers wherein at least one of such monomers contains a carboxylic acid group; and

(D) a curing amount of at least one curing agent for component (A) which is different from either component (B) or the prereaction product of components (B) and (C);

characterized by incorporating into said composition;

(C) a stabilizing amount of at least one stabilizer compound which is

(a) at least one Group IA, IIA, IIB, IIIA, VIB or VIII of the periodic table of the elements metal salt of an organic carboxylic acid;

(b) at least one of zinc carbonate, zinc oxide, sodium carbonate or potassium carbonate; or

(c) any combination of (a) and (b).

3. A powder coating composition which is essentially free of pigment(s) and filler(s) comprising
(A) at least one epoxy resin containing an average of more than one vicinal epoxy group per molecule and at least one aromatic ring in its backbone;
(B) at least one polymer prepared from one or more ethylenically unsaturated monomers wherein at least one of such monomers contains a carboxylic acid group;
(D) at least one curing agent for component (A) which is different from either component (B) or the prereaction product of components (B) and (C); and
(E) at least one or more additional component(s) selected from the group consisting of flow control agent, leveling aid, and promoter or catalyst;
characterized by incorporating into said composition;
(C) a stabilizing amount of at least one stabilizer compound which is
(a) at least one Group IA, IIA, IIB, IIIA, VIB or VIII of the periodic table of the elements metal salt of an organic carboxylic acid;
(b) at least one of zinc carbonate, zinc oxide, sodium carbonate or potassium carbonate; or
(c) any combination of (a) and (b).

4. A powder coating composition which contains substantial quantities of pigment(s) or filler(s) or both comprising
(A) at least one epoxy resin containing an average of more than one vicinal epoxy group per molecule and at least one aromatic ring in its backbone;
(B) at least one polymer prepared from one or more ethylenically unsaturated monomers wherein at least one of such monomers contains a carboxylic acid group;
(D) at least one curing agent for component (A) which is different from either component (B) or the prereaction product of components (B) and (C); and
(E) at least one or more additional component(s) including pigment, filler, flow control agent, leveling aid or other additive;
characterized by incorporating into said composition;
(C) a stabilizing amount of at least one stabilizer compound which is
(a) at least one Group IA, IIA, IIB, IIIA, VIB or VIII of the periodic table of the elements metal salt of an organic carboxylic acid;
(b) at least one of zinc carbonate, zinc oxide, sodium carbonate or potassium carbonate; or
(c) any combination of (a) and (b).

5. A composition of Claim 1, 2, 3 or 4 wherein

(a) component (A) is a diglycidyl ether of: a dihydric phenol, a bisphenol, a phenol- or substituted phenol-aldehyde resin, or a phenol- or substituted phenol-unsaturated diene resin;

(b) component (B) is a polymer resulting from polymerizing a monomer mixture containing ethylene and an aliphatic, cycloaliphatic or aromatic carboxylic acid;

(c) component (C) is zinc oxide, sodium carbonate, zinc carbonate, potassium carbonate, or sodium, lithium, potassium, zinc, calcium, magnesium, nickel, aluminum or chromium salt of a saturated or unsaturated aliphatic or cycloaliphatic or aromatic organic carboxylic acid having from about 1 to about 30 carbon atoms per molecule, or a combination of any two or more of such compounds;

(d) component (D) is a guanidine, biguanide, aliphatic amine, aromatic amine, compound containing an average of more than one phenolic hydroxyl group per molecule, aliphatic, cycloaliphatic or aromatic di-or poly-carboxylic acid anhydride, or any combination of two or more of such curing agents;

(e) component (A) is employed in an amount of from about 66 to about 99 percent by weight based upon the combined weight of components (A) and (B); .

(f) component (B) is employed in an amount of from about 1 to about 34 percent by weight based upon the combined weight of components (A) and (B);

(g) Component (C) is employed in an amount sufficient to provide a ratio of metal equivalents per carboxyl equivalents of

(i) in Claim 1, 2 or 4, at least about 0.04:1; or

(ii) in Claim 3, at least about 0.5:1; and

(h) component (D) is employed in an amount which is sufficient to provide a ratio of equivalents of this curing agent plus component (B) or ionomers thereof per epoxide equivalent of from about 0.8:1 to about 3:1.

6. A composition of Claim 5 wherein

(a) component (A) is a diglycidyl ether of a bisphenol;

(b) component (B) is a polymer resulting from polymerizing a monomer mixture containing ethylene and either acrylic or methacrylic acid;

(c) component (C) is zinc oxide, sodium carbonate, zinc carbonate, potassium carbonate, zinc acetate, zinc propionate, zinc stearate, sodium acetate, calcium propionate;

(d) component (D) is dicyandiamide, o-tolubiguanide, acid functional polyesters, compounds containing more than one phenolic group per molecule, or any combination of two or more of such curing agents;

(e) component (A) is employed in an amount of from about 80 to about 96 percent by weight based upon the combined weight of components (A) and (B);

(f) component (B) is employed in an amount of from about 4 to about 20 percent by weight based upon the combined weight of components (A) and (B);

(g) Component (C) is employed in an amount sufficient to provide a ratio of metal equivalents per carboxyl equivalents of

(i) in Claim 1, 2 or 4, from about 0.08:1 to about 6:1; or

(ii) in Claim 3, from about 0.6:1 to about 6:1; and

(h) component (D) is employed in an amount which provides a ratio of equivalents of this curing agent plus component (B) or ionomers thereof per epoxide equivalent of from about 0.9:1 to about 2.5:1.

7. A composition of Claim 5 wherein

(a) component (A) is a diglycidyl ether of bisphenol A, bisphenol F or bisphenol K;

(b) component (B) is a polymer resulting from polymerizing a monomer mixture containing ethylene and acrylic acid;

(c) component (C) is zinc carbonate, zinc acetate, zinc propionate, zinc stearate, sodium acetate, calcium propionate or any combination thereof;

(d) component (D) is dicyandiamide or an imidazole accelerated dicyandiamide;

(e) component (A) is employed in an amount of from about 80 to about 92 percent by weight based upon the combined weight of components (A) and (B); and

(f) component (B) is employed in an amount of from about 8 to about 20 percent by weight based upon the combined weight of components (A) and (B);

(g) Component (C) is employed in an amount sufficient to provide a ratio of metal equivalents per carboxyl equivalents of

  (i) in Claim 1, 2 or 4, from about 0.15:1 to about 1:1; or

  (ii) in Claim 3, from about 0.7:1 to about 1:1; and

(h) component (D) is employed in an amount which provides a ratio of equivalents of this curing agent plus component (B) or ionomers thereof per epoxide equivalent of from about 1:1 to about 2:1.

8. A composition suitable as a curing agent for epoxy resins which comprises

(1) at least one polymer prepared from one or more ethylenically unsaturated monomers wherein at least one of such monomers contains a carboxylic acid group; and

(2) at least one curing agent for said epoxy resin which curing agent is different from component (1);

characterized by incorporating into said curing agent composition

(3) a stabilizing amount of at least one stabilizer compound which is

  (a) at least one Group IA, IIA, IIB, IIIA, VIB or VIII of the periodic table of the elements metal salt of an organic carboxylic acid;

  (b) at least one of zinc carbonate, zinc oxide, sodium carbonate or potassium carbonate; or

  (c) any combination of (a) and (b).

9. A composition of Claim 8 wherein

(a) component (1) is present in an amount of from about 1 to about 99 percent by weight based upon the combined weight of components (1) and (2);

(b) component (2) is present in an amount of from about 99 to about 1 percent by weight based upon the combined weight of components (1) and (2); and

(c) component (3) is employed in an amount sufficient to provide a ratio of metal equivalents per carboxyl equivalent of at least about 0.04:1.

10. A composition of Claim 8 wherein

(a) component (1) is present in an amount of from about 3 to about 96 percent by weight based upon the combined weight of components (1) and (2);

(b) component (2) is present in an amount of from about 97 to about 4 percent by weight based upon the combined weight of components (1) and (2); and

(c) component (3) is employed in an amount sufficient to provide a ratio of metal equivalents per carboxyl equivalent of from about 0.08:1 to about 6:1.

11. A composition of Claim 8 wherein

(a) component (1) is present in an amount of from about 25 to about 90 percent by weight based upon components (1) and (2); and

(b) component (2) is present in an amount of from about 75 to about 10 percent by weight based upon components (1) and (2; and

(c) component (3) is employed in an amount sufficient to provide a ratio of metal equivalents per carboxyl equivalent of from about 0.15:1 to about 1:1.

12. A composition of Claim 11 wherein a curing promoter or catalyst is employed.

13. The product resulting from curing the curable compositions of Claim 3 or 4.

14. The product resulting from curing the curable compositions of Claim 5.

15. The product resulting from curing the curable compositions of Claim 6.

16. The product resulting from curing the curable compositions of Claim 7.

18. An article coated with the powder coating compositions of Claim 3 or 4.

19. An article coated with the powder coating compositions of Claim 5.

20. An article coated with the powder coating compositions of Claim 6.

21. An article coated with the powder coating compositions of Claim 7.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 93/00702

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C09D167/00; C08L63/00; C08K5/09; C08K3/22
C08K3/26

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C09D ; C08L ; C08K

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
A	US,A,4 419 495 (DAVIS) 6 December 1983 cited in the application see claims 1-12 ---	1-21
A	PATENT ABSTRACTS OF JAPAN vol. 6, no. 143 (C-117)(1021) 3 August 1982 & JP,A,57 065 764 (TOUYOU KOUHAN K.K.) see abstract ---	1-21
A	BE,A,661 435 (S.A. SOBEMI) 16 July 1965 see claims 1,2 -----	1-21

° Special categories of cited documents : [10]

"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

"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

IV. CERTIFICATION

1

Date of the Actual Completion of the International Search 11 MAY 1993	Date of Mailing of this International Search Report 28. 05. 93
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer GLANDDIER A.

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 9300702
SA 70067

11/05/93

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-4419495	06-12-83	None		
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