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[54] POWDER PAINT WITH EPOXY AND HYDROXY COPOLYMER AND MIXTURE OF DICARBOXYLIC ACIDS AND POLYANHYDRIDES

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Related U.S. Patent Documents

Reissue of:

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U.S. Applications:

[63] Continuation-in-part of Ser. No. 394,881, Sep. 6, 1973, abandoned.

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[52] **U.S. Cl.** **525/327.3**; 525/386; 525/934; 524/904

[58] **Field of Search** .... 526/273; 260/830 R, 260/836; 525/329, 386

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,752,870	8/1973	Labana	260/836
3,770,848	11/1973	Labana et al.	260/836
3,781,379	12/1973	Theodore et al.	260/836
3,876,587	4/1975	Matsui et al.	260/78.4 D

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[57] **ABSTRACT**

Improved powder paint compositions are disclosed which comprise a particulate mixture of (1) a qualitatively difunctional copolymer of about 5 to about 20 weight percent of a glycidyl ester of a monoethylenically unsaturated acid, about 2 to about 10 weight percent of C_5–C_7 hydroxyalkyl acrylates and/or C_5–C_7 hydroxyalkyl methacrylates, and about 70 to about 93 weight percent monoethylenically unsaturated monomers consisting essentially of monofunctional monomers selected from the group consisting of esters of a C_1–C_8 monohydric alcohol and acrylic acid, esters of a C_1–C_8 monohydric alcohol and methacrylic acid and C_8–C_{12} monovinyl hydrocarbons, (2) a C_4–C_{20} saturated, straight chain, aliphatic dicarboxylic acid which is present in an amount that provides about 0.1 to about 0.6 carboxyl group per functional group on said copolymer, and (3) a polyanhydride, i.e., a homopolymer of a monomeric anhydride of a dicarboxylic acid, having molecular weight in the range of about 1000 to about 5000 which is present in an amount that provides about 0.2 to about 1.1 anhydride groups per [epoxy] *functional* group on said copolymer.

17 Claims, No Drawings

POWDER PAINT WITH EPOXY AND HYDROXY COPOLYMER AND MIXTURE OF DICARBOXYLIC ACIDS AND POLYANHYDRIDES

Matter enclosed in heavy brackets [ ] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue.

This application is a Continuation-In-Part of application Ser. No. 394,881 filed Sept. 6, 1973, now abandoned.

BACKGROUND OF THE INVENTION

Powder coating compositions are extremely desirable for use in painting substrates in that they are essentially free of organic solvents conventionally utilized in liquid paint systems. Thus, they give off little, if any, volatile material to the environment when heat cured.

Powder coating compositions comprising (1) a copolymer of a glycidyl acrylate and other monofunctional olefinically unsaturated monomers, (2) an anhydride crosslinking agent, and (3) a polymeric flow control agent were heretofore described in U.S. Pat. No. 3,781,379 issued Dec. 25, 1973 to S. S. Labana and A. N. Theodore, the inventors herein.

Powder coating compositions comprising (1) a copolymer of a glycidyl acrylate and other monofunctional olefinically unsaturated monomers, (2) a dicarboxylic acid crosslinking agent, and (3) a polymeric flow control agent were heretofore described in U.S. Pat. No. 3,752,870 to S. S. Labana, a coinventor herein.

Powder coating compositions comprising (1) a copolymer of a glycidyl acrylate and other monofunctional olefinically unsaturated monomers, (2) a crosslinking agent comprising a mixture of a monocarboxylic acid and a dicarboxylic acid, and (3) a polymeric flow control agent were heretofore described in U.S. Pat. No. 3,730,930 to Santokh S. Labana, a coinventor herein.

Powder coating compositions comprising (1) a copolymer of a hydroxy acrylate and other monofunctional olefinically unsaturated monomers, (2) a crosslinking agent selected from anhydrides, dicarboxylic acids, and melamines and (3) a polymeric flow control agent were heretofore described in copending U.S. patent application Ser. No. 407,128 filed Oct. 17, 1973 by Santokh S. Labana, a coinventor herein and Yun F. Chang.

THE INVENTION

It now has been discovered that powder paints having certain unexpected advantages relative to the aforedescribed powder paint compositions can be obtained by converting the qualitatively monofunctional (epoxy functional) copolymer to a qualitatively difunctional (epoxy and hydroxy functional) copolymer and employing such difunctional copolymer in combination with a combination of crosslinking agents, i.e., a dicarboxylic acid and a polyanhydride.

Substitution of the polyanhydride for a portion of the dicarboxylic acids which otherwise would be required provides a powder paint having improved leveling characteristics and further characterized by increased gel time and increased adhesion.

Further improvement in the homogeneity of the powders, can be obtained by having the copolymer both epoxy-functional and hydroxy-functional. Such powders can be cured at lower temperatures and provide coatings having improved mechanical properties and solvent resistance. This provides the copolymer with both a difference in functional groups and an increase in total functionality and increased polarity. The latter provides, in combination with the crosslinking agents, a higher degree of compatibility (aiding homogeneous mixing) of the complete coating composition including pigment dispersion.

Those powders are effectively prepared by spray drying in that they resist phase separation. They may also be processed by melt blending and vacuum drying techniques. They are easily and effectively mixed by extrusion or mill rolling.

The functionality of the copolymer is provided by constituent epoxy-functional acrylates and methacrylates and hydroxy-functional acrylates and methacrylates. For simplicity, except in those instances wherein a specific compound is named, the term "acrylate" is used in this specification to include esters of both acrylic and methacrylic acid, i.e., acrylates and methacrylates.

DETAILED DESCRIPTION OF THE INVENTION

The epoxy and hydroxy functional copolymers used in the practice of this invention contain between about 5 and about 20, preferably between 8 and 15, weight percent of a glycidyl ester of a monoethylenically unsaturated carboxylic acid, e.g., a glycidyl acrylate and glycidyl methacrylate, about 2 to about 10 weight percent of a C_5–C_7 hydroxyalkyl acrylates and/or C_5–C_7 hydroxyalkyl methacrylates, i.e., esters of C_2–C_3 dihydric alcohols and acrylic or methacrylic acid, and about 70 to about 93 weight percent monoethylenically unsaturated monomers consisting essentially of monofunctional monomers selected from the group consisting of esters of a C_1–C_8 monohydric alcohol and acrylic acid, esters of a C_1–C_8 monohydric alcohol and methacrylic acid and C_8–C_{12} monovinyl hydrocarbons such as styrene, vinyl toluene, t-butyl styrene, chlorostyrene and alpha methyl styrene. The preferred hydroxy acrylates are 2-hydroxyethyl methacrylate and 2-hydroxypropyl methacrylate. In the preferred embodiment in excess of 50 weight percent of such monofunctional, monoethylenically unsaturated monomers are esters of a C_1–C_8 monohydric alcohol and either acrylic or methacrylic acid. Other vinyl monomers such as vinyl chloride, acrylonitrile, methacrylonitrile, and vinyl acetate may be used as modifying monomers. When employed, these comprise about 0 to about 30 percent by weight of the monomer mixture but, ordinarily, the remainder monomers will consist exclusively of the aforementioned esters of a C_1–C_8 monohydric alcohol and acrylic or methacrylic acid or a mixture of such esters and C_8–C_{12} monovinyl hydrocarbons.

These copolymers have a glass transition temperature in the range of 40° C. to 90° C., preferably between 50° C. and 80° C., and a molecular weight ($\overline{M}_n$) in the range of about 1500 to about 15,000, preferably about 2500 to about 6000.

When dicarboxylic acids have been used as the sole crosslinking agent for epoxy-functional copolymers, it has been found advantageous to employ the acid in an amount such that about 0.3 to about 1.2 carboxyl groups are present for each epoxy group in the copolymer.

In this invention, a portion of the dicarboxylic acid crosslinking agent is replaced by a functionall equivalent amount of a polyanhydride. Thus, a mixture of the prepolymer and crosslinking agent in accordance with this invention advantageously contains the dicarboxylic acid in an amount sufficient to provide about 0.1 to about 0.6 carboxyl groups per functional group on the prepolymer and the polyanhydride in an amount sufficient to provide about 0.2 to about 1.1 anhydrode groups per same.

These powder coating compositions include as crosslinking agent for the aforedescribed copolymers saturated, straight chain, aliphatic, dicarboxylic acid containing 4 to 20 carbon atoms per molecule.

The preferred dicarboxylic acids are those containing from 5 to 13 carbon atoms per molecule. In still greater detail, the most desirable acids are adipic acid, pimelic acid, suberic acid, azelaic acid, sebasic acid, undecanoic acid and brassylic acid.

The preferred polyanhydrides are poly (adipic anhydride), poly (azelaic anhydride), and poly (sebasic anhydride) but others having molecular weight up to about 5000 are useful. Those having molecular weight in the range of about 1,000 to about 2500 are preferred.

These powder coating compositions advantageously contain a flow control agent as a part of the powder coating mixture. The flow control agent is a polymer having a molecular weight ($\overline{M}_n$) of at least 1000 and comprises at least 0.05 weight percent of the mixture. The flow control agent has a glass transition temperature at least 20° C. below the glass transition temperature of the mixture's copolymer.

One group of suitable flow control agents are acrylic polymers. Preferred acrylic polymers which may be used for the flow control agent are polylauryl acrylate, polybutyl acrylate, poly (2-ethylhexyl acrylate), polylauryl methacrylate and polyisodecyl methacrylate.

The flow control agent may also be a fluorinated polymer having a surface tension, at the baking temperature of the powder, lower than that of the copolymer utilized in the mixture. Preferred flow control agents, if the agent is a fluorinated polymer are esters of polyethyleneglycol or polypropyleneglycol and fluorinated fatty acids. For example, an ester of polyethyleneglycol of molecular weight of over 2500 and perfluoro octanoic acid is a useful flow control agent. Polymer siloxanes of molecular weight of over 1000 (advantageously 1,000 to 20,000) may also be useful as flow control agents, e.g. poly (dimethyl siloxane) or poly (methylphenyl) siloxane.

A coating composition formed in accordance with the teachings of this invention may include a small weight percent of a catalyst in order to increase the crosslinking rate of the powder coating composition at the baking temperature thereof. Baking temperatures will ordinarily be in the range of 130° to 200° C. and the catalyst should produce a gel time for the powder coating composition at the baking temperature to be used which is at least 1 minute but no greater than 20 minutes. This gel time is preferably in the range of 1 to 12 minutes and most preferably between about 2 and about 8 minutes.

Some catalysts which are suitable for use in the powder coating compositions include tetraalkylammonium salts, imidazole type catalyst, tertiary amines and metal salts of organic carboxylic acids. The tetraalkylammonium salt catalysts include the following: tetrabutyl ammonium chloride (bromide or iodide), tetraethyl ammonium chloride (bromide or iodide), trimethylbenzylammonium chloride, dodecyl dimethyl (2-phenoxyethyl) ammonium bromide, diethyl (2-hydroxy ethyl) methyl ammonium bromide. Suitable catalysts of the imidazole type include: 2-methyl-4-ethyl imidazole, 2-methyl imidazole, imidazole, 2-[(N-benzylanilino) methyl]-2-imidazoline phosphate, and 2-benzyl-2-imidazoline hydrochloride. Suitable tertiary amine catalysts for the powder coating compositions of this invention include: triethylenediamine, N,N-diethylcyclohexylamine and N-methyl morpholine. The metal salts of organic carboxylic acid which are catalysts for the powder coatings of this invention include, but are not limited to: stannous octoate, zinc naphthenate, cobalt naphthenate, zinc octoate, stannous 2-ethylhexyoate, phenylmercuric propionate, lead neodecanoate, dibutyl tin dilaurate and lithium benzoate.

The catalyst used in an individual powder coating composition is generally solid at room temperature and has a melting point of from 50° C. to 200° C.

Conventional non-metallic and metallic pigments can be used with these powder coating compositions. Such are conventionally employed in an amount such as to constitute between about 6 and 35 weight percent of the total mixture depending on the pigment selected and the gloss required for the baked coating.

Since individual powder coating compositions of this invention can be applied to an article to be painted by electrostatic methods, one may desire to include a small weight percentage of an antistatic agent in such compositions. In particular, the antistatic agent is included in a range from 0.05 weight percent of the total powder composition. Suitable antistatic agents include, but are not limited to, tetraalkylammonium salts as discussed previously and which also serve as catalysts. Other suitable antistatic agents include: alkyl-poly (ethyleneoxy) phosphate or alkylauryl poly (ethyleneoxy) phosphates as, for example, ethyl benzyl poly (ethyleneoxy) phosphate: polyethyleneimine, poly (2-vinyl pyrollidone), pyridinium chloride, poly (vinyl pyridium chloride), polyvinyl alcohol or inorganic salts.

A plasticizer may be used in a powder coating composition of this invention if desired. The type of plasticizers used very often include adipates, phosphates, phthalates, sebacates, polyesters derived from adipic acid or azelaic acid, and epoxy or epoxidized plasticizers. Some of these plasticizers are: dihexyl adipate, diisooctyl adipate, dicyclohexyl adipate, triphenylphosphate, tricresylphosphate, tributylphosphate, dibutylphthalate, dioctylphthalate, butyl octyl phthalate, dioctyl sebacate, butyl benzyl sebacate, dibenzyl sebacate, butanediol-1,4-diglycidyl ether, diglycidyl ether of bisphenol A and its polymers and cellulose acetate butyrate.

Having described the various materials which are employed in formulating the powder coating compositions of this invention, a plurality of examples are hereinafter set forth to illustrate various individual powder coating compositions. In each of the examples, the molecular weight of the copolymer is between 1500 and 15000 and the glass transition temperature of the copolymer is between 40° C. and 90° C.

EXAMPLE 1

An epoxy-functional and hydroxy-functional copolymer is prepared from the below listed components in the manner hereinafter set forth:

Reactants	Amounts, grams	Percent by Weight Of Total Reactants
glycidyl methacrylate	30	15
hydroxyethyl methacrylate	10	5
butyl methacrylate	80	40
methyl methacrylate	80	40

The above-mentioned monomers are admixed in the proportions above set forth and 11.0 grams of 2,2'-azobis(2-methylpropionitrile), hereinafter called AIBN, are added to the monomer mixture. The mixture (solution) is slowly added to 200 ml. of toluene heated to 80°-90° C. which is being stirred vigorously under a nitrogen atmosphere. A condenser is provided at the top of the toluene container to condense the toluene vapors and return the condensed toluene to the container. The monomer mixture is added through a regulating valve and the rate of addition is controlled to maintain a reaction temperature of 90°-110° C. with the rest of the heat supplied from an external heater. After the addition of the monomer mixture is completed (3 hours), 0.8 gram of AIBN dissolved in 10 ml. acetone is added over an one-half hour period and refluxing is continued for two additional hours.

The resultant toluene-polymer solution is diluted with 200 mls. acetone and coagulated in two liters of hexane. The white powder is dried in the vacuum oven at 55° C. for 2 hours. The molecular weight of this copolymer is determined to be $\overline{M}_w/\overline{M}_n=6700/3200$ and WPE (molecular weight per epoxide group) is about 1000.

This dry copolymer, hereinafter called Copolymer A, is mixed with the following ingredients in the proportions hereinafter set forth to form a coating powder.

Ingredients	Amounts, grams
Copolymer A	50
Poly(azelaic anhydride)	5.0
Azelaic acid	2.1
Titanium dioxide	4.50
Ferrite yellow	4.0
Poly(2-ethylhexyl acylate), $\overline{M}_n$ = 11000	0.42

This mixture is ball-milled for 5 hours and mill rolled for 10 minutes at 110° C. Subsequently, the cooled material is granulated and converted to a particle size range of 5-30 microns with a fluid energy mill. This powder demonstrates excellent non-caking characteristics, is uniform in appearance, and demonstrates a high gel time.

This powder is sprayed electrostatically on a grounded steel panel by using an electrostatic powder spray gun operating at 50 KV charging voltage. The powder coated panels are cured at 160° C. for 20 minutes.

The cured coatings have good adhesion to the steel panels. They also have good impact strength and are not soluble in xylene, toluene, methyl ethyl ketone, or gasoline. The appearance of these coated surfaces is excellent and free of "orange peel" effect.

EXAMPLE 2

Powder coating materials of Example 1 including the copolymer and all other ingredients are dispersed in 45 mls. toluene and reduced with acetone to a homogeneous mixture containing 30% total solids. After processing this mixture with a spray dryer, a powder is obtained that contains less 1.5% solvent. This powder is deposited on steel panels and cured at 160° C. for 25 minutes. The resulting coating has good solvent resistance an appearance.

EXAMPLE 3

The procedure of Example 1 is repeated except that a functionally equivalent amount of glycidyl acrylate is substituted for the glycidyl methacrylate used to form the copolymer.

EXAMPLE 4

The procedure of Example 1 is repeated except for the difference that a functionally equivalent amount of adipic acid is substituted for the azelaic acid in the coating material formulation.

EXAMPLE 5

The procedure of Example 1 is repeated except for the difference that a functionally equivalent amount of pimelic acid is substituted for the azelaic acid in the coating material formulation.

EXAMPLE 6

The procedure of Example 1 is repeated except for the difference that a functionally equivalent amount of suberic acid is substituted for the azelaic acid in the coating material formulation.

EXAMPLE 7

The procedure of Example 1 is repeated except for the difference that a functionally equivalent amount of sebasic acid is substituted for the azelaic acid in the coating material formulation.

EXAMPLE 8

The procedure of Example 1 is repeated except for the difference that a functionally equivalent amount of undecanoic acid is substituted for the azelaic acid in the coating material formulation.

EXAMPLE 9

The procedure of Example 1 is repeated except for the difference that a functionally equivalent amount of brassylic acid is substituted for the azelaic acid in the coating material formulation.

EXAMPLE 10

The procedure of Example 1 is repeated except for the difference that a functionally equivalent amount of poly (adipic anhydride) is substituted for the poly (azelaic anhydride) in the coating material formulation.

EXAMPLE 11

The procedure of Example 1 is repeated except for the differences that the composition of the copolymer and the composition of the coating material differ as hereinafter set forth:

The composition of the copolymer, hereinafter called Copolymer B, is as follows:

Reactants	Amounts, grams	Percent by Weight Of Total Reactants
Glycidyl methacrylate	30	15
Hydroxyethyl methacrylate	4	2
Butyl methacrylate	80	40

-continued

Reactants	Amounts, grams	Percent by Weight Of Total Reactants
Methyl methacrylate	86	43

The composition of the coating material is as follows:

Ingredients	Amounts, grams
Copolymer B	50.0
Poly(azelaic anhydride)	4.7
Azelaic acid	2.35
Titanium dioxide	4.50
Ferrite yellow	4.0
Poly(2-ethylhexyl acrylate)	0.42

EXAMPLE 12

The procedure of Example 1 is repeated except for the differences that the composition of the copolymer and the composition of the coating material differ as hereinafter set forth:

The composition of the copolymer, hereinafter called Copolymer C, is as follows:

Reactants	Amounts, grams	Percent by Weight Of Total Reactants
Glycidyl methacrylate	30	15
Hydroxyethyl methacrylate	20	10
Butyl methacrylate	80	40
Methyl methacrylate	70	35

The composition of the coating material is as follows:

Ingredients	Amounts, grams
Copolymer C	50.0
Poly(azelaic anhydride)	4.4
Azelaic acid	1.4
Titanium Dioxide	4.50
Ferrite yellow	4.0
Poly(2-ethylhexyl acrylate)	0.42

EXAMPLE 13

The procedures of Example 1 are repeated except for the difference that a chemically equivalent amount of hydroxyethyl acrylate is substituted for the hydroxyethyl methacrylate component of Copolymer C.

EXAMPLE 14

The procedures of Example 1 are repeated except for the difference that a chemically equivalent amount of hydroxypropyl acrylate is substituted for the hydroxyethyl methacrylate component of Copolymer C.

EXAMPLE 15

The procedures of Example 1 are repeated except for the difference that a chemically equivalent amount of hydroxypropyl methacrylate is substituted for the hydroxyethyl methacrylate component of Copolymer C.

EXAMPLE 16

The procedures of Example 1 are repeated with the single difference that an equivalent amount of poly

(butyl acrylate), $\overline{M}_n=9000$ is substituted for the poly (2-ethylhexyl acrylate) flow control agent.

EXAMPLE 17

The procedures of Example 1 are repeated with the single difference that an equivalent amount of poly (lauryl methacrylate) $\overline{M}_n=6000$ is substituted for the poly (2-ethyl hexyl acrylate) flow control agent.

EXAMPLE 18

The procedures of Example 1 are repeated with the single difference that an equivalent amount of poly (isodecyl methacrylate), $\overline{M}_n=5000$, is substituted for the poly (2-ethylhexyl acrylate) flow control agent.

EXAMPLE 19

The procedures of Example 1 are repeated with the single difference that an equivalent amount of polyethylene glycol perfluoro octonate, $\overline{M}_n=3400$, is substituted for the poly (2-ethylhexyl acrylate) flow control agent.

EXAMPLE 20

The procedures of Example 1 are repeated with the single difference that an equivalent amount of poly (methyl siloxane) is substituted for the poly (2-ethylhexyl acrylate) flow control agent.

EXAMPLE 21

The procedures of Example 1 are repeated with the single difference that the flow control agent poly (2-ethylhexyl acrylate), is reduced from 0.42 grams to 0.25 grams.

EXAMPLE 22

The procedures of Example 1 are repeated with the single difference that the flow control agent, poly (2-ethylhexyl acrylate) is increased from 0.42 to 0.75 grams.

EXAMPLE 23

The procedure of Example 1 are repeated with the single difference that the flow control agent, poly (2-ethylhexyl acrylate), is increased from 0.42 grams to 1.0 grams.

EXAMPLE 24

The procedures of Example 1 are repeated with the single difference that the flow control agent, poly (2-ethylexyl acrylate), is increased from 0.42 grams to 1.5 grams.

EXAMPLE 25

The procedure of Example 1 is repeated except for the difference that a functionally equivalent amount of poly (sebasic anhydride) is substituted for the poly (azelaic anhydride) in the coating material formulation.

EXAMPLE 26

The procedure of Example 1 is repeated with the single difference that the copolymer is formed from the following monomers:

Reactants	Percent by Weight Of Total Reactants
glycidyl methacrylate	20
hydroxyethyl methacrylate	2

-continued

Reactants	Percent by Weight Of Total Reactants
isobutyl acrylate	25
alpha methyl styrene	15
methacrylonitrile	15
methyl methacrylate	23

EXAMPLE 27

The procedure of Example 1 is repeated with the single difference that the copolymer is formed from the following monomers:

Reactants	Percent By Weight Of Total Reactants
glycidyl methacrylate	12
hydroxyethyl methacrylate	3
2-ethylhexyl acrylate	10
acrylonitrile	25
methyl methacrylate	50

EXAMPLE 28

The procedure of Example 1 is repeated with the single difference that the copolymer is formed from the following monomers as follows:

Reactants	Percent by Weight Of Total Reactants
glycidyl methacrylate	10
hydroxyethyl methacrylate	10
vinyl toluene	5
butyl methacrylate	35
methyl methacrylate	40

The term "polyanhydride" as used herein means a homopolymer of a monomeric anhydride of a dicarboxylic acid.

Many modifications of this invention will be apparent to those skilled in the art in view of this specification. It is intended that all such modifications which fall within the scope of this invention be included within the appended claims.

We claim:

1. In a thermosettable powder paint which exclusive of pigments, catalysts, antistatic agents, plasticizers and flow control agents, the same being conventional nonreactive additives to a thermosettable powder paint, consists essentially of a coreactive particulate mixture of

1. a [qualitatively difunctional] copolymer of about 5 to about 20 weight percent of a glycidyl ester of a monoethylenically unsaturated acid and about 95 to about 80 weight percent of monoethylenically unsaturated monomers and having a glass transition temperature in the range of about 40° C. to about 90° C. and a molecular weight (M_n) in the range of about 1500 to about 15,000, and
2. a C_4–C_{20} saturated, straight chain, aliphatic dicarboxylic acid,

the improvement wherein

A. said copolymer is qualitatively difunctional and said other monoethylenically unsaturated monomers consist essentially of difunctional monomers selected from the group consisting of C_5–C_7 hydroxyalkyl acrylates and C_5–C_7 hydroxyalkyl methacrylates in an amount comprising about 2 to about 10 weight percent of said copolymer and monofunctional monomers selected from the group consisting of esters of a C_1–C_8 monohydric alcohol and acrylic acid, esters of a C_1–C_8 monohydric alcohol and methacrylic acid and C_8–C_{12} monovinyl hydrocarbons, and

B. there is substituted for a portion of said dicarboxylic acid a polyanhydride having molecular weight in the range of about 1000 to about 5000 and the resultant mixture of said dicarboxylic acid and said polyanhydride is [porportional] *proportional* and quantified such that said dicarboxylic acid is present in an amount that provides about 0.1 to about 0.6 carboxyl groups per [epoxy] *functional* group on said copolymer and said polyanhydride is present in an amount that provides about 0.2 to about 1.1 anhydride pgroups per [epoxy] *functional* group on said polymer.

2. A powder paint in accordance with claim 1 wherein said dicarboxylic acid is present in an amount sufficient to provide about 0.4 to about 0.6 carboxyl group for each [epoxy] *functional* group on said copolymer.

3. A powder paint in accordance with claim 1 wherein said polyanhydride has molecular weight ($\overline{M}_n$ in the range of about 1000 to about 2500.

4. A powder paint in accordance with claim 1 wherein said copolymer has molecular weight ($\overline{M}_n$) in the range of about 2500 to about 6000.

5. A powder paint in accordance with claim 1 wherein said glycidyl ester is an ester selected from the group consisting of glycidyl acrylate and glycidyl methacrylate.

6. A thermosettable powder paint which comprises a coreactive mixture of:

1. a qualitatively difunctional copolymer having a glass transition temperature in the range of about 40° C. to about 90° C. and a molecular weight (M_n) in the range of about 1,500 to about 15,000, said copolymer being formed from a monomer mixture consisting essentially of

(a) between about 5 and about 20 weight percent of a glycidyl ester of a monoethylenically unsaturated acid;

(b) between about 2 and about 10 weight percent of difunctional monomers selected from the group consisting of C_5–C_7 hydroxyalkyl acrylates and C_5–C_7 hydroxyalkyl methacrylates;

(c) between about 70 and about 93 weight percent of monoethylenically unsaturated monomers consisting essentially of monofunctional monomers selected from the group consisting of esters of a C_1–C_8 monohydric alcohol and acrylic acid, esters of a C_1–C_8 monohydric alcohol and methacrylic acid and C_8–C_{12} monovinyl hydrocarbons; and

(d) up to 30 weight percent of modifying monomers selected from the group consisting of vinyl chloride, acrylonitrile, methacrylonitrile and vinyl acetate;

2. a mixture of (a) C_4–C_{20} saturated, straight chain, aliphatic dicarboxylic acids and (b) polyanhydride having a molecular weight (M_n) in the range of up to about 5,000, said /mixture being proportional and quantified such that said dicarboxylic acid is present in an amount that provides about 0.1 to about 0.6 carboxyl groups per functional group on said copolymer and said polyanhydride is present in an amount that provides about 0.2 to about 1.1 anhydride groups per functional group on said copolymer.

7. A powder paint in accordance with claim 6 wherein said copolymer has a glass transition temperature in the range of about 50° C. to about 80° C. and a molecular weight (M_n) in the range of about 2,500 to about 6,000.

8. A powder paint in accordance with claim 6 wherein said glycidyl ester is an ester selected from the group consisting of glycidyl acrylate and glycidyl methylate and is included in said monomer mixture in an amount ranging from about 8 to about 15 weight percent.

9. A powder paint in accordance with claim 1 wherein greater than 50 weight percent of said monofunctional, monoethylenically unsaturated monomers of said monomer mixture are exters of a C_1–C_8 monohydric alcohol and either acrylic or methacrylic acid.

10. A powder paint in accordance with claim 1 wherein said C_8–C_{12} monovinyl hydrocarbons are selected from the group consisting of styrene, vinyltoluene, t-butylstyrene, chlorostyrene and alphamethylstyrene.

11. A powder paint in accordance with claim 1 wherein said polyanhydride has a molecular weight (M_n) in the range of about 1,000 to about 2,500.

12. A powder paint in accordance with claim 1 wherein said saturated, straight chain, aliphatic dicarboxylic acid contains 5 to 13 carbons.

13. A powder paint in accordance with claim 1 wherein said saturated, straight chain, aliphatic dicarboxylic acids are selected from the group consisting of adipic acid, pimelic acid, suberic acid, azelaic acid, sebasic acid, undecanoic acid and brassylic acid.

14. A power paint in accordance with claim 1 wherein said polyanhydrides are selected from the group consisting of poly(adipic anhydrides), poly(azelaic anhydrides), and poly(sebasic anhydrides).

15. A thermosettable powder paint which, exclusive of pigments, catalysts, antistatic agents, plastizers, flow control agents and other unreactive additives, consists essentially of a coreactive mixture of:

1. A qualitatively difunctional copolymer having a glass transition temperature in the range of about 50° C. to about 80° C. and a molecular weight (M_n) in the range of about 2,500 to about 6,000, said copolymer being formed from a monomer mixture consisting essentially of

(a) between about 8 and about 15 weight percent of a glycidyl ester of a monoethylenically unsaturated carboxylic acid;

(b) between about 2 and about 10 weight percent of difunctional monomers selected from the group consisting of C_5–C_7 hydroxyalkyl acrylates and C_5–C_7 hydroxyalkyl methacrylates; and

(c) between about 75 and about 90 weight percent of monoethylenically unsaturated monomers consisting essentially of monofunctional monomers selected from the group consisting of (i) esters of a C_1–C_8 monohydric alcohol and acrylic acid, (ii) esters of a C_1–C_8 monohydric alcohol and methacrylic acid, and (iii) C_8–C_{12} monovinyl hydrocarbons, the total of said monofunctional monomers (i) and (ii) comprising at least 50 weight percent of said monofunctional monoethylenically unsaturated monomers of said monomer mixture; and

2. A mixture of (a) C_5–C_{13} saturated, straight chain, aliphatic dicarboxylic acids and (b) polyanhydrides having a molecular weight in the range of about 1,000 to about 2,500, said mixture being proportional and quantified such that said dicarboxylic acid is present in an amount that provides about 0.1 to about 0.6 carboxyl groups per functional group on said copolymer and said polyanhydride is present in an amount that provides about 0.2 to about 1.1 anhydride groups per functional group on said copolymer.

16. A powder paint in accordance with claim 15 wherein said glycidyl ester is selected from the group consisting of glycidyl mthacrylate and glycidyl acrylate.

17. A powder paint in accordance with claim 15 wherein said C_5–C_{13} saturated, straight chain, aliphatic dicarboxylic acids are selected from the group consisting of adipic acid, pimelic acid, suberic acid, azelaic acid, sebasic acid, undecanoic acid and brassylic acid and wherein said polyanhydrides are selected from the group consisting of poly(adipic anhydride), poly(azelaic anhydride), and poly(-sebasic anhydride).

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