EUROPEAN PATENT SPECIFICATION

Imide modified epoxy resins
Imid-modifizierte Epoxyharze
Resines époxydes modifiées par une imide

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References cited:
US-A- 4 579 916

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Description

The present invention pertains to modified epoxy resins and their use in coating compositions. Powder coatings are increasingly becoming an important segment of the coatings industry. They offer a wide range of advantages over conventional solvent borne coatings, such as the absence of volatile organic compounds, 95-98 percent recovery of over-sprayed powder, superior corrosion and chemical resistance, and the like. One major disadvantage, however, particularly for polyester/epoxy hybrid decorative coatings, is their lack of flow-out during cure and the resulting uneven or "orange-peel" appearance. This poor appearance is caused predominantly by the high melt viscosity of the solid carboxyl functional polyester resin and the unsatisfactorily high melt viscosity of the solid epoxy resin used to cure the polyester resin. There are several solid epoxy resins based upon bisphenol A which have low melt viscosities, such as D.E.R.™ 661 and D.E.R.™ 662 solid epoxy resins available from The Dow Chemical Company and EPON™ 1001 and EPON™ 1002 solid epoxy resins available from Shell Chemical Company. Solid epoxy resins are typically available for powder coatings as a finely divided solid flake, chip or granule. These resins can conceivably be used for powder coatings to provide smooth finishes. However, because of their low softening points, they are found to not be stable upon prolonged periods of storage at ambient temperatures. If stored for long periods of time, the resin flakes, chips or granules tend to clump together (sinter) rendering them unusable until mechanically broken apart.


The coatings industry considers standard epoxy resins which have Mettler softening points of 90°C and above to be storage stable whereas those having Mettler softening points below 85°C require refrigerated storage. Those standard resins having Mettler softening points between 85°C and 90°C may or may not require special storage facilities.

It would be desirable to have available solid epoxy resins which have physical storage stability (a Mettler softening point of at least 85°C) while possessing a relatively low melt viscosity. Because of the inherent storage problem associated with low melt viscosity epoxy resins, it would be desirable to have available epoxy resins which not only have very low melt viscosities, but also have adequate physical storage stability as evidenced by their high softening points.

This object is attained by a solid modified epoxy resin obtainable by reacting

(a) a solid epoxy resin having an average of more than one vicinal epoxide group per molecule with
(b) a monoimide of a dicarboxylic acid,

characterized in that

the monoimide is free of allyl and methallyl groups which are not member of an unsaturated cycloaliphatic ring and is employed in an amount of from 0,5 to 10 percent by weight based on the combined weights of component (a) and (b) and the resulting solid modified epoxy resin having a Mettler softening point of at least 85°C.

These resins would advantageously provide high flow-out and consequently impart very smooth finishes without the need for special resin storage facilities.

The reaction raises the Mettler softening point to at least 85°C when the resin before modification has a Mettler softening point below 85°C or when the softening point of the unmodified resin is above 85°C, an amount sufficient to raise the softening point by at least 2°C.

The present invention also pertains to curable compositions containing the aforementioned monoimide modified epoxy resins and a curing quantity of a curing agent therefor.

The present invention also pertains to the use of the curable composition as coating compositions containing the aforementioned monoimide modified epoxy resins.

The present invention therefore provides for solid epoxy resins which exhibit an improvement in physical storage stability without a significant increase in melt viscosity.

If desired, these resins can conveniently be prepared by reacting a relatively low molecular weight epoxy resin with an organic compound having an average of 2 aromatic hydroxyl groups per molecule, hereafter referred to as a dihydric phenol, in the presence of a suitable advancement catalyst at temperatures of from 50°C to 250°C, suitably from 100°C to 200°C, more suitably from 150°C to 175°C for a period of time to essentially complete the advancement reaction, suitably from 1 to 24, more suitably from 2 to 6, most suitably from 3 to 4 hours. The epoxy resin and the organic compound having an average of 2 aromatic hydroxyl groups per molecule are reacted in amounts which provide a ratio of aromatic hydroxyl groups to epoxy groups of from 0.1:1 to 0.9:1, suitably from 0.3:1 to 0.7:1, more suitably from 0.4:1 to 0.6:1. The resultant products have Mettler softening points of at least 85°C, preferably at least 90°C.

Any epoxy resin having an average of more than one vicinal epoxy group per molecule which can be reacted with a dihydric phenol to form a solid epoxy resin can be modified as described herein. Particularly suitable are those epoxy resins having the following Formulas I, II, III and IV:
wherein each A is independently a divalent hydrocarbon group having from 1 to 10, suitably from 1 to 6, carbon atoms, -O-, -S-, -S-S-, -SO-, -SO_2- or -CO-. Q is a trivalent hydrocarbon group having from 1 to 10 carbon atoms; each A' is independently a hydrocarbon group having from 1 to 10, suitably from 1 to 4, carbon atoms; each R is independently hydrogen or an alkyl group having from 1 to 4 carbon atoms; each X is independently hydrogen, a hydrocarbonyl or hydrocarboxyloxy group having from 1 to 10, suitably from 1 to 4 carbon atoms, bromine, chlorine or fluorine; m has an average value of from zero to 15; m' has an average value from 0.001 to 5, suitably from 0.001 to 3; and n has a value of zero or 1.

The term hydrocarbonyl as employed herein means any aliphatic, cycloaliphatic, aromatic, aryl substituted aliphatic or cycloaliphatic, or aliphatic or cycloaliphatic substituted aromatic groups. Likewise, the term hydrocarboxyloxy means a hydrocarbonyl group having an oxygen linkage between it and the object to which it is attached.

The epoxy resins which can be modified according to the present invention can be purchased commercially from several sources, e.g. The Dow Chemical Company, Shell Chemical Company or Ciba-Geigy Corp., to name a few.

Suitable dihydric phenols which can be employed herein to prepare solid epoxy resins by reaction with liquid epoxy resins include, for example, those represented by the following formulas V and VI:
wherein each A, X and n is as defined above.

Suitable catalysts for reacting the epoxy resin with the dihydric phenol include any acid or base (Lewis, Brønsted-Lowry type, nitrogen-, phosphorus-, oxygen-, or sulfur-containing bases such as tertiary amines; primary, secondary or tertiary phosphines; metal salts of alcohols, phenols, carboxylic acids or water; thioethers and the like) or any compound which will catalyze the reaction between an epoxy group and a phenolic hydroxyl group such as, for example, imidazoles, tertiary amines, quaternary ammonium compounds, phosphonium compounds, phosphines, or combinations thereof. Suitable imidazoles include, for example, 2-methylimidazole, 2-ethyl-4-methylimidazole, 2-ethylimidazole, 1-methylimidazole, 1-propylimidazole, 2-phénylimidazole, and combinations thereof. Suitable tertiary amines include, for example, N,N-dimethylbenzylamine, N,N-dimethylamiline, triethylamine, tripropylamine, triphehylamine, and combinations thereof. Suitable quaternary ammonium catalysts which can be employed herein include, for example, benzyl trimethyl ammonium chloride, benzyl trimethyl ammonium bromide, tetrabutyl ammonium chloride, and combinations thereof. Particularly suitable phosphonium compounds include, for example, ethyltriphenyl phosphonium chloride, ethyltriphenyl phosphonium bromide, ethyltriphenyl phosphonium iodide, ethyltriphenyl phosphonium acetate-acetic acid complex, tetrabutyl phosphonium chloride, tetrabutyl phosphonium bromide, tetrabutyl phosphonium iodide, tetrabutyl phosphonium acetate-acetic acid complex, and combinations thereof. Suitable catalysts which can be employed herein include, for example, those disclosed in U.S. Patents 3,326,672; 3,341,580; 3,379,684; 3,477,990; 3,547,881; 3,948,855; 4,048,141; 4,093,650; 4,131,633; 4,132,706; 4,171,420; 4,177,216; 4,302,574; 4,320,222; 4,366,295; and 4,389,520.

Instead of preparing the solid epoxy resin for modification as described herein, one can just as well employ commercially available solid epoxy resins as mentioned above. These epoxy resins can have the formulas I and II described above wherein the value of m is from 2 to 15, more suitably from 2 to 10, most suitably from 3 to 6, or formula III where m' has a value of at least 3.

The reaction between the monoimide-containing compound and the solid epoxy resin can be conducted in the presence of a suitable catalyst for reacting an epoxy (oxirane) group with an imide group. The reaction is suitably conducted at a temperature of from 100°C to 250°C, suitably from 125°C to 200°C, more suitably from 150°C to 175°C for a period of time to essentially completely the addition reaction, suitably from 0.25 to 4, more suitably from 0.25 to 2, most suitably from 0.5 to 1 hour(s). Higher temperatures require less reaction time than do lower temperatures. Temperatures above 250°C can result in an undesired reaction between epoxy groups and hydroxyl groups of the modified epoxy resin which can result in an excess molecular weight increase of the polymer.

At temperatures below 100°C, the reaction is unsatisfactorily slow. In some epoxy resins, the imide may be insoluble at temperatures below 100°C and thus will not appreciably react. In addition, at these temperatures, the mixture may be too viscous for effective mixing.

The imide compound is employed in an amount which is sufficient to raise the Mettler Softening point to at least 85°C, or if the softening point is already above 85°C, to raise the Mettler softening point by at least 2°C. Usually from 0.5 to 10, suitably from 1 to 8, more suitably from 2 to 6, percent of the monoimide compound based on the combined weight of the imide compound and the epoxy resin is sufficient.

Suitable catalysts for effecting the reaction between the epoxy groups of the epoxy resin and an imide group include, for example, those previously described as being suitable for the reaction between an epoxy resin and a phenolic hydroxyl group. Particularly suitable catalysts include, for example, ethyltriphenyl phosphonium chloride, ethyltriphenyl phosphonium bromide, ethyltriphenyl phosphonium iodide, ethyltriphenyl phosphonium acetate-acetic acid complex, ethyltriphenyl phosphonium phosphate-phosphoric acid complex, tetrabutyl phosphonium chloride, tetrabutyl phosphonium bromide, tetrabutyl phosphonium iodide, tetrabutyl phosphonium acetate-acetic acid complex, tetrabutyl phosphonium phosphate-phosphoric acid complex, and those catalysts disclosed in U.S. Patent 3,962,182.

Suitable monooimide compounds which can be employed herein include, for example, those represented by the following formula VII.
wherein each \( R^1, R^2, R^3, R^4 \) is independently hydrogen or a hydrocarbyl group having from 1 to 20, suitably from 1 to 10, more suitably from 1 to 5, carbon atoms or \( R^2 \) and \( R^3 \) can be combined to form a saturated or unsaturated cycloaliphatic ring or an aromatic ring or another bond between the carbon atoms to which they are attached.

Particularly suitable monomer compounds include, for example, maleimide, phthalimide, succinimide, tetrahydrophthalimide, dihydrophthalimide, hexahydrophthalimide, naphthalenedicarboximide, pentanedicarboximide, hexanedicarboximide, 3-methyl-1,2-benzene dicarboximide, 4-methyl-1,2-benzene dicarboximide, 4-phenyl-1,2-benzene dicarboximide, 1,2-cyclobutane-dicarboximide, 1,2-cyclopentane-dicarboximide, 1,2-cyclohexanedicarboximide, 1,2-cycloheptane-dicarboximide, 3-methyl-1,2-cyclohexyldicarboximide, 3-methyl-azacyclohexane-2,6-dione, 4-methyl-aza cyclohexane-2,6-dione, 3-ethyl-azacyclopentane-2,5-dione, 3-ethyl-4-methyl-azacyclopentane-2,5-dione, 3,4-dimethyl azacyclopentene-2,5-dione, and combinations thereof.

The modified epoxy resins of the present invention can be cured with any suitable curing agent for epoxy resins including, for example, primary and secondary polyamines, carboxylic acids and anhydrides thereof, phenolic hydroxyl-containing compounds, ethylene-acrylic acid copolymers, ethylene-methacrylic acid copolymers, styrene-acrylic acid copolymers, styrene-methacrylic acid copolymers, polyisocyanates, guanidines, biguanides, urea-aldehyde resins, melamine-aldehyde resins, alkoxylated urea-aldehyde resins, alkoxylated melamine-aldehyde resins, polynicarbazoles, tertiary amines, aromatic polyamines such as methylenedianiline and diaminodiphenylsulfone, sulfonylimides, phosphites and partial esters thereof, phosphates, Lewis acids such as boron trifluoride and complexes thereof, combinations thereof and the like. Particularly suitable curing agents include, for example, dicyanodiamide, phenolic compounds such as phenol-formaldehyde novolac resins, cresol-formaldehyde novolac resins, D.E.H.™ 81, D.E.H.™ 82, D.E.H.™ 84 and D.E.H.™ 85 curing agents available from The Dow Chemical Company, imidazoles such as 2-methylimidazole, 2-phenylimidazole and reaction products of 2-methylimidazole or 2-phenylimidazole with liquid epoxy resins, trimellitic anhydride, pyromellitic dianhydride, phthalic anhydride, maleic anhydride, succinic anhydride, chlorendic anhydride, carboxy functional polyester resins, and combinations thereof. The curing agents are employed in an amount which will effectively cure the composition containing the modified epoxy resin. These amounts will depend upon the particular modified epoxy resin and curing agent employed; however, suitable amounts include, for example, from 0.1 to 1.5, more suitably from 0.5 to 1.25, most suitably from 0.75 to 1, equivalent(s) of curing agent per equivalent of epoxy resin.

The modified epoxy resins of the present invention can be blended with other materials such as solvents or diluents, fillers, pigments, dyes, flow modifiers, thickeners, reinforcing agents, leveling agents, extenders, antistatic agents, or other polymers such as unmodified epoxy resins, polyethylene, polystyrene, polypolypropylene, ethylene-alkyl acrylate copolymers, nylons, polyester resins, poly(vinyl chloride) or poly(vinylidene chloride) resins, and combinations thereof.

These additives, when employed are added in functional equivalent amounts e.g., the pigments and/or dyes are added in quantities which will provide the composition with the desired color; however, they are suitably employed in amounts of from 5 to 70, suitably from 10 to 60, more suitably from 30 to 50, percent by weight based upon the weight of complete or total coating mixture.

Solvents or diluents which can be employed in coating applications other than powder coatings include, for example, hydrocarbons, ketones, glycol ethers, alcohols, ethers, and combinations thereof. Particularly suitable solvents or diluents include, for example, toluene, benzene, xylene, methyl ethyl ketone, methyl isobutyl ketone, diethyl ether, dipropyl glycol, methanol, ethanol, propanol, isopropyl alcohol, sec-butyl alcohol, tert-butyl alcohol, ethyl ether, ethyl methyl ether, propyl ether, butyl ether, hexyl ether, and combinations thereof.

The modifiers such as thickeners, flow modifiers and the like can be suitably employed in amounts of from 0.1 to 5, suitably from 0.5 to 3, more suitably from 0.75 to 2, percent by weight based upon the weight of the total coating mixture.

The fillers, when employed, can be suitably employed in amounts of from 5 to 70, suitably from 10 to 60, more suitably from 30 to 50, percent by weight based upon the weight of the total coating mixture.
EXAMPLE 1

In a 2-liter 5-necked round-bottom flask equipped with a mechanical stirrer, thermometer, temperature controlled heating mantel, nitrogen purge, and reflux condenser, were placed 800.2 g (4.23 epoxide equiv.) of a diglycidyl ether of bisphenol A having an epoxide equivalent weight (EEW) of 189 and 274.3 g (2.41 hydroxyl equiv.) of Bisphenol A (ER grade). The mixture was heated to 100°C with stirring under nitrogen atmosphere. The temperature was maintained at 100°C until dissolution of the Bisphenol A. A catalyst, (a 70 weight percent solution of ethyl triphenyl-phosphonium acetate-acetic acid complex in methanol), 1.0 ml. was then added while maintaining stirring. The temperature controller was set to 150°C and the voltage applied to the heating mantel was adjusted so that the temperature of the reaction mixture raised at an initial rate of no greater than 1°C - 2°C per minute. The reaction mixture was allowed to exotherm and then cool to 170°C. (Peak temperature ranged from 170°C 200°C). The temperature was maintained at this temperature and a sample of the resin was drawn for EEW and softening point determination. The unmodified resin had an EEW of 580 and a Mettler softening point of 82°C. Phthalimide (5.0 weight percent) was then added to the molten resin and a small exothermic reaction occurred which caused the temperature of the reaction mixture to rise, ~10°C. After the exotherm, the reaction mixture was allowed to cool to 170°C and was held at this temperature for 20-30 minutes and then poured out and allowed to cool to room temperature. The resulting clear, pale yellow resin has an EEW of 772, Mettler softening point of 93.3°C, and a melt viscosity (150°C, Kinematic) of 1435 centistokes (0.001435 m²/s).

EXAMPLES 2-13 and COMPARATIVE EXPERIMENTS A-D

Examples 2 - 13 and Comparative Experiments A-D were prepared in a manner similar to Example 1 using the reagent quantities shown on Table I. The Comparative Experiments do not employ an imide. The resulting resins EEWs, Mettler softening points, and viscosities are also shown in Table I.
TABLE I

<table>
<thead>
<tr>
<th>Example No. or Comp. Expt. Letter</th>
<th>Base Resin</th>
<th>Modified Resin</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>DGEBA(^a) grams</td>
<td>Bis A grams</td>
</tr>
<tr>
<td>1</td>
<td>800.2</td>
<td>274.3</td>
</tr>
<tr>
<td>Comp. Expt. A(^*)</td>
<td>800</td>
<td>302</td>
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<tr>
<td>2</td>
<td>977.3</td>
<td>322.7</td>
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<td>Comp. Expt. B(^*)</td>
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<tr>
<td>3</td>
<td>955.7</td>
<td>304.3</td>
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<tr>
<td>4</td>
<td>900.0</td>
<td>308.5</td>
</tr>
<tr>
<td>Comp. Expt. C(^*)</td>
<td>723.4</td>
<td>276.6</td>
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<tr>
<td>5</td>
<td>986.6</td>
<td>313.4</td>
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<td>6</td>
<td>908.9</td>
<td>311.6</td>
</tr>
<tr>
<td>7</td>
<td>900.0</td>
<td>308.5</td>
</tr>
<tr>
<td>8(^e)</td>
<td>986.6</td>
<td>313.4</td>
</tr>
<tr>
<td>9</td>
<td>800.2</td>
<td>274.3</td>
</tr>
<tr>
<td>10</td>
<td>800.2</td>
<td>274.3</td>
</tr>
<tr>
<td>Comp. Expt. D(^*)</td>
<td>712.8</td>
<td>287.2</td>
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<tr>
<td>11</td>
<td>2213.5</td>
<td>703.1</td>
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<tr>
<td>12</td>
<td>2218.4</td>
<td>713.8</td>
</tr>
<tr>
<td>13</td>
<td>985.6(^f)</td>
<td>319.3</td>
</tr>
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</table>

*Not an example of the present invention.

\(^a\) Diglycidyl ether of Bisphenol A having an EEW of 189 (liquid, no Mettler softening point).

\(^b\) Phthalimide.

\(^c\) Mettler softening point.

\(^d\) Kinematic melt viscosity in centistokes measured at 150°C (1 centistoke = 0.000001 m²/s)

\(^e\) Phthalimide added prior to advancement.

\(^f\) Diglycidyl ether of Bisphenol A having an EEW of 183 instead of 189 (liquid, no Mettler softening point).

The data in Table I demonstrates that epoxy resins which have been modified with an imide have desirably reduced melt viscosities as compared to epoxy resins which have not been modified with an imide and which have comparable softening points.
EXAMPLE 14

A diglycidyl ether of Bisphenol A having an EEW of 189 (900 g, 4.76 epoxide equiv.) and Bisphenol A (308.5 g, 2.71 phenolic OH equiv.) were mixed and allowed to react as in Example 1. After complete reaction of the liquid resin and Bisphenol A, 42.8 g (3.4 weight percent) succinimide was added to the molten resin with stirring at 170°C. A slight exothermic reaction occurred. After the reaction mixture temperature returned to 170°C, the mixture was allowed to stir at this temperature for ~15 minutes, and allowed to cool to room temperature. A pale yellow, transparent resin resulted which has an EEW of 783, Mettler softening point of 93.6°C and a melt viscosity (150°C, Kinematic) of 1571 centistokes (0.001671 m²/s). The resin, before succinimide addition, had an EEW of 583 and a Mettler softening point of 81°C.

EXAMPLE 15

Example 15 was prepared in a manner suitable to Example 14 except that 450.0 g (2.36 epoxide equiv.) of the diglycidyl ether of Bisphenol A and 154.3 g (1.35 phenolic OH equiv.) of Bisphenol A were used and tetrahydrophthalimide (32.5 g, 5.1 weight percent) was used in place of succinimide. The resulting pale yellow, transparent resin had an EEW of 808, Mettler softening point of 93.9°C, and a melt viscosity (150°C, Kinematic) of 1767 centistokes (0.001767 m²/s). The resin before reaction with tetrahydrophthalimide had an EEW of 650 and a Mettler softening point of 85°C.

EXAMPLE 16

A powder coating was prepared from the resin prepared in Example 12. Example 12 resin (23.4 weight percent), Scaco P2610 (35.1 weight percent, a carboxyl functional polyester resin), titanium dioxide (40.0 weight percent), benzoin (0.7 weight percent), and Acrylon™MFP (0.8 weight percent, a flow modifier) were weighed out and dry blended. The mixture was then melt mixed using a Buss Condux PLK 46 single screw extruder, operated at 120 rpm with Zone 1 set at 70°C and Zone 2 set at 110°C. The extrudate was passed through BCI Chill Rolls, cooled, and crushed. The crushed extrudate was then ground into a fine powder using a Brinkman Centrifugal Grinding Mill utilizing the 24 tooth grinding attachment and classified by sieving through No. 140 (150 mesh) standard sieves (wire cloth). The powder coating was then applied via electrostatic spray with a Gemas Ag Type 710 Laboratory Unit (set at 60 - 70 kV) on the 4" x 12" x 20 gauge (101.6 mm x 304.8 mm x 0.9 mm) cold rolled steel, clean treatment, Parker test panels. The powder coated panels were then cured at 180°C for 30 minutes in a Blue M Touchmatic convection oven. After removal from the oven, the panels were allowed to cool and the coating properties were evaluated. The resulting powder coating has equivalent coating properties with superior smoothness as compared to a similar powder coating made from standard epoxy resin (See Comparative Experiment E). Coating evaluation data is found in Table II.

EXAMPLE 17

A powder coating was prepared using the method described in Example 16 with the following change in ingredients. Example 12 resin (19.4 weight percent), Scaco P2610 (29.1 weight percent), titanium dioxide (50 weight percent), benzoin (0.7 weight percent), Acrylon MFP (0.8 weight percent). The coating resulting from this powder has good physical properties and an appearance equivalent to a similar powder coating made from standard epoxy resin. Coating evaluation data is found in Table II.

EXAMPLE 18

A powder coating was prepared using the method described in Example 16 with the following change in ingredients. Example 12 resin (15.4 weight percent), Scaco P2610 (23.1 weight percent), titanium dioxide (60 weight percent), benzoin (0.7 weight percent), Acrylon MFP (0.8 weight percent). Coating evaluation data is found in Table II.

COMPARATIVE EXPERIMENT E (Not an Example of the Present Invention)

A powder coating was prepared using the method described in Example 16 with the following change in ingredients. A diglycidyl ether of bisphenol A having an EEW of 700 commercially available from The Dow Chemical Company as D.E.R.™662UH (23.4 weight percent), Scaco P2610 (35.1 weight percent), titanium dioxide (40 weight percent), benzoin 0.7 weight percent), Acrylon MFP (0.8 weight percent). Coating evaluation data for this powder coating is found in Table II.
EXAMPLE 19

A powder coating was prepared by first melting Example 12 resin and then mixing in 2 weight percent BYK 361 (a flow modifier). Once thoroughly mixed, the molten resin was allowed to cool and then formulated using the method described in Example 16. The amounts of the ingredients were as follows: Example 12 resin containing BYK 361 (23.7 weight percent), Scaco P2610 (35.6 weight percent), titanium dioxide (40 weight percent), benzoin (0.7 weight percent). The coating prepared from this powder has superior smoothness as compared to a similar powder prepared from standard epoxy resin which contains 2 weight percent BYK 361 (see Comparative Experiment F). Coating evaluation data for this powder coating is found in Table II.

COMPARATIVE EXPERIMENT F (Not an Example of the Present Invention)

A powder coating was prepared by first melting a diglycidyl ether of bisphenol A having an EEW of 700 commercially available from The Dow Chemical Company as D.E.R.™ 662UH and then mixing in 2 weight percent BYK 361. Once thoroughly mixed, the molten resin was allowed to cool and then formulated using the method described in Example 16. Coating evaluation data for this powder coating is found in Table II.

<table>
<thead>
<tr>
<th>TABLE II</th>
</tr>
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<tbody>
<tr>
<td>TEST</td>
</tr>
<tr>
<td>EXAMPLE OR COMPARATIVE EXPERIMENT</td>
</tr>
<tr>
<td>16</td>
</tr>
<tr>
<td>----------------------------------</td>
</tr>
<tr>
<td>Impact (F/R)(^a)</td>
</tr>
<tr>
<td>Gloss (20°/60°)</td>
</tr>
<tr>
<td>Cross Hatch Adhesion (% Loss)</td>
</tr>
<tr>
<td>MEK Db Rbs(^b)</td>
</tr>
<tr>
<td>Pill Flow (mm)(^c)</td>
</tr>
<tr>
<td>Y11 (Initial)(^d)</td>
</tr>
<tr>
<td>Y10B (30 min. OB)(^e)</td>
</tr>
<tr>
<td>Gel Time (sec)(^f)</td>
</tr>
<tr>
<td>Pencil Hardness</td>
</tr>
</tbody>
</table>

\(^a\) Not an example of the present invention.
\(^b\) Forward and reverse impact.
\(^c\) Methyl ethyl ketone double rubs.
\(^d\) 0.75g pill (6mm x 12 mm diameter) inclined at 60° in a 300°F (149°C) oven for 15 minutes.
\(^e\) Yellowness index, initial reading.
\(^f\) Yellowness index reading after 30 minute overbake at 180°C.

EXAMPLE 20

A solid diglycidyl ether of bisphenol A having an EEW of 535, a melt viscosity at 150°C of 920 cSt (0.00092 m²/S) and a Mettler softening point of 78°C was reacted with 5 weight percent phthalimide at 170°C for 2 hours. The resultant
modified, solid epoxy resin has a Mettler softening point of 88°C.

EXAMPLE 21

A solid glycidyl ether of bisphenol A having an EEW of 671, a melt viscosity of 1813 cSt (0.001813 m²/s) at 150°C, and a Mettler softening point of 93°C was reacted with 1.0 weight percent phthalimide at 170°C for 50 minutes. The resultant modified, solid epoxy resin has Mettler softening point of 96°C.

Three typical solid epoxy resins (Comparative Experiments G-I) and two resins of this invention (Examples 20 and 21) were evaluated using the accelerated storage stability test method described below. The results of this study are shown in Table III in which the time required for each sample to sinter is shown. Three of these resins are commercially available solid epoxy resins available from The Dow Chemical Company, as D.E.R.™ 661 epoxy resin (Comparative Experiment G), D.E.R.™ 662 epoxy resin (Comparative Experiment H), and D.E.R.™ 662UH epoxy resin (Comparative Experiment I). These resins are in the form of solid chips or flakes ranging in size from 0.25 to 3 cm in diameter. Comparative Experiment G, has a Mettler softening point of 79°C, is known to cake or sinter during prolonged periods of storage at ambient storage temperatures which can range from 60°F to 125°F (15°C to 52°C). At higher storage temperatures, physical storage stability is reduced and the resin chips cake quickly. The resin of Comparative Experiment G is considered to be insufficiently physically storage stable. The resin of Comparative Experiment H has a Mettler softening point of 85°C, is considered to be only marginally storage stable and will cake or sinter at temperatures in the mid to high range of those typically found in a warehouse. Thus, it is not considered to be physically storage stable under most typical storage conditions. The resin of Comparative Experiment I has a Mettler softening point of 94°C and is known to be more physically storage stable under warehousing conditions.

ACCELERATED STORAGE STABILITY TEST

The epoxy resins were ground and sieved through an 80 mesh screen (180 micron or less). The powdered resins (25.0 g each) were then sealed in clear, 2 oz. (0.000059 m³) glass bottles and placed in a 40°C water bath so that the water level was above the level of the powder but not above the top of the bottles. The water temperature was maintained at 40°C for three days and then raised 3°C every three days until all of the powders had sintered. To determine the time required to sinter, the samples were removed from the bath on a regular basis (every several hours for the first day at each temperature), dried and allowed to cool for several minutes. The bottles were agitated lightly and the fluidity of the powder noted. If the samples no longer were free flowing, the bottle caps were removed and the samples were examined by lightly prodding them with a spatula. The samples were considered to be completely sintered when light prodding could no longer brake down the powder mass. The time required to reach this point was then recorded.

<table>
<thead>
<tr>
<th>EXAMPLE OR COMPARATIVE EXPERIMENT</th>
<th>METTLER SOFTENING POINT (°C)</th>
<th>TIME TO SINTER (hours)</th>
<th>MELT VISCOSITY (cSt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G*</td>
<td>79</td>
<td>3</td>
<td>600</td>
</tr>
<tr>
<td>H*</td>
<td>85</td>
<td>32</td>
<td>1000</td>
</tr>
<tr>
<td>I*</td>
<td>94</td>
<td>216</td>
<td>2200</td>
</tr>
<tr>
<td>20</td>
<td>88</td>
<td>170</td>
<td>920</td>
</tr>
<tr>
<td>21</td>
<td>96</td>
<td>336</td>
<td>2260</td>
</tr>
</tbody>
</table>

*Not an example of the present invention.

*aMeasured at 150°C (1cSt = 0.000001 m²/s).

The resin of Example 20 remains a non-sintered, flowable powder for more than five times longer than the marginally storage stable resin of Comparative Experiment H as indicated in Table III. The resin of Example 20 and Comparative Experiment H have comparable Mettler softening points, 88°C and 85°C respectively. The resin of Example 21, having a softening point and melt viscosity comparable to Comparative Experiment I, remained a non-sintered, free flowing powder for 120 hours longer than the resin of Comparative Experiment I.
Claims

1. A solid modified epoxy resin obtainable by reacting

   (a) a solid epoxy resin having an average of more than one vicinal epoxide group per molecule with
   (b) a monomide of a dicarboxylic acid,

   characterized in that

   the monomide is free of allyl and methallyl groups which are not a member of an unsaturated cycloaliphatic ring and
   is employed in an amount of from 0.5 to 10 percent by weight based on the combined weights of component (a)
   and (b) and the resulting solid modified epoxy resin having a Mettler softening point of at least 85°C.

2. A modified, solid epoxy resin of Claim 1 wherein said solid epoxy resin prior to modification is obtainable by reacting

   (A) an epoxy resin represented by the following Formulas I, II, III or IV or any combination thereof

   ...
wherein each A is independently a divalent hydrocarbon group having from 1 to 10 carbon atoms, -O-, -S-, -S-S-, -SO-, -SO₂- or -CO₂-. Q is a trivalent hydrocarbon group having from 1 to 10 carbon atoms; each A’ is independently a divalent hydrocarbon group having from 1 to 10 carbon atoms; each R is independently hydrogen or an alkyl group having from 1 to 4 carbon atoms; each X is independently hydrogen, a hydrocarbyl or hydrocarbylxy group having from 1 to 10 carbon atoms, bromine, chlorine or fluoride; m has an average value of from zero to 15; m’ has an average value from 0.001 to 5; and n has a value of zero or 1; with (B) an organic compound having an average of 2 aromatic hydroxyl groups per molecule represented by the following formulas (V) or (VI) or any combination thereof.

wherein each A and X is as defined above; and wherein components (A) and (B) are employed in quantities which provide a ratio of phenolic hydroxyl groups to epoxy groups of from 0.1:1 to 0.9:1.

3. A modified, solid epoxy resin of Claim 2 wherein component (A) is a diglycidyl ether of bisphenol A; component (B) is bisphenol A, and components (A) and (B) are employed in quantities which provide a ratio of phenolic hydroxyl
4. A modified, solid epoxy resin of Claim 2 wherein said epoxy resin is an epoxy resin represented by formulas I or II or a combination thereof wherein each A is independently a divalent hydrocarbon group having from 1 to 10 carbon atoms, \(-\text{SO}_2\), \(-\text{SO}_3\), \(-\text{S}-\), \(-\text{SO}_4\), \(-\text{CO}_2\), each R is independently hydrogen or an alkyl group having from 1 to 4 carbon atoms; each X is independently hydrogen, a hydrocarbonyl or hydrocarboxyloxy group having from 1 to 10 carbon atoms, bromine, chlorine or fluorine; m has an average value of from 2 to 15; and n has a value of zero or 1.

5. A modified, solid epoxy resin of Claim 1, 2, 3, or 4, wherein the monoiide is one or more of those represented by the following formula VII

\[
\text{FORMULA VII}
\]

\[
\begin{align*}
\text{R}_1 & \text{O} \\
\text{R}_2 & \text{C} \quad \text{C} \\
& \text{NH} \\
\text{R}_3 & \text{C} \quad \text{C} \\
& \text{R}_4 \text{O}
\end{align*}
\]

wherein each \(\text{R}_1\), \(\text{R}_2\), \(\text{R}_3\), \(\text{R}_4\), is independently hydrogen or a hydrocarbonyl group having from 1 to 20 carbon atoms or \(\text{R}_2\) and \(\text{R}_3\) can be combined to form a saturated or unsaturated cycloaliphatic ring or an aromatic ring.

6. A modified, solid epoxy resin of Claim 5 wherein the monoiide is phthalimide, succinimide, tetrahydrophthalimide, 2,3-naphthalenedicarboximide, pentanedicarboximide, hexanedicarboximide, 3-methyl-1,2-benzene-dicarboximide, 1,2-cyclohexane-dicarboximide, 1,2-cyclpentanedicarboximide, 3-methyl-1,2-cyclopentane-dicarboximide, 3-methyl-1-azacyclopentane-2,5-dione, or any combination thereof, and is employed in an amount of from 2 to 5 percent by weight based upon the combined weight of monoiide compound and epoxy resin.

7. A curable composition which comprises (i) at least one modified, solid epoxy resin of Claim 1, 2, 3, or 4; and (ii) a curing quantity of at least one curing agent for component (i) selected from a primary aliphatic polyamine, a secondary aliphatic polyamine, a tertiary amine, a carboxylic acid, a carboxylic acid anhydride, a phenolic hydroxy-containing compound, a guanidine, a bisguanidine, a urea-aldehyde resin, a melamine-aldehyde resin, a melamine aldehyde resin, a aromatic polyamine, a sulfanilamide, a phosphate acid, a phosphate ester, phosphite, Lewis acid and a combination thereof.

8. A curable composition which comprises (i) at least one modified, solid epoxy resin of Claim 5; and (ii) a curing quantity of at least one curing agent for component (i) selected from biquanidines, guanidines, imidazoles, ethylene-acrylic acid copolymers, ethylene-methacrylic acid copolymers, styrene-acrylic acid copolymers, styrene-methacrylic acid copolymers, polyisocyanates, and combinations thereof.

9. A curable composition which comprises (i) at least one modified solid epoxy resin of Claim 5; and (ii) a curing quantity of at least one curing agent selected from dicyandiamide, methyleneedianiline, dianinodiphenylsulfone, phenol-formaldehyde novolac resins, cresol-formaldehyde novolac resins, 2-methylimidazole, 2-phenylimidazole, trimellitic anhydride, pyromellitic anhydride, phthalic anhydride, maleic anhydride, succinic anhydride, and a combination thereof.

10. A curable composition which comprises (i) at least one modified, solid epoxy resin of Claim 6; and (ii) a curing quantity of at least one curing agent for component (i) which curing agent is a carboxyl functional polyester resin.

11. Use of the curable composition of any of the claims 7 to 10 as coating composition, wherein at least one additive is added which is selected from the group consisting of solvents or diluents, fillers, pigments, dyes, flow modifiers, thickeners, leveling agents, extenders, reinforcing agents, antistatic agents, curing agents, catalysts or fluidizing agents.
Patentansprüche

1. Ein festes, modifiziertes Epoxyharz, erhältlich durch Umsetzen
   (a) eines festen Epoxyharzes mit im Mittel mehr als einer vicinalen Epoxidgruppe pro Molekül mit
   (b) einem Monoimid einer Dicarboxylsäure,

dadurch gekennzeichnet,
   daß das Monoimid frei von Allyl- und Methallylgruppen ist, die nicht Teil eines ungesättigten cycloaliphatischen
   Rings sind, und in einer Menge von 0,5 bis 10 Gew.-%, bezogen auf die Gesamtmasse der Komponenten (a) und
   (b), eingesetzt wird und das resultierende feste, modifizierte Epoxyharz einen Mettler-Erweichungspunkt von wenig-
   stens 85°C aufweist.

2. Modifiziertes, festes Epoxyharz nach Anspruch 1, wobei dieses feste Epoxyharz vor der Modifizierung erhältlich ist
   durch Umsetzen (A) eines Epoxyharzes, wiedergegeben durch folgende Formeln I, II, III oder IV oder jegliche Kombi-
   nation davon.
wobei jedes A unabhängig eine divalente Kohlenwasserstoffgruppe mit 1 bis 10 Kohlenstoffatomen, -O-, -S-, -S-S-, -SO-, -SO₂- oder -CO- ist, Q eine trivale Kohlenwasserstoffgruppe mit 1 bis 10 Kohlenstoffatomen, jedes A' unabhängig eine divalente Kohlenwasserstoffgruppe mit 1 bis 10 Kohlenstoffatomen, jedes R unabhängig Wasserstoff oder eine Alkylgruppe mit 1 bis 4 Kohlenstoffatomen ist, jedes X unabhängig Wasserstoff, eine Hydrocarbyloxy- oder Hydrocarbyloxyxygruppe mit 1 bis 10 Kohlenstoffatomen, Brom, Chlor oder Fluor ist, m einen Mittelwert von 0 bis 15 aufweist, m' einen Mittelwert von 0,001 bis 5 aufweist und n einen Wert von 0 oder 1 hat, mit (B) einer organischen Verbindung mit im Mittel 2 aromatischen Hydroxylgruppen pro Molekül wiedergegeben durch folgende Formeln V oder VI oder jegliche Kombination davon.

FORMEL V

FORMEL VI

wobei jedes A und X wie oben definiert ist und wobei die Komponenten (A) und (B) in Mengen eingesetzt werden, die zu einem Verhältnis von phenolischen Hydroxylgruppen zu Epoxylgruppen von 0,1:1 bis 0,9:1 führen.
3. Modifiziertes, festes Epoxyharz nach Anspruch 2, wobei die Komponente (A) ein Diglycidylether von Bisphenol A ist, die Komponente (B) Bisphenol A ist und Komponenten (A) und (B) in Mengen eingesetzt werden, die zu einem Verhältnis von phenolischen Hydroxylgruppen zu Epoxygruppen von 0,4:1 bis 0,7:1 führen.

4. Modifiziertes, festes Epoxyharz nach Anspruch 2, wobei dieses Epoxyharz ein Epoxyharz, wiedergegeben durch Formeln I oder II oder eine Kombination davon, ist, wobei jedes A unabhängig eine divalente Kohlenwasserstoffgruppe mit 1 bis 10 Kohlenstoffatomen, -O-, -S-, -S-S-, -SO₂-, -SO₃- oder -CO₂- ist, jedes R unabhängig Wasserstoff oder eine Alkylgruppe mit 1 bis 4 Kohlenstoffatomen ist, jedes X unabhängig Wasserstoff, eine Hydrocarbonyl- oder Hydrocarbonylxyloxygruppe mit 1 bis 10 Kohlenstoffatomen, Brom, Chlor oder Fluor ist, m einen Molgewicht von 2 bis 15 aufweist und n einen Wert von 0 oder 1 aufweist.

5. Modifiziertes, festes Epoxyharz nach Anspruch 1, 2, 3 oder 4, wobei das Monoimid eines oder mehrere derer ist, die durch die folgende Formel VII wiedergegeben sind

\[
\text{VII}
\]

\[
\begin{align*}
\text{R}^1 & \quad \text{O} \\
\text{R}^2 & \quad \text{C} \\
\text{C} & \quad \text{C} \\
\text{R}^3 & \quad \text{NH} \\
\text{R}^4 & \quad \text{O}
\end{align*}
\]

worin jedes \(\text{R}^1\), \(\text{R}^2\), \(\text{R}^3\) und \(\text{R}^4\) unabhängig Wasserstoff oder eine Hydrocarbonylgruppe mit 1 bis 20 Kohlenstoffatomen ist oder \(\text{R}^2\) und \(\text{R}^3\) kombiniert werden können, um einen gesättigten oder ungesättigten cykloaliphatischen Ring oder einen aromatischen Ring zu bilden.

6. Modifiziertes, festes Epoxyharz nach Anspruch 5, wobei das Monoimid Phthalimid, Succinimid, Tetrahydrophthalimid, 2,3-Naphthalendicarboximid, Pentandicarboximid, Hexandicarboximid, 3-Methyl-1,2-benzoldicarboximid, 1,2-Cyclohexandicarboximid, 1,2-Cyclopentandicarboximid, 3-Methyl-1,2-cyclopentandicarboximid, 3-Methylazacyclopentan-2,5-dion oder jegliche Kombination davon ist und in einer Menge von 2 bis 5 Gew.-%, bezogen auf die Gesamtmasse der Monoimidverbindung und Epoxyharz, eingesetzt wird.

7. Härzbare Zusammensetzung, die (i) wenigstens ein modifiziertes, festes Epoxyharz nach Anspruch 1, 2, 3 oder 4 und (ii) eine härrende Menge wenigstens eines härterungs mittels für die Komponente (i), ausgewählt aus einem primären aliphatischen Amin, einem sekundären aliphatischen Polymatin einem tertiären Amin, einem Carbon säure oder einem Carbonsäurederivat, einer Verbindung mit phenolischen Hydroxylgruppen, Guanidin, Biguanid, Harnstoffaldehydehydrat, Melaminaldehydehydrat, aromatischem Polymatin, Sulfansalimid, partiell veresterter Phosphorsäure, Phosphatester, Phosphit, Lewis Säure und Kombinationen davon, enthält.

8. Härzbare Zusammensetzung, die (i) wenigstens ein modifiziertes, festes Epoxyharz nach Anspruch 5 und (ii) eine härrende Menge wenigstens eines härterungs mittels für die Komponente (i), ausgewählt aus Biguanid, Guanidinen, Imidazonen, Ethylen-Acrylsäure-Copolymeren, EthylenMethacrylsäure-Copolymeren, Styrol-Acrylsäure-Copolymeren, Styrol-Methacrylsäure-Copolymeren, Polyisocyanaten und Kombinationen davon, enthält.


10. Härzbare Zusammensetzung, die (i) wenigstens ein modifiziertes, festes Epoxyharz nach Anspruch 6 und (ii) eine härrende Menge wenigstens eines härterungs mittels für die Komponente (i) enthält, wobei das härterungs mittel ein carboxyfunktionelles Polyesterharz ist.

11. Verwendung der härzbaren Zusammensetzung nach einem der Ansprüche 7 bis 10 als Beschichtungszusammen-
setzung, wobei wenigstens ein Additiv zugesetzt ist, das ausgewählt ist aus der Gruppe bestehend aus Lösungsmitteln oder Verdünnungsmitteln, Füllstoffen, Pigmenten, Farbstoffen, Flußregulierungsmitteln, Verdickungsmitteln, Verlaufsmitteln, Streckungsmitteln, Verstärkungsmitteln, antistatischen Mitteln, Härtungsmitteln, Katalysatoren oder Verflüssigungsmitteln.

**Revendications**

1. Résine époxy modifiée solide, que l'on peut obtenir en faisant réagir (a) une résine époxy solide présentant en moyenne plus d'un groupe époxyde vicinal par molécule, avec (b) un monomide d'un acide dicarboxylique, caractérisé en ce que le monomide est exempt de groupes allylé et méthallylé qui ne font pas partie d'un noyau cycloaliphatique insaturé et est employé en une proportion de 0,5 à 10 % en poids par rapport aux poids combinés des constituants (a) et (b), et en ce que la résine époxy modifiée solide résultante présente un point de ramollissement Mettler d'au moins 85°C.

2. Résine époxy solide modifiée selon la revendication 1, pour laquelle ladite résine époxy solide avant la modification peut être obtenue par réaction de (A) une résine époxy représentée par l'une quelconque des formules suivantes I, II, III et IV, ou une combinaison quelconque de telles résines:
formules dans lesquelles chaque A représente indépendamment un groupe hydrocarboné divalent ayant de 1 à 10 atomes de carbone, -O-, -S-, -SO-, -SO₂- ou -CO-, Q représente un groupe hydrocarboné trivalent ayant de 1 à 10 atomes de carbone, chaque A' représente indépendamment un groupe hydrocarboné divalent ayant de 1 à 10 atomes de carbone, chaque R représente indépendamment un atome d'hydrogène ou un groupe alkyle ayant de 1 à 4 atomes de carbone, chaque X représente indépendamment un atome d'hydrogène, de brome, de chloro ou de fluor, ou un groupe hydrocarbyle ou hydrocarbyleoxy ayant de 1 à 10 atomes de carbone, m a une valeur moyenne de 0 à 15, m' a une valeur moyenne de 0,001 à 5, et n a une valeur de 0 ou 1,
avec (B) un composé organique ayant en moyenne 2 groupes hydroxyde aromatiques par molécule, représenté par l'une quelconque des formules suivantes (V) et (VI), ou une combinaison quelconque de tels composés :
formules dans lesquelles chaque A et chaque X est tel que défini précédemment, les constituants (A) et (B) étant employés en des quantités qui fournissent un rapport des groupes hydroxylé phénoliques aux groupes époxy de 0,1 à 0,9.

3. Résine époxy solide modifiée selon la revendication 2, pour laquelle le constituant (A) est un éther diglycidyle de bisphénol A, le constituant (B) est le bisphénol A, et les constituants (A) et (B) sont employés en des quantités qui fournissent un rapport des groupes hydroxylé phénoliques aux groupes époxy de 0,1 à 0,9.

4. Résine époxy solide modifiée selon la revendication 2, pour laquelle ladite résine époxy est une résine époxy représentée par la formule I ou II, ou une combinaison de telles résines, les symboles des formules ayant les significations suivantes : chaque A représente indépendamment un groupe hydrocarboné divalent ayant de 1 à 10 atomes de carbone, -O-, -S-, -S-S-, -SO-, -SO2- ou -CO- ; chaque R représente indépendamment un atome d'hydrogène ou un groupe alkyle ayant de 1 à 4 atomes de carbone ; chaque X représente indépendamment un atome d'hydrogène, de brome, de chlore ou de fluor, ou un groupe hydrocarbure ou hydrocarbureoxy ayant de 1 à 10 atomes de carbone ; m a une valeur moyenne de 2 à 15 et n a une valeur de 0 ou 1.

5. Résine époxy solide modifiée selon l'une quelconque des revendications 1 à 4, pour laquelle le monoimide est constitué d'un ou plusieurs composés représentés par la formule suivante VII :

\[
\begin{align*}
R^1 & \quad O \\
| & \quad | \\
R^2 & \quad C \quad C \quad \quad \text{NH} \\
| & \quad | \\
R^3 & \quad C \quad C \\
| & \quad | \\
R^4 & \quad O \\
\end{align*}
\]

(VII)

dans laquelle chacun des groupes R¹, R², R³ et R⁴ représente indépendamment un atome d'hydrogène ou un groupe hydrocarbure ayant de 1 à 20 atomes de carbone, ou bien R² et R³ peuvent être combinés pour former un noyau cycloaliphatique saturé ou insaturé, ou un noyau aromatique.

6. Résine époxy solide modifiée selon la revendication 5, pour laquelle le monoimide est le phthalimide, le succinimide, le tétrahydrophthalimide, le 2,3-naphthalénedicarboximide, le pentanedicarboximide, l'hexanedicarboximide, le 3-méthyl-1,2-benzène-dicarboximide, le 1,2-cyclohexanedicarboximide, le 1,2-cyclopentanedicarboximide, le 3-méthyl-1,2-cyclopentan-dicarboximide, le 3-méthyl-azacyclopentane-2,5-dione, ou une combinaison quelconque de ces composés, et est employé en une proportion de 2 à 5 % en poids par rapport aux poids combinés de composé monoimide et de résine époxy.

7. Composition durcissable qui comprend (i) au moins une résine époxy solide modifiée selon l'une quelconque des revendications 1 à 4, et (ii) une quantité durcissante d'au moins un agent de durcissement pour le constituant (i), choisi parmi les polynamines aliphatiques primaires, les polynamines aliphatiques secondaires, les amines tertiaires, les acides carboxyliques ou les anhydrides d'acides carboxyliques, les composés contenant un groupe hydroxylé phénolique, les guanidines, les biguanidies, les résines urée-aléhyde, les résines mélimino-aléhyde, les polyamines aromatiques, le sulfanilamide, les phosphates acides, les esters phosphates, les phosphites, les acides de Lewis et leurs combinaisons.

8. Composition durcissable qui comprend (i) au moins une résine époxy solide modifiée selon la revendication 5, et (ii) une quantité durcissante d'au moins un agent de durcissement pour le constituant (i), choisi parmi les biguanidies, les guanidines, les imidazoles, les copolymères éthylène-acide acrylique, les copolymères éthylène-acide méthacrylique, les copolymères styrène-acide acrylique, les copolymères styrène-acide méthacrylique, les polyisocyanates et leurs combinaisons.

9. Composition durcissable qui comprend (i) au moins une résine époxy solide modifiée selon la revendication 5, et (ii) une quantité durcissante d'au moins un agent de durcissement choisi parmi le dicyandiamide, la méthylénediamine, la diaminodiphenyl-sulfone, les résines novoloxes phénol-formaléhyde, les résines novoloxes crésol-formaléhyde, le 2-méthyl-imidazole, le 2-phénylimidazole, l’anhydride trimellitique, l’anhydride pyromellitique, l’anhy-
dride phthalique, l'anhydride maléique, l'anhydride succinique et leurs combinaisons.

10. Composition durcissable qui comprend (i) au moins une résine époxy solide modifiée selon la revendication 6, et (ii) une quantité durcissante d'au moins un agent de durcissement pour le constituant (i), ledit agent de durcissement étant une résine polyester à fonctions carboxyle.

11. Utilisation de la composition durcissable selon l'une quelconque des revendications 7 à 10 comme composition de revêtement, utilisation pour laquelle est ajouté au moins un additif qui est choisi parmi les solvants ou diluants, les charges, les pigments, les colorants, les agents modifiant l'écoulement, les épaisseurs, les agents niveleurs, les diluants, les agents de renforcement, les agents antistatiques, les agents de durcissement, les catalyseurs et les agents de fluidification.