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PATENT SPECIFICATION

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NO DRAWINGS

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COMPLETE SPECIFICATION

Epoxy Resin Compositions and Cured Products thereof with improved Impact Strength

We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a Company organised under the laws of The Netherlands of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to new epoxy resin compositions which are curable at elevated temperature, and to shaped articles such as castings and laminates having improved chemical and physical properties, in particular improved impact strength, and manufactured with use of the new compositions. Resins containing epoxy groups in the molecule are well-known in the art under the names polyepoxide, or epoxy, epoxide or ethoxyline resin. In particular, those epoxy resins which are the reaction product of polyhydric alcohols or phenols with epihalogeno-hydrins are commercially available, such as, for instance, polyglycidyl ethers prepared by reaction of bis(4-hydroxyphenyl)-2,2-propane and epichlorohydrin.

Epoxy resins can be cured at elevated temperature by polycarboxylic acid anhydrides to make coatings, mouldings, castings and laminates with useful properties such as high temperature resistance, excellent electrical and mechanical properties and light colour. Anhydrides used for this purpose include phthalic anhydride, partly or completely hydrogenated phthalic anhydride, pyromellitic dianhydride, endomethylenetetrahydrophthalic anhydride and alkylated or chlorinated derivatives thereof. Specific advantages of polycarboxylic anhydrides, as compared with other types of curing agents are low volatility and absence of dermatitic effects of the anhydrides, and further long pot-life, low viscosity, and low shrinkage of the mixtures with epoxy resins during cure.

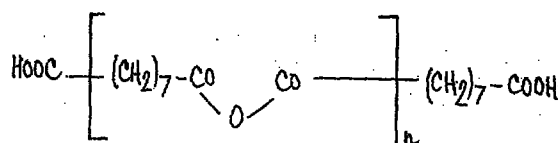
The known epoxy resin-polycarboxylic anhydride compositions provide hard and tough castings and laminates which are suitable for many purposes, but there is still a need for a composition which is suitable for the manufacture of articles with improved impact strength, in particular when also a high heat resistance is required.

It has now been found that articles having improved impact strength and high heat resistance can be made by using the heat-curable compositions of the invention which comprise (1) an epoxy resin having an epoxy equivalency greater than one and (2) a mixture of polymeric azelaic acid anhydride and a monomeric polycarboxylic acid anhydride.

The epoxy resins used in the compositions of the invention are compounds having an epoxy equivalency greater than one, i.e. having on average more than one epoxy group per molecule. The epoxy resins may contain in addition hydroxyl groups as other reactive groups in the molecule. Preferred are polyglycidyl ethers such as polyglycidyl ethers of glycerol, resorcinol, hydroquinone, pyrocatechol, bis(4-hydroxyphenyl)propane, bis(4-hydroxyphenyl)methane, bis(4-hydroxyphenyl) sulphone, and novolac resins. Polyglycidyl ethers of bis(4-hydroxyphenyl)-2,2-propane which have an epoxy equivalency greater than one and which have a melting point lower than 50°C are preferred. Mixtures of polyglycidyl ethers may also be used.

Very suitable epoxy resins are also mixtures of polyglycidyl ethers with minor amounts, i.e. from 1 to 20% by weight, of monoglycidyl compounds, such as butyl glycidyl ether, phenyl glycidyl ether, and glycidyl esters of saturated aliphatic monocarboxylic acids in which the carboxyl group is attached to a tertiary or quaternary carbon atom. Other examples of epoxy resins are polyglycidyl esters of polycarboxylic acids, such as diglycidyl terephthalate; epoxidized esters of unsaturated alcohols with unsaturated monocarboxylic acids such as 3,4-epoxy-6-methylcyclohexylmethyl 3,4-epoxy-6-methylcyclohexanecarboxylate; and epoxidized polyolefins.

The polymeric azelaic acid anhydride used in the compositions of the invention has the general formula



wherein n is a number of from 2 to 40 or more. Preferred is a polymeric product having a molecular weight range from approximately 500 to approximately 4000, the major amount having a molecular weight close to 2000.

Suitable monomeric polycarboxylic anhydrides for use in admixture with polymeric azelaic anhydride in the compositions of the invention include phthalic anhydride, hexahydrophthalic anhydride and methylenedimethylene tetrahydrophthalic anhydride, since these dicarboxylic anhydrides provide relatively high heat distortion points of the cured resins. Preferred are polycarboxylic anhydrides which are low melting solids or liquids at room temperature or which dissolve readily in the epoxy resin at temperatures below 100°C. Particularly preferred is hexahydrophthalic anhydride. Other di- and tetracarboxylic anhydrides may also be used.

The weight ratio of polymeric azelaic anhydride and monomeric polycarboxylic anhydride in the compositions of the invention is preferably from 10:1 to 1:10, and more preferably from 3:1 to 1:3, for example 1:1.

The amount of polymeric azelaic anhydride plus monomeric polycarboxylic anhydride in relation to the epoxy resin may vary. In order to obtain as complete a cross-linking as possible this amount is preferably from 50 to 100% by weight of epoxy resin. Particularly preferred are those amounts of combined polycarboxylic anhydrides which provide 0.7 to 1.1 mols of dicarboxylic anhydride equivalent per epoxy equivalent, i.e. 1.4 to 2.2 carboxyl equivalent per epoxy equivalent.

Accelerators may be added to the compositions of the invention in order to accelerate the cure and to obtain shorter curing cycles in the manufacture of articles. Suitable accelerators are tertiary amines such as benzyldimethylamine and 2,4,6-tri(dimethylaminomethyl)phenol. The amount of amine accelerator is usually between 0.5 and 5.0% by weight of the combined polycarboxylic anhydrides.

In preparing the compositions of the invention the mixture of polymeric azelaic acid anhydride and monomeric polycarboxylic acid anhydride, may be added to the epoxy resin, or the resin may be added to the mixture of anhydrides. If the components of the compositions are normally liquids the mixing is being carried out by stirring. If one of the components of the compositions is a solid, the other being a liquid, it is preferred to mix the components at a temperature which allows the solid component to dissolve readily in the liquid component of the composition.

The composition of the invention may be used to manufacture shaped articles by laminating, casting, moulding and coating techniques. If desired, diluents, fillers, pigments, plasticizers and flexibilizers may be added to the compositions. The compositions of the invention are in particular suitable to prepare laminates, and have excellent adhesion and good wetting properties for reinforcing materials, and low shrinkage during cure. Suitable fibrous reinforcing materials are glass fibres, polyamide fibres and polyester fibres.

The fibrous reinforcing material can be impregnated with the liquid or liquefied composition of the invention, if desired at elevated temperature and brought into shape by moulding, filament winding, injection into moulds, and other techniques if required under pressure. After cure at elevated temperature laminated shaped articles with high dimensional stability, excellent chemical resistance, high impact strength, high compressive, tensile and flexural strength, good fatigue resistance, high heat resistance in particular heat resistance under load, and good electrical properties are obtained. In the laminated article the fibrous reinforcing material is embedded in

the cured resinous composition. By such techniques using the compositions of the invention laminated articles such as bodies for cars and ships, pipes, and containers, for example, bottles, cylinders, drums and tanks, of outstanding shock resistance can be manufactured. Such pipes and containers can be used for transport and storage of gases, liquids, and solids, if desired under pressure, and are especially suitable for those applications where rough handling is likely to occur.

The invention may be further illustrated by the following Examples.

EXAMPLE I

A mixture of the following components was prepared: 128.5 parts by weight of a polyglycidyl ether of bis(4-hydroxyphenyl)-2,2-propane having an epoxy equivalency of 1.75, a viscosity of 150 poises at 25°C and an average molecular weight of 350,

50 parts by weight of hexahydrophthalic anhydride,

50 parts by weight of polymeric azelaic acid anhydride having an average molecular weight of 2000, and a melting point of approximately 60°C,

3.4 parts by weight of 2,4,6-tri(dimethylaminomethyl)-phenol (accelerator).

The mixture was cured for two hours at 100°C followed by 3 hours at 150°C. After curing, the following properties were found:

IZOD notched impact strength: 10.9 kg.cm/cm²

Elongation at break: 7.5%

Ultimate tensile strength: 580 kg/cm²

Flexural yield strength: 1000 kg/cm²

The specimen tested did not break under the condition of a test for determining the ultimate flexural strength. Extraction of a sample with boiling methyl ethyl ketone for 3 hours gave 0.5% of soluble material. For comparison a mixture of 100 parts by weight of the above-mentioned polyglycidyl ether with 80 parts of hexahydrophthalic anhydride and 1 part by weight of 2,4,6-tri(dimethylaminomethyl)-phenol was prepared and cured at the same conditions as mentioned above. The cured composition showed an IZOD notched impact strength of only 6.8 kg.cm/cm² and an elongation at break of 4.1%.

EXAMPLE II

A mixture of the following components was prepared:

127 parts by weight of the polyglycidyl ether of bis(4-hydroxyphenyl)-2,2-propane used in Example I,

75 parts by weight of hexahydrophthalic anhydride

25 parts by weight of the polymeric azelaic acid anhydride used in Example I,

3.4 parts by weight of 2,4,6-tri(dimethylaminomethyl)phenol.

The mixture was cured for two hours at 100°C followed by 3 hours at 150°C. After curing, the following properties were found:

IZOD notched impact strength: 8.3 kg.cm/cm²

Elongation at break: 4.1%

Ultimate tensile strength: 710 kg/cm²

Flexural yield strength: 1170 kg/cm²

Vicat softening temperature: 101°C (5 kg load, 0.1 mm penetration)

Extraction of a sample with boiling methyl ethyl ketone for 3 hours gave 0.5% of soluble material.

By reversing the amounts of hexahydrophthalic anhydride and polymeric azelaic acid anhydride the IZOD notched impact strength of the cured composition was found to be 10.9 kg.cm/cm².

EXAMPLE III

A mixture of the following components was prepared:

122 parts by weight of the polyglycidyl ether of bis(4-hydroxyphenyl)-2,2-propane used in Example I,

50 parts by weight of methylenedimethylenetetrahydrophthalic anhydride,

50 parts by weight of the polymeric azelaic acid anhydride used in Example I,

3.3 parts by weight of benzyldimethylamine (accelerator).

The mixture was cured for two hours at 100°C followed by 6 hours at 150°C.

After curing, the following properties were found:

IZOD notched impact strength: 8.2 kg.cm/cm²
 Ultimate tensile strength: 545 kg/cm²
 Flexural yield strength: 1060 kg/cm²

The mixture from 100 parts by weight of polyglycidyl ether of bis(4-hydroxyphenyl)-2,2-propane, 90 parts by weight of methylenedimethylenetetrahydrophthalic anhydride, and 1.9 parts by weight of benzyldimethylamine had an IZOD notched impact strength of only 3.4 kg.cm/cm² after curing under the same conditions.

EXAMPLE IV

A mixture of the following components was prepared:
 133 parts by weight of the polyglycidyl ether of bis(4-hydroxyphenyl)-2,2-propane used in Example I,

25 parts by weight of phthalic anhydride

75 parts by weight of the polymeric azelaic acid anhydride used in Example I,

3.5 parts by weight of benzyldimethylamine (accelerator).

The mixture was cured for 2 hours at 100°C followed by 6 hours at 150°C. After curing the following properties were found:

IZOD notched impact strength: 12.1 kg.cm/cm²
 Ultimate tensile strength: 400 kg/cm²
 Flexural yield strength: 875 kg/cm²

A similar mixture containing as the curing agent mixture 50 parts by weight of each, phthalic anhydride and polymeric azelaic acid anhydride, showed after curing under the same conditions the following properties:

IZOD notched impact strength: 8.5 kg.cm/cm²
 Ultimate tensile strength: 620 kg/cm²
 Flexural yield strength: 1095 kg/cm²

For comparison a mixture was prepared consisting of 100 parts by weight of the polyglycidyl ether of bis(4-hydroxyphenyl)-2,2-propane, 75 parts by weight of phthalic anhydride and 0.2 parts by weight of benzyldimethylamine. After curing under the same conditions a sample showed an IZOD notched impact strength of only 5.0 kg.cm/cm².

WHAT WE CLAIM IS:—

1. A composition of matter curable by heat comprising (1) an epoxy resin having an epoxy equivalency greater than one and (2) a mixture of polymeric azelaic acid anhydride with a monomeric polycarboxylic acid anhydride.

2. A composition as claimed in claim 1, wherein the epoxy resin is a polyglycidyl ether of bis(4-hydroxyphenyl)-2,2-propane.

3. A composition as claimed in claim 2, wherein the polyglycidyl ether has a melting point lower than 50°C.

4. A composition as claimed in any one of claims 1 to 3, wherein the polymeric azelaic acid anhydride has a molecular weight ranging from approximately 500 to approximately 4000.

5. A composition as claimed in any one of claims 1 to 4, wherein the monomeric polycarboxylic acid anhydride is hexahydrophthalic anhydride.

6. A composition as claimed in any one of claims 1 to 4, wherein the monomeric polycarboxylic anhydride is methylenedimethylenetetrahydrophthalic anhydride.

7. A composition as claimed in any one of claims 1 to 4, wherein the monomeric polycarboxylic anhydride is phthalic anhydride.

8. A composition as claimed in any one of claims 1 to 7, wherein the weight ratio of polymeric azelaic acid anhydride to monomeric polycarboxylic acid anhydride is in the range from 10:1 to 1:10.

9. A composition as claimed in claim 8, wherein the weight ratio of polymeric azelaic acid anhydride to monomeric polycarboxylic anhydride is in the range from 3:1 to 1:3.

10. A composition as claimed in any one of claims 1 to 9, wherein the amount of polymeric azelaic acid anhydride plus monomeric polycarboxylic acid anhydride is from 50 to 100 percent by weight of the epoxy resin.



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After curing, the following properties were found:

IZOD notched impact strength: 8.2 kg.cm/cm²

Ultimate tensile strength: 545 kg/cm²

Flexural yield strength: 1060 kg/cm²

- 5 The mixture from 100 parts by weight of polyglycidyl ether of bis(4-hydroxyphenyl)-2,2-propane, 90 parts by weight of methylenedimethylenetetrahydrophthalic anhydride, and 1.9 parts by weight of benzyldimethylamine had an IZOD notched impact strength of only 3.4 kg.cm/cm² after curing under the same conditions.

EXAMPLE IV

- 10 A mixture of the following components was prepared:

133 parts by weight of the polyglycidyl ether of bis(4-hydroxyphenyl)-2,2-propane used in Example I,

25 parts by weight of phthalic anhydride

75 parts by weight of the polymeric azelaic acid anhydride used in Example I,

- 15 3.5 parts by weight of benzyldimethylamine (accelerator).

The mixture was cured for 2 hours at 100°C followed by 6 hours at 150°C. After curing the following properties were found:

IZOD notched impact strength: 12.1 kg.cm/cm²

Ultimate tensile strength: 400 kg/cm²

- 20 Flexural yield strength: 875 kg/cm²

A similar mixture containing as the curing agent mixture 50 parts by weight of each, phthalic anhydride and polymeric azelaic acid anhydride, showed after curing under the same conditions the following properties:

IZOD notched impact strength: 8.5 kg.cm/cm²

- 25 Ultimate tensile strength: 620 kg/cm²

Flexural yield strength: 1095 kg/cm²

- 30 For comparison a mixture was prepared consisting of 100 parts by weight of the polyglycidyl ether of bis(4-hydroxyphenyl)-2,2-propane, 75 parts by weight of phthalic anhydride and 0.2 parts by weight of benzyldimethylamine. After curing under the same conditions a sample showed an IZOD notched impact strength of only 5.0 kg.cm/cm².

WHAT WE CLAIM IS:—

- 35 1. A composition of matter curable by heat comprising (1) an epoxy resin having an epoxy equivalency greater than one and (2) a mixture of polymeric azelaic acid anhydride with a monomeric polycarboxylic acid anhydride.

2. A composition as claimed in claim 1, wherein the epoxy resin is a polyglycidyl ether of bis(4-hydroxyphenyl)-2,2-propane.

- 40 3. A composition as claimed in claim 2, wherein the polyglycidyl ether has a melting point lower than 50°C.

4. A composition as claimed in any one of claims 1 to 3, wherein the polymeric azelaic acid anhydride has a molecular weight ranging from approximately 500 to approximately 4000.

- 45 5. A composition as claimed in any one of claims 1 to 4, wherein the monomeric polycarboxylic acid anhydride is hexahydrophthalic anhydride.

6. A composition as claimed in any one of claims 1 to 4, wherein the monomeric polycarboxylic anhydride is methylenedimethylenetetrahydrophthalic anhydride.

7. A composition as claimed in any one of claims 1 to 4, wherein the monomeric polycarboxylic anhydride is phthalic anhydride.

- 50 8. A composition as claimed in any one of claims 1 to 7, wherein the weight ratio of polymeric azelaic acid anhydride to monomeric polycarboxylic acid anhydride is in the range from 10:1 to 1:10.

9. A composition as claimed in claim 8, wherein the weight ratio of polymeric azelaic acid anhydride to monomeric polycarboxylic anhydride is in the range from 3:1 to 1:3.

- 55 10. A composition as claimed in any one of claims 1 to 9, wherein the amount of polymeric azelaic acid anhydride plus monomeric polycarboxylic acid anhydride is from 50 to 100 percent by weight of the epoxy resin.

11. A composition as claimed in any one of claims 1 to 10, comprising in addition a curing accelerator.

12. A curing agent for epoxy resins comprising a mixture of polymeric azelaic acid anhydride having a molecular weight in the range from 500 to 4000 with a monomeric polycarboxylic acid anhydride.

13. A process for curing a composition as claimed in any of claims 1—11, comprising heating said composition.

14. A process for making a laminated article which comprises impregnating a fibrous reinforcing material with a composition as claimed in any one of claims 1 to 11, bringing the impregnated fibrous reinforcing material into shape, and hardening at elevated temperature.

15. Shaped article, wholly or partly made as claimed in claim 14.

16. Shaped article, comprising a fibrous reinforcing material embedded in a cured resinous composition as claimed in any one of claims 1 to 11.

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