

## Cycloaliphatic Epoxy Resins

The present invention relates to novel solid cycloaliphatic epoxy resins with improved properties and their use in thermoset powder coatings.

Cycloaliphatic epoxy resins find use in important fields like electric/electronic equipment and appliances, filament winding and coatings.

In coating applications, cycloaliphatic epoxy resins are used mainly in coatings for high performance outdoor applications, due to their very high resistance to atmospheric agents and ultraviolet radiation.

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Powder coating is becoming increasingly popular because it avoids the use of solvents and the pollution problems associated therewith. In thermoset powder coatings, epoxy resins are used as crosslinking agents in conjunction with carboxyl-terminated polyester resins. The most widely used epoxy crosslinking agent is triglycidyl isocyanurate (TGIC; compare, for example, EP-A 0 107 888). This compound, which is a solid with a softening point in the 90–100 °C range, has good technical properties but gives rise to toxicological problems. Furthermore, it is a suspect mutagenic agent (positive AMES test).

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On the other hand, existing cycloaliphatic epoxy resins like the well-known 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate, which is a liquid with low viscosity, are not suitable for this application.

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US-A 5 244 985 assigned to New Japan Chemical describes the preparation of a family of epoxidized polyesters containing epoxycyclohexane moieties with a molecular weight between 1000 and 10000. The products described in the patent examples are liquids. For this reason they are suitable for use with liquid carboxylic anhydrides, for UV curing, or as plasticisers for PVC. They are not suitable, however, for powder coating applications.

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Therefore, it is the object of the present invention to provide substitutes for TGIC which are free from toxicity problems and have physicochemical and performance characteristics suitable for thermoset powder coatings, which means that they can be incorporated in stable powder compositions which have no tendency to agglomerate.

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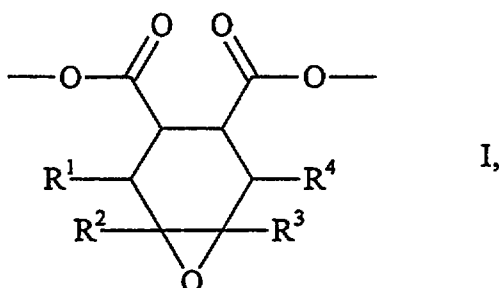
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This object has been accomplished by the solid epoxidized polyester resin according to claim 1 and the processes for its production according to claims 7 and 8.

It has been found that by using an appropriate production process it is possible to prepare a family of epoxidized polyesters which are solid and suitable for thermoset powder coating applications.

These solid epoxidized polyester resins comprise at least one epoxidized ester which contains, per molecule, two or more dicarboxylic cycloaliphatic moieties of the general formula

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wherein

$R^1$  and  $R^4$  are independently selected from the group consisting of hydrogen and methyl or  $R^1$  and  $R^4$  together are methylene,

$R^2$  and  $R^3$  are independently selected from the group consisting of hydrogen and methyl. The dicarboxylic cycloaliphatic moieties are bonded by their open valencies to moieties independently selected from the group consisting of hydrogen, linear or branched  $C_{1-8}$  alkyls, linear or branched linking  $C_{2-8}$  alkanediyls, linear or branched (cross-) linking  $C_{3-8}$  alkanetriyls, linear or branched (cross-) linking  $C_{4-8}$  alkanetetrayls and linking or crosslinking moieties of the general formula  $X(Y-)_n$  wherein  $n$  is an integer from 2 to 4,  $X$  is a di-, tri- or tetravalent group containing at least one isocyclic or heterocyclic ring and  $Y$  is a direct bond or a  $-(CH_2)_m-$  group wherein  $m$  is an integer from 1 to 4. Here and in the following, the term "open valence" means any valence of a moiety that is (formally) available for engaging in a bond to another moiety. In the molecule as a whole, there are of course no open valencies. As the epoxidized esters contain at least two cycloaliphatic moieties, they comprise "terminal" carboxylate functions which are bonded to  $C_{1-8}$  alkyl or hydrogen, forming a  $C_{1-8}$  alkylester or a free carbox-

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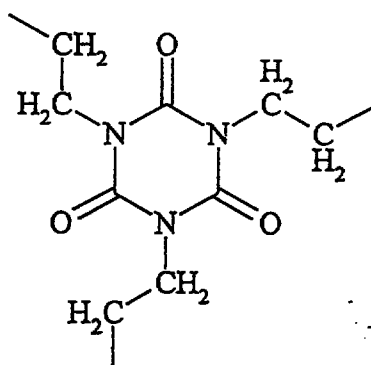
- ylic acid function, respectively, and "inner" carboxylate functions which are linked or cross-linked by the above-mentioned diyls, triyls, tetrayls or di-, tri- or tetravalent moieties. In this context, linear or branched  $C_{1-8}$  alkyl means any alkyl group having up to 8 carbon atoms and any possible number of branches, for example methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, pentyl, 3-methylbutyl (isoamyl), tert-pentyl, neopentyl, hexyl, octyl or 2-ethylhexyl. Accordingly, linear or branched  $C_{2-8}$  alkanediyl means any alkanediyl group having 2 to 8 carbon atoms and any possible number of branches, except those having two open valences at the same carbon atom, for example 1,2-ethanediyl, 1,2-propanediyl, 1,3-propanediyl, 1,2-butanediyl, 1,3-butanediyl, 1,4-butanediyl, 2,3-butanediyl, 2-methyl-1,3-propanediyl, 3-methyl-1,3-butanediyl, 1,2-hexanediyl, 1,6-hexanediyl or 2,2-dimethyl-1,3-propanediyl. Accordingly, linear or branched  $C_{3-8}$  alkanetriyl means any alkanetriyl group having 3 to 8 carbon atoms and any possible number of branches, except those having two or three open valences at the same carbon atom, for example 1,2,3-propanetriyl or 2,2-dimethylbutane-1,1',1''-triyl. Accordingly, linear or branched  $C_{4-8}$  alkanetetrayl means any alkanetetrayl group having 4 to 8 carbon atoms and any possible number of branches, except those having two or three open valences at the same carbon atom, for example 1,2,3,4-butanetetrayl and 2,2-dimethylpropane-1,1',1'',3-tetrayl. The term "di-, tri- or tetravalent group containing at least one isocyclic or heterocyclic ring" means any organic moiety having 2 to 4 open valencies and containing any number of isocyclic or heterocyclic rings, for example triazine rings.
- According to the invention, the epoxidized polyester resins are essentially free of monomeric products. To be understood as monomeric products are compounds containing only one cycloaliphatic moiety of the type defined above, especially those wherein both open valencies are bound to hydrogen or  $C_{1-8}$  alkyl, and any hydroxy compounds from the synthesis of the polyester resin. "Essentially free of monomeric products" is to be understood as containing less than 5 wt %, preferably less than 3 wt % of those products.

Preferably, one of the substituents  $R^1$  to  $R^4$  is hydrogen or a methyl group and the remaining of  $R^1$  to  $R^4$  are hydrogens. The compounds according to this embodiment are derived from tetrahydrophthalic and methyltetrahydrophthalic acids.

Also preferred are resins wherein R<sup>1</sup> and R<sup>4</sup> together are methylene, one of R<sup>2</sup> and R<sup>3</sup> is hydrogen or methyl and the other one is hydrogen. These compounds are derived from nadic (= bicyclo[2.2.2]hept-5-ene-2,3-dicarboxylic) and methylnadic acids.

- 5 The C<sub>1-8</sub> alkyls are preferably selected from methyl, ethyl, propyl, isopropyl, butyl, isobutyl and 2-ethylhexyl. Most preferably, isobutyl is employed as C<sub>1-8</sub> alkyl. The linking C<sub>2-8</sub> alkanediyls, if present, are preferably selected from 1,2-ethanediyl, 1,2-propanediyl, 1,3-propanediyl, 1,2-butanediyl, 1,3-butanediyl, 1,4-butanediyl, 2,3-butanediyl, 3-methyl-1,3-butanediyl, 1,2-hexanediyl, 1,6-hexanediyl and 2,2-dimethyl-1,3-propanediyl. The (cross-) linking C<sub>3-8</sub> alkanetriyls, if present, are preferably selected from 1,2,3-propanetriyl and 2,2-dimethylbutane-1,1',1''-triyl. The (cross-) linking C<sub>4-8</sub> alkanetetrayls, if present, are preferably selected from 1,2,3,4-butanetetrayl and 2,2-dimethylpropane-1,1',1'',3-tetrayl.

As linking or crosslinking moieties of the general formula  $X(Y-)_n$ , if present, isocyanurate  
15 groups of the formula



are preferred.

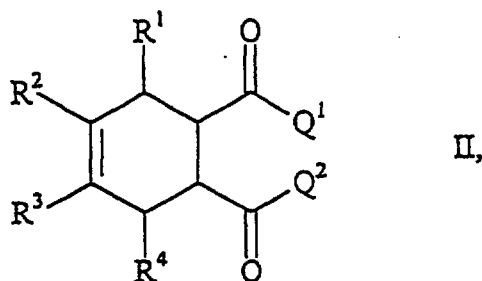
- 20 Preferably, the solid epoxidized polyester resin according to the invention has an acid number of not more than 2 mg KOH/g, more preferably, not more than 1 mg KOH/g. This means that essentially no free carboxyl groups are present.

The (weight-averaged) molecular weight, as determined by gel permeation chromatography, is typically between about 500 and 10000, preferably between 1000 and 5000.

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According to the invention, the solid epoxidized polyester resins may be prepared by

i) reacting an unsaturated dicarboxylic acid or acid derivative of the general formula



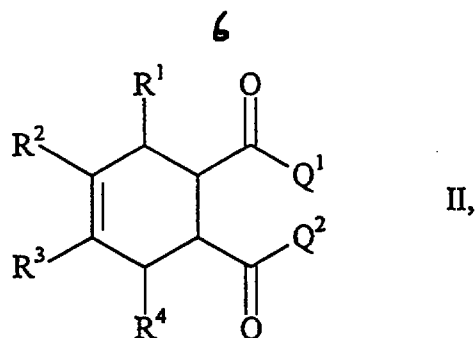
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wherein  $R^1$  to  $R^4$  are as defined above and  $Q^1$  and  $Q^2$  are independently selected from the group consisting of hydroxy and  $C_{1-8}$  alkoxy or  $Q^1$  and  $Q^2$  together are  $-O-$ , with at least one hydroxy compound selected from the group consisting of linear or branched  $C_{2-8}$  alkanediols, linear or branched  $C_{3-8}$  alkanetriols, linear or branched  $C_{4-8}$  alkanetetraols and hydroxy compounds of the general formula  $X(Y-OH)_n$  wherein  $n$  is an integer from 2 to 4,  $X$  is a di-, tri- or tetraivalent group containing at least one isocyclic or heterocyclic ring and each  $Y$  is a direct bond or a  $-(CH_2)_m-$  group wherein  $m$  is an integer from 1 to 4; and a linear or branched  $C_{1-8}$  alkanol,

ii) removing essentially all monomeric byproducts, and  
 15 iii) epoxidizing the resulting unsaturated polyester.

In this process, the unsaturated dicarboxylic acids may be employed as such ( $Q^1 = Q^2 = OH$ ) or in form of their di- $C_{1-8}$ -alkyl esters ( $Q^1 = Q^2 = C_{1-8}$  alkyl) or anhydrides ( $Q^1 + Q^2 = -O-$ ). Accordingly, the first step is a direct esterification if an acid or an anhydride is employed, and a transesterification if a dialkyl ester is used as starting material. In the former case, the linear or branched  $C_{1-8}$  alkanol is required to esterify the "terminal" carboxylic functions of the resulting polyester.

Another process for preparing the solid epoxidized polyester resins according to the invention comprises the steps of  
 25 i) reacting an unsaturated dicarboxylic acid ester of the general formula



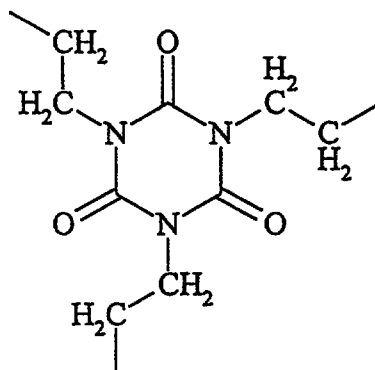
- wherein  $R^1$  to  $R^4$  are as defined in claim 1 and  $Q^1$  and  $Q^2$  are  $C_{1-8}$  alkoxy groups, with at least one hydroxy compound selected from the group consisting of linear or branched  $C_{2-8}$  alkanediols, linear or branched  $C_{3-8}$  alkanetriols, linear or branched  $C_{4-8}$  alkanetraols and hydroxy compounds of the general formula  $X(Y-OH)_n$  wherein  $n$  is an integer from 2 to 4,  $X$  is a di-, tri- or tetravalent group containing at least one isocyclic or heterocyclic ring and each  $Y$  is a direct bond or a  $-(CH_2)_m-$  group wherein  $m$  is an integer from 1 to 4,
- ii) removing essentially all monomeric byproducts, and
  - 10 iii) epoxidizing the resulting unsaturated polyester by reacting it with a peroxy compound.
- In this case, dialkyl esters are used as starting materials and therefore only transesterification reactions are required in the first step. In the resulting polyester, the "terminal" carboxylic functions still carry the alkyl groups that had been present in the starting dialkyl ester.
- 15 Depending on the type of  $C_{1-8}$  alkyl groups or (cross-) linking di-, tri- or tetravalent groups to be introduced, suitable hydroxy compounds are used as starting materials.

The preferred methyl, ethyl, propyl, isopropyl, butyl, isobutyl and 2-ethylhexyl groups are introduced by using methanol, ethanol, propanol, isopropyl alcohol, butanol, isobutyl alcohol (especially preferred) and 2-ethylhexanol, respectively. The preferred 1,2-ethanediyl, 1,2-propanediyl, 1,3-propanediyl, 1,2-butanediyl, 1,3-butanediyl, 1,4-butanediyl, 2,3-butanediyl, 3-methyl-1,3-butanediyl, 1,2-hexanediyl, 1,6-hexanediyl and 2,2-dimethyl-1,3-propanediyl groups are introduced by using ethylene glycol, propylene glycol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 2,3-butanediol, 3-methyl-1,3-butanediol, 1,2-hexanediol and 2,2-dimethyl-1,3-propanediol (neopentyl glycol), respectively. The preferred 1,2,3-propanetriyl and 2,2-dimethylbutane-1,1',1''-triyl groups are introduced by using glycerol and trimethylolpropane, respectively. The preferred 1,2,3,4-butanetetrayl and 2,2-di-

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methylpropane-1,1,1,3-tetra-yl groups are introduced by using threitol/erythritol and penta-erythritol, respectively.

The preferred groups of the formula



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are introduced by using tris(2-hydroxyethyl) isocyanurate as a hydroxy compound.

In the second step of the preparation of the epoxidized polyester resin, the molecular mass distribution of the crude polyester is modified by eliminating the molecules with lower molecular mass, e. g., the monomeric dialkyl esters.

Preferably, the molecules with lower molecular mass are removed by distillation. This distillation is advantageously performed under high vacuum. After the destillation, the residue has a relatively narrow molecular mass distribution. Other possible methods for eliminating the low molecular mass products are, for example, liquid chromatography or membrane separation processes such as ultrafiltration.

In the third step, the unsaturated ester precursor with a narrow molecular weight distribution is epoxidized by reacting it with a peroxy compound.

As a peroxy compound, both organic and inorganic peroxy compounds may be used. Preferably peroxycarboxylic acids such as peracetic acid or m-chloroperbenzoic acid are used as peroxy compounds. Monoperphthalic acid is especially preferred.

Hydrogen peroxide is also a preferred peroxy compound. When hydrogen peroxide is used, a phase transfer catalyst may be used. Examples of suitable phase transfer catalysts are described in *J. Polym. Sci., Part A: Polym. Chem.* 1993, 31, 1825-1838.

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The epoxidation reaction is advantageously carried out in an inert solvent. Suitable inert solvents are, for example, alkyl alkanoates, halogenated hydrocarbons, cycloaliphatic hydrocarbons, aromatic hydrocarbons or alcohols.

- 5 In powder coating, the coating powder usually comprises a thermosetting binder composition and further ingredients such as catalysts, pigments, fillers and auxiliary materials. The thermosetting binder composition may be a one-component binder composition which can be used as such or a two-component binder composition which comprises a hardener and a reactive polymer. The terms "one-component" and "two-component" in this context are independent  
10 of the actual chemical composition, i. e., a one-component binder composition may consist of several compounds. In addition, each component of a two-component binder composition may consist of several compounds.

- Preferred compositions which are suitable for both one-component binder compositions and,  
15 as hardener component, two-component binder compositions comprise at least one solid epoxidized polyester resin according to the invention and, optionally, a catalyst. Suitable catalysts for this type of composition are, for example, Lewis acids such as boron trifluoride complexes or Lewis bases such as tertiary amines.

- 20 In an especially preferred embodiment of the invention, the solid epoxidized polyester compounds according to the invention are used in compositions further comprising at least one polymer capable of reacting with epoxy groups.

- As polymers capable of reacting with epoxy groups, preferably polymers containing carboxy  
25 groups, polymers containing anhydride groups, polymers containing hydroxy groups, polymers containing amino and/or amido groups or (other) polymers containing epoxy groups are employed.

- Especially preferred polymers capable of reacting with epoxy groups are polymers based on  
30 polyesters, polyacrylates or polyethers which are modified so as to contain the above func-

tional groups. Depending on the type of functional groups present in the reactive polymers, suitable catalysts known in the art may be used to expedite the curing process.

Particularly preferred as polymers capable of reacting with epoxy groups are carboxylated polyesters with an acid number of 10 to 70 mg KOH/g resin and a glass transition temperature  $T_g$  of 50 to 70 °C. Resins of this type are available from Vianova Resins, a company of the Hoechst Group, under the trademark Alftalat®.

The compositions comprising at least one solid epoxidized polyester resin according to the invention and at least one polymer capable of reacting with epoxy groups may be blends with no substantial degree of crosslinking between the epoxidized polyester resin and the other polymer. These blends are often called masterbatches.

In another embodiment, the compositions are pre-polymerized, i. e., crosslinking has taken place to some extent, but without considerably impairing the thermosetting properties of the composition. Accordingly, these compositions are often called prepolymer compositions.

The masterbatch compositions may be prepared by — separately or together — melting the solid epoxidized polyester resin and the polymer capable of reacting with epoxy groups, mixing the melts thoroughly, solidifying and comminuting the composition. Especially the mixing should be performed at a temperature where no substantial crosslinking occurs.

The prepolymer compositions may be prepared by — separately or together — melting the solid epoxidized polyester resin and the polymer capable of reacting with epoxy groups, mixing the melts thoroughly, keeping the mixture at a temperature where crosslinking is possible for a time sufficient to achieve the desired degree of crosslinking, solidifying the mixture and comminuting it.

Both the solid epoxidized polyester resins as such and the above compositions may be used in thermosetting one-component binder compositions suitable for powder coating. When used as such, i. e., without additional polymer capable of reacting with epoxy groups, the solid ep-

oxidized polyester compounds according to the invention yield homopolymerized epoxy resins on curing.

In addition, both the solid epoxidized polyester resins as such and the above compositions  
5 may be used as hardener components in thermosetting two-component binder compositions suitable for powder coating which comprise a hardener component, a reactive polymer component which comprises at least one reactive polymer capable of reacting with epoxy groups and, optionally, a catalyst. If masterbatch or prepolymer compositions are employed as hardener components, the reactive polymer in the second component may be the same as that  
10 comprised in the hardener or a different one.

In the two-component binder compositions, preferred polymers capable of reacting with epoxy groups are polymers containing carboxy groups, polymers containing anhydride groups, polymers containing hydroxy groups, polymers containing amino and/or amido  
15 groups or (other) polymers containing epoxy groups.

Especially preferred polymers capable of reacting with epoxy groups are polymers based on polyesters, polyacrylates or polyethers which are modified so as to contain the above functional groups.  
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Particularly preferred as polymers capable of reacting with epoxy groups are carboxylated polyesters with an acid number of 10 to 70 mg KOH/g resin and a glass transition temperature  $T_g$  of 50 to 70 °C. Resins of this type are available from Vianova Resins, a company of the Hoechst Group, under the trademark Alftalat®.  
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Especially suitable for powder coating are powder coating compositions comprising a one-component or two-component binder composition as described above and one or more substance(s) such as pigments, catalysts, curing agents, including polymers capable of reacting with epoxy groups, fillers, and auxiliary materials. Auxiliary materials include materials such  
30 as flow improvers, antioxidants etc.

The powder coating compositions may be prepared by methods known in the art, for example by mixing and extruding the components in a heated extruder and subsequently comminuting the solid extrudate to a particle size suitable for the usual coating techniques.

- 5 The coating process may be carried out by applying the powder coating composition on a substrate, for example by electrostatic spraying or another known method, and curing the coating by subjecting it to heat for a sufficient time at a suitable temperature to obtain a completely cured coating.
- 10 The invention will be further described based on the following non-limiting examples. The molecular masses have been determined by gel permeation chromatography (GPC). The relative peak areas refer to the resolved peaks (at high retention times) only, whereas the averaged molecular masses have been determined from the complete elution diagrams.

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#### **Comparative Example A**

**Preparation of a polyester from 1,2,3,6-tetrahydrophthalic acid, ethylene glycol and isobutyl alcohol without distilling low boiling fraction**

- 20 A flask was charged with 456.3 g (3 mol) of 1,2,3,6-tetrahydrophthalic anhydride (THPA), 124.1 g (2 mol) of ethylene glycol, 148.2 g (2 mol) of isobutyl alcohol and 20 g of xylene. The mixture was heated and the temperature was gradually raised to 230 °C. The esterification reaction was carried out distilling off the water formed until the acid number of the mixture was 15 mg KOH/g. Then 0.5 g of stannous oxide was added. After ca. 12 h, the xylene was
- 25 distilled off at 230 °C under vacuum, from 1000 to 136 mbar. The reaction mixture was filtered and 675 g of polyester were obtained.

Iodine number: 110 (calculated: 113)

Acid number: 1 mg KOH/g

Viscosity at 100 °C: 60 mPa·s

- 30 Viscosity at 70 °C: 300 mPa·s

$\overline{M}_w$  1100

Molecular mass distribution (GPC, relative peak areas)

|   |          |            |
|---|----------|------------|
| 5 | <i>M</i> | 280 (15%)  |
|   |          | 450 (36%)  |
|   |          | 650 (24%)  |
|   |          | 850 (16%)  |
|   |          | 1100 (9%). |

### Comparative Example B

#### 10 Epoxidation of the polyester obtained in Comparative Example A

Crude polyester of 1,2,3,6-tetrahydrophthalic acid, ethylene glycol and isobutyl alcohol obtained in comparative example A (225 g, 1 eq) was dissolved in 450 g of ethyl acetate at 50 °C. Solid monoperphthalic acid (95% purity, 249 g, 1.3 mol) was added portionwise during 15 1 h. By immersing the reaction flask in cold water the temperature of the stirred reaction mixture was maintained at 50 °C. When the exothermic reaction ceased, the flask was immersed in a warm bath and the reaction mixture was allowed to stand at 50 °C for another 2 h. After cooling to room temperature, the reaction mixture was filtered and the filtrate washed with aqueous sodium carbonate and then with water. The organic layer was concentrated in 20 vacuo and dried at 80 °C/13 mbar to give 245 g of epoxy resin.

Oxirane content: 5.9 wt %

Iodine number: 0.8

Acid number: 0.5 mg KOH/g

Viscosity at 100 °C: 300 mPa·s

25 Viscosity at 70 °C: 7000 mPa·s

$\overline{M}_w$  1100

Molecular mass distribution (GPC, relative peak areas)

|    |          |           |
|----|----------|-----------|
| 30 | <i>M</i> | 280 (15%) |
|    |          | 450 (35%) |
|    |          | 650 (25%) |
|    |          | 850 (15%) |

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1100 (10%).

### Example 1

#### 5 Polyester of 1,2,3,6-tetrahydrophthalic acid, ethylene glycol and isobutyl alcohol

A flask was charged with 456.3 g (3 mol) of 1,2,3,6-tetrahydrophthalic anhydride (THPA), 124.1 g (2 mol) of ethylene glycol, 148.2 g (2 mol) of isobutyl alcohol and 20 g of xylene. The mixture was heated and the temperature was gradually raised to 230 °C. The esterification  
 10 reaction was carried out distilling off the water formed until the acid number of the mixture was 15 mg KOH/g. Then 0.5 g of stannous oxide was added. After ca. 12 h, the xylene and 110 g of diisobutyl tetrahydrophthalate were distilled off under vacuum at 230 °C, gradually reducing the pressure from 1000 to 13 mbar). The reaction mixture was filtered and 565 g of polyester were obtained:

|    |                                                        |                       |
|----|--------------------------------------------------------|-----------------------|
| 15 | Iodine number:                                         | 114 (calculated: 113) |
|    | Acid number:                                           | 1 mg KOH/g            |
|    | Viscosity at 100 °C:                                   | 90 mPa·s              |
|    | Viscosity at 70 °C:                                    | 600 mPa·s             |
|    | $\overline{M}_w$                                       | 1400                  |
| 20 | Molecular mass distribution (GPC, relative peak areas) |                       |
|    | $M$                                                    | 280 (2%)              |
|    |                                                        | 450 (20%)             |
|    |                                                        | 650 (15%)             |
|    |                                                        | 850 (15%)             |
| 25 |                                                        | 1100 (48%).           |

**Example 2**

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**Epoxidation of the polyester obtained in Example 1**

Crude polyester of 1,2,3,6-tetrahydrophthalic acid, ethylene glycol and isobutyl alcohol obtained in example 1 (224 g, 1 eq) was dissolved in 450 g of ethyl acetate at 50 °C. Solid monoperphthalic acid (95% purity, 249 g, 1.3 mol) was added portionwise during 1 h. By immersing the reaction flask in cold water the temperature of the stirred reaction mixture was maintained at 50 °C. When the exothermic reaction ceased, the flask was immersed in a warm bath and the reaction mixture was allowed to stand at 50 °C for another 2 h. After cooling to room temperature, the reaction mixture was filtered and the filtrate washed with aqueous sodium carbonate and then with water. The organic layer was concentrated in vacuo and dried at 80 °C/13 mbar to give 240 g of solid epoxy resin with a softening point of ca. 60 °C.

Oxirane content: 6.3 wt %

Iodine number: 0.3

15 Acid number: 0

Viscosity at 100 °C: 2700 mPa·s

Viscosity at 70 °C: 64000 mPa·s

$\overline{M}_w$  1500

Molecular mass distribution (GPC, relative peak areas)

|    |          |             |
|----|----------|-------------|
| 20 | <i>M</i> | 280 (2%)    |
|    |          | 450 (20%)   |
|    |          | 650 (15%)   |
|    |          | 850 (15%)   |
|    |          | 1100 (48%). |

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**Comparative Example C****Preparation of a polyester of 1,2,3,6-tetrahydrophthalic acid, neopentyl glycol and isobutyl alcohol without distilling low boiling fraction**

- 5 A flask was charged with 456.3 g (3 mol) of 1,2,3,6-tetrahydrophthalic anhydride (THPA), 208.3 g (2 mol) of neopentyl glycol, 148.2 g (2 mol) of isobutyl alcohol and 20 g of xylene. The mixture was heated and the temperature was gradually raised to 230 °C. The esterification reaction was carried out distilling off the water formed until the acid number of the mixture was 15 mg KOH/g. Then 0.5 g of stannous oxide was added. After ca. 12 h, the xylene was
- 10 distilled off at 230 °C under vacuum, from 1000 to 136 mbar. The reaction mixture was filtered and 760 g of polyester were obtained.

Iodine number: 98 (calculated: 100)

Acid number: 0.4 mg KOH/g

Viscosity at 100 °C: 110 mPa·s

- 15 Viscosity at 70 °C: 700 mPa·s

$\overline{M}_w$  1400

Molecular mass distribution (GPC, relative peak areas)

- |     |             |
|-----|-------------|
| $M$ | 280 (26%)   |
| 20  | 470 (31%)   |
|     | 700 (17%)   |
|     | 1000 (8%)   |
|     | 1300 (18%). |

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**Comparative Example D****Epoxidation of the polyester obtained in Comparative Example C**

- 30 The crude polyester of 1,2,3,6-tetrahydrophthalic acid, neopentyl glycol and isobutyl obtained in comparative example C (258 g, 1 eq) was dissolved in 500 g of ethyl acetate at 50 °C. Solid monoperphthalic acid (95% purity, 249 g, 1.3 mol) was added portionwise during 1 h. By

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immersing the reaction flask in cold water the temperature of the stirred reaction mixture was maintained at 50 °C. When the exothermic reaction ceased, the flask was immersed in a warm bath and the reaction mixture was allowed to stand at 50 °C for another 2 h. After cooling to room temperature, the reaction mixture was filtered and the filtrate washed with aqueous sodium carbonate and then with water. The organic layer was concentrated in vacuo and dried at 80 °C/13 mbar to give 271 g of epoxy resin.

Oxirane content: 4.9 wt %

Iodine number: 1

Acid number: 0

10 Viscosity at 100 °C: 2500 mPa·s

$\bar{M}_w$  1800

Molecular mass distribution (GPC, relative peak areas)

$M$  280 (25%)

470 (30%)

15 700 (18%)

1000 (7%)

1300 (20%).

### 20 Example 3

#### Polyester of 1,2,3,6-tetrahydrophthalic acid, neopentyl glycol and isobutyl alcohol

A flask was charged with 456.3 g (3 mol) of 1,2,3,6-tetrahydrophthalic anhydride (THPA), 208.3 g (2 mol) of neopentyl glycol, 148.2 g (2 mol) of isobutyl alcohol and 20 g of xylene.

25 The mixture was heated and the temperature was gradually raised to 230 °C. The esterification reaction was carried out distilling off the water formed until the acid number of the mixture was 15 mg KOH/g. Then 0.5 g of stannous oxide was added. After ca. 12 h, the xylene and 160 g of diisobutyl tetrahydrophthalate were distilled off under vacuum at 230 °C, gradually reducing the pressure from 1000 to 13 mbar. The reaction mixture was filtered and 760 g of polyester were obtained.

30 Iodine number: 100 (calculated: 100)

17

|    |                                                        |            |
|----|--------------------------------------------------------|------------|
|    | Acid number:                                           | 0          |
|    | Viscosity at 100 °C:                                   | 250 mPa·s  |
|    | Viscosity at 70 °C:                                    | 2200 mPa·s |
|    | $\overline{M}_w$                                       | 1500       |
| 5  | Molecular mass distribution (GPC, relative peak areas) |            |
|    | $M$                                                    | 280 (2%)   |
|    |                                                        | 470 (50%)  |
|    |                                                        | 700 (30%)  |
|    |                                                        | 1000 (15%) |
| 10 |                                                        | 1300 (3%). |

**Example 4****Epoxidation of the polyester obtained in Example 3**

15

Crude polyester of 1,2,3,6-tetrahydrophthalic acid, neopentyl glycol and isobutyl alcohol obtained in example 3 (253 g, 1 eq) was dissolved in 500 g of ethyl acetate at 50 °C. Solid monoperphthalic acid (95% purity, 249 g, 1.3 mol) was added portionwise during 1 h. By immersing the reaction flask in cold water the temperature of the stirred reaction mixture was maintained at 50 °C. When the exothermic reaction ceased, the flask was immersed in a warm bath and the reaction mixture was allowed to stand at 50 °C for another 2 h. After cooling to room temperature, the reaction mixture was filtered and the filtrate washed with aqueous sodium carbonate and then with water. The organic layer was concentrated in vacuum and dried at 80 °C/13 mbar to give 266 g of epoxy resin.

|    |                                                        |              |
|----|--------------------------------------------------------|--------------|
| 25 | Oxirane content:                                       | 5.3 wt %     |
|    | Iodine number:                                         | 1.3          |
|    | Acid number:                                           | 0            |
|    | Viscosity at 100 °C:                                   | 6150 mPa·s   |
|    | Viscosity at 70 °C:                                    | 132000 mPa·s |
| 30 | $\overline{M}_w$                                       | 1700         |
|    | Molecular mass distribution (GPC, relative peak areas) |              |

|          |            |
|----------|------------|
| <i>M</i> | 280 (2%)   |
|          | 470 (45%)  |
|          | 700 (29%)  |
|          | 1000 (18%) |
| 5        | 1300 (6%). |

**Example 5****Polyester of 1,2,3,6-tetrahydrophthalic acid, trimethylolpropane and isobutyl alcohol**

10

A flask was charged with 1369 g (9 mol) of 1,2,3,6-tetrahydrophthalic anhydride (THPA), 404.5 g (3 mol) of trimethylolpropane (= 2-ethyl-2-(hydroxymethyl)-1,3-propanediol), 699 g (9.4 mol) of isobutyl alcohol and 35 g of xylene. The mixture was heated and the temperature was gradually raised to 230 °C. The esterification reaction was carried out distilling off the

15 water formed until the acid number of the mixture was 18 mg KOH/g. Then 1.2 g of stannous oxide was added. After ca. 24 h, the xylene and 589 g of diisobutyl tetrahydrophthalate were distilled off under vacuum at 230 °C, gradually reducing the pressure from 1000 to 13 mbar. The reaction mixture was filtered and 1677 g of polyester were obtained.

Iodine number: 101.5 (calculated: 102.5)

20 Acid number: 1 mg KOH/g

Viscosity at 100 °C: 2260 mPa·s

$\overline{M}_w$  2050

25 **Example 6****Polyester of 1,2,3,6-tetrahydrophthalic acid, trimethylolpropane and isobutyl alcohol**

A flask was charged with 1056 g (7 mol) of 1,2,3,6-tetrahydrophthalic anhydride (THPA), 582 g (2 mol) of diisobutyl tetrahydrophthalate, 404.5 g (3 mol) of trimethylolpropane, 388 g

30 (5.2 mol) of isobutyl alcohol and 40 g of xylene. The mixture was heated and the temperature was gradually raised to 230 °C. The esterification reaction was carried out distilling off the

water formed until the acid number of the mixture was 18 mg KOH/g. Then 1.3 g of stannous oxide was added. After ca. 24 h, the xylene and 695 g of diisobutyl tetrahydrophthalate were distilled off under vacuum at 230 °C, gradually reducing the pressure from 1000 to 13 mbar. The reaction mixture was filtered and 1501 g of polyester were obtained.

5 Iodine number: 102.3 (calculated: 102.5)

Acid number: 1 mg KOH/g

Viscosity at 100 °C: 71300 mPa·s

$\overline{M}_w$  2600

10

### Example 7

#### Epoxidation of the polyester obtained in Example 6

Crude polyester of 1,2,3,6-tetrahydrophthalic acid, trimethylolpropane and isobutyl alcohol  
15 obtained in example 6 (100 g, 0.4 eq) was dissolved in 255 g of xylene with 1 g of methyl-  
trioctylammonium chloride at 40 °C. To this mixture 115 g of an aqueous solution containing  
hydrogen peroxide (0.54 mol), sodium tungstate (0.02 mol) and phosphoric acid (0.06 mol)  
was quickly added. By immersing the reaction flask in cold water the temperature of the  
stirred reaction mixture was maintained at 40 °C. When the exothermic reaction ceased, the  
20 flask was immersed in a warm bath and the reaction mixture was allowed to stand at 40 °C for  
4 h. After cooling the organic layer was concentrated in vacuum to give 110 g of solid epoxy  
resin with a softening point of about 80 °C.

Oxirane content: 4.8 wt %

Iodine number: 2.5

25 Acid number: 0

Viscosity at 100 °C: 13400 mPa·s

$\overline{M}_w$  2700

**Example 8****Epoxidation of the polyester obtained in Example 6**

Crude polyester of 1,2,3,6-tetrahydrophthalic acid, trimethylolpropane and isobutyl alcohol  
5 obtained in example 6 (100 g, 0.4 eq) was dissolved in 200 g of ethyl acetate at 50 °C.  
Solid monoperphthalic acid (95% purity, 100 g, 0.52 mol) was added portionwise during 1 h.  
By immersing the reaction flask in cold water the temperature of the stirred reaction mixture  
was maintained at 50 °C. When the exothermic reaction ceased, the flask was immersed in a  
warm bath and the reaction mixture was allowed to stand at 50 °C for another 2 h. After cool-  
10 ing to room temperature, the reaction mixture was filtered and the filtrate washed with aque-  
ous sodium carbonate and then with water. The organic layer was concentrated in vacuum and  
dried at 80 °C/13 mbar to give 103.3 g of solid epoxy resin with a softening point of about  
80 °C.

Oxirane content: 5.1 wt %

15 Iodine number: 1

Acid number: 0

Viscosity at 100 °C: 39500 mPa·s

$\overline{M}_w$  2700

20

**Example 9****Polyester of 1,2,3,6-tetrahydrophthalic acid, pentaerythritol and isobutyl alcohol**

A flask was charged with 1217 g (8 mol) of 1,2,3,6-tetrahydrophthalic anhydride (THPA),  
25 273 g (2 mol) of pentaerythritol (= 2,2-bis(hydroxymethyl)-1,3-propanediol), 594 g (8 mol) of  
isobutyl alcohol and 37 g of xylene. The mixture was heated and the temperature was gradu-  
ally raised to 230 °C. The esterification reaction was carried out distilling off the water formed  
until the acid number of the mixture was 22 mg KOH/g. Then 1.5 g of stannous oxide was  
added. After ca. 24 h, the xylene and 540 g of diisobutyl tetrahydrophthalate were distilled off  
30 under vacuum at 230 °C, gradually reducing the pressure from 1000 to 13 mbar. The reaction  
mixture was filtered and 1400 g of polyester were obtained.

Iodine number: 103.5 (calculated: 107)  
Acid number: 1.7 mg KOH/g  
Viscosity at 100 °C: 138000 mPa·s  
 $\overline{M}_w$  2300

5

**Example 10****Epoxidation of the polyester obtained in Example 9**

- 10 Crude polyester of 1,2,3,6-tetrahydrophthalic acid, pentaerythritol and isobutyl alcohol obtained in example 9 (149 g, 0.6 eq) was dissolved in 300 g of ethyl acetate at 50 °C. Solid monoperphthalic acid (95% purity, 150 g, 0.78 mol) was added portionwise during 1 h. By immersing the reaction flask in cold water the temperature of the stirred reaction mixture was maintained at 50 °C. When the exothermic reaction ceased, the flask was immersed in a  
15 warm bath and the reaction mixture was allowed to stand at 50 °C for another 2 h. After cooling to room temperature, the reaction mixture was filtered and the filtrate washed with aqueous sodium carbonate and then with water. The organic layer was concentrated in vacuum and dried at 80 °C/13 mbar to give 160 g of solid epoxy resin.

- Oxirane content: 5.8 wt %  
20 Iodine number: 0.9  
Acid number: 0  
Melting point: 123 °C  
 $\overline{M}_w$  2900

25

**Example 11****Polyester of 1,2,3,6-tetrahydrophthalic acid, tris(hydroxyethyl) isocyanurate and isobutyl alcohol**

- 30 A flask was charged with 913 g (6 mol) of 1,2,3,6-tetrahydrophthalic anhydride (THPA), 523 g (2 mol) of tris(hydroxyethyl) isocyanurate, 445 g (6 mol) of isobutyl alcohol and 50 g of

xylene. The mixture was heated and the temperature was gradually raised to 230 °C. The esterification reaction was carried out distilling off the water formed until the acid number of the mixture was 21 mg KOH/g. Then 1g of stannous oxide was added. After ca. 15 h, the xylene and 435 g of diisobutyl tetrahydrophthalate were distilled off under vacuum at 230 °C, gradually reducing the pressure from 1000 to 13 mbar. The reaction mixture was filtered and 1340 g of polyester were obtained.

Iodine number: 83 (calculated: 86)

Acid number: 0.53 mg KOH/g

Viscosity at 100 °C: 26350 mPa·s

10  $\overline{M}_w$  1400

Colour 8 Gardner

### Example 12

#### 15 Epoxidation of the polyester obtained in Example 11

Crude polyester of 1,2,3,6-tetrahydrophthalic acid, tris(hydroxyethyl) isocyanurate and isobutyl alcohol obtained in example 11 (306 g, 1 eq) was dissolved in 600 g of ethyl acetate at 50 °C. Solid monoperphthalic acid (95% purity, 249 g, 1.30 mol) was added portionwise during 1 h. By immersing the reaction flask in cold water the temperature of the stirred reaction mixture was maintained at 50 °C. When the exothermic reaction ceased, the flask was immersed in a warm bath and the reaction mixture was allowed to stand at 50 °C for another 2 h. After cooling to room temperature, the reaction mixture was filtered and the filtrate washed with aqueous sodium carbonate and then with water. The organic layer was concentrated in vacuo and dried at 80 °C/13 mbar to give 330 g of solid epoxy resin.

25 Melting point: 98 °C

Oxirane content: 4.6 wt %

Iodine number: 2

Acid number: 0

30 Viscosity at 100 °C: 970000 mPa·s

$\overline{M}_w$  1700

Colour

3 Gardner

**Example 13**

- 5    **Preparation of a pre-polymer binder/hardener from the epoxy ester of Example 2 and a carboxylated polyester**

In a reactor equipped with stirrer 2 parts of the epoxidized polyester of Example 2 were charged under light nitrogen flow and the temperature was increased up to 80–90 °C until the epoxy ester was melted, then 1 part of the carboxylated polyester resin Alftalat<sup>®</sup> 01634 (Vianova Resins) was added until complete homogenisation of the resin was reached. The temperature of the mixture was further increased to a maximum of 130–140 °C and the mixture was kept at this temperature for about 15 min (upon prolonged heating, the mixture tends to gelatinize). After this time the reaction mixture was quickly discharged, cooled to room temperature and ground to give a pre-polymer which may be used as a one-component binder or as a hardener in a two-component binder for powder coating.

**Example 14**

- 20    **Preparation of a pre-polymer binder/hardener from the epoxy ester of Example 4 and a carboxylated polyester**

The procedure of Example 13 was repeated with the epoxidized polyester of Example 4 using the same ratio of epoxide to Alftalat<sup>®</sup> 01634.

**Example 15**

**Preparation of a masterbatch binder/hardener from the epoxy ester of Example 8 and a carboxylated polyester**

- 5 In a reactor equipped with stirrer 9.4 parts of the epoxidized polyester resin of Example 8 were charged under light nitrogen flow and the temperature was increased up to 80–90 °C until the epoxide was molten. In a second reactor equipped with a stirrer 1 part of the carboxylated polyester resin Alftalat® 01634 was charged under light nitrogen flow and the temperature was increased to about 130–140 °C until the resin was molten. Then the contents of the
- 10 reactors were rapidly and thoroughly mixed while being discharged into the same container. After cooling and solidification, the mixture was ground to give a masterbatch that may be used as a one-component binder or as a hardener in a two-component binder for powder coating.

15

**Example 16**

**Preparation of a masterbatch binder/hardener from the epoxy ester of Example 12 and a carboxylated polyester**

- 20 The procedure of Example 15 was repeated using the epoxidized polyester resin of Example 12 and the same ratio of epoxide to Alftalat® 01634.

**Example 17**

- 25 **Powder compositions for coating and coating tests performed therewith**

- A series of powder coating tests were performed using the following powder compositions (in parts by weight). Each composition comprises a two-component binder which in turn comprises a reactive polyester resin ("Polyester") and a epoxy-containing hardener ("Hardener").
- 30 For each binder composition, with the exception of that in the reference composition, the

compound or composition used as hardener is identified by the corresponding Example No. in parentheses.

The components used in the compositions were:

5

Alftalat<sup>®</sup> 01634: carboxylated polyester resin, acid number ~ 35 mg KOH/g,  $T_g \sim 65^\circ\text{C}$

Alftalat<sup>®</sup> AN 989: carboxylated polyester resin, acid number ~ 35 mg KOH/g,  $T_g \sim 60^\circ\text{C}$

Alftalat<sup>®</sup> AN 770: carboxylated polyester resin, acid number ~ 35 mg KOH/g,  $T_g \sim 50^\circ\text{C}$

Alftalat<sup>®</sup> AN 995: carboxylated polyester resin, acid number ~ 25 mg KOH/g,  $T_g \sim 55^\circ\text{C}$

10 

Alftalat<sup>®</sup> VAN 997: carboxylated polyester resin, acid number ~ 35 mg KOH/g,  $T_g \sim 55^\circ\text{C}$

Additol<sup>®</sup> XL 496: flow promoting agent

(Alftalat and Additol are registered trademarks of Vianova Resins, a company of the Hoechst Group.)

15 

Irganox<sup>®</sup> 1010: antioxidant

(Irganox is a registered trademark of Ciba Ltd.)

Kronos<sup>®</sup> 2160: titanium dioxide filler

(Kronos is a registered trademark of NL Industries Inc.)

20

#### REFERENCE COMPOSITION

25

|    |                                                       |      |
|----|-------------------------------------------------------|------|
|    | Polyester: Alftalat <sup>®</sup> AN 989               | 569  |
| 25 | Hardener: Araldite <sup>®</sup> PT 810 (= TGIC, Ciba) | 43   |
|    | Additol <sup>®</sup> XL 496                           | 30   |
|    | Irganox <sup>®</sup> 1010                             | 3    |
|    | Benzoin                                               | 5    |
|    | Kronos <sup>®</sup> 2160                              | 350  |
| 30 | Ratio polyester/hardener                              | 93/7 |

## TEST NUMBER 1

|   |                                         |       |
|---|-----------------------------------------|-------|
|   | Polyester: Alftalat <sup>®</sup> AN 770 | 465   |
|   | Hardener (Ex. 13)                       | 155   |
| 5 | Additol <sup>®</sup> XL 496             | 30    |
|   | Benzoin                                 | 5     |
|   | Kronos <sup>®</sup> 2160                | 345   |
|   | Ratio polyester/hardener                | 75/25 |

10

## TEST NUMBER 2

|    |                                         |       |
|----|-----------------------------------------|-------|
|    | Polyester: Alftalat <sup>®</sup> AN 770 | 465   |
| 15 | Hardener (Ex. 14)                       | 155   |
|    | Additol <sup>®</sup> XL 496             | 30    |
|    | Benzoin                                 | 5     |
|    | Kronos <sup>®</sup> 2160                | 345   |
| 20 | Ratio polyester/hardener                | 75/25 |

## TEST NUMBER 3

|    |                                         |       |
|----|-----------------------------------------|-------|
| 25 | Polyester: Alftalat <sup>®</sup> AN 770 | 465   |
|    | Hardener (Ex. 15)                       | 155   |
|    | Additol <sup>®</sup> XL 496             | 30    |
|    | Benzoin                                 | 5     |
|    | Kronos <sup>®</sup> 2160                | 345   |
| 30 | Ratio polyester/hardener                | 75/25 |

## TEST NUMBER 4

|   |                             |       |
|---|-----------------------------|-------|
|   | Polyester: Alftalat® AN 770 | 496   |
|   | Hardener (Ex. 8)            | 124   |
| 5 | Additol® XL 496             | 30    |
|   | Benzoin                     | 5     |
|   | Kronos® 2160                | 345   |
|   | Ratio polyester/hardener    | 80/20 |

10

## TEST NUMBER 5

|    |                              |       |
|----|------------------------------|-------|
|    | Polyester: Alftalat® VAN 995 | 496   |
| 15 | Hardener (Ex. 8)             | 124   |
|    | Additol® XL 496              | 30    |
|    | Benzoin                      | 5     |
|    | Kronos® 2160                 | 345   |
| 20 | Ratio polyester/hardener     | 80/20 |

## TEST NUMBER 6

|    |                             |       |
|----|-----------------------------|-------|
| 25 | Polyester: Alftalat® AN 989 | 496   |
|    | Hardener (Ex. 8)            | 124   |
|    | Additol® XL 496             | 30    |
|    | Benzoin                     | 5     |
|    | Kronos® 2160                | 345   |
| 30 | Ratio polyester/hardener    | 80/20 |

## TEST NUMBER 7

|   |                             |       |
|---|-----------------------------|-------|
|   | Polyester: Alftalat® AN 770 | 465   |
|   | Hardener (Ex. 16)           | 155   |
| 5 | Additol® XL 496             | 30    |
|   | Benzoin                     | 5     |
|   | Kronos® 2160                | 345   |
|   | Ratio polyester/hardener    | 75/25 |

10

## TEST NUMBER 8

|    |                             |       |
|----|-----------------------------|-------|
|    | Polyester: Alftalat® AN 770 | 496   |
| 15 | Hardener (Ex. 12)           | 124   |
|    | Additol® XL 496             | 30    |
|    | Benzoin                     | 5     |
|    | Kronos® 2160                | 345   |
| 20 | Ratio polyester/hardener    | 80/20 |

## TEST NUMBER 9

|    |                             |       |
|----|-----------------------------|-------|
| 25 | Polyester: Alftalat® AN 770 | 496   |
|    | Hardener (Ex. 10)           | 124   |
|    | Additol® XL 496             | 30    |
|    | Benzoin                     | 5     |
|    | Kronos® 2160                | 345   |
| 30 | Ratio polyester/hardener    | 80/20 |

The powders of the above mentioned compositions were extruded using the following conditions:

Twin screw extruder.

Temperatures [°C]: 80/100/100 (3 heating elements)

5 Feeding ratio [%]: 30

Rotation speed [ $\text{min}^{-1}$ ]: 300

The extrudate was cooled, micronized and sieved ( $<125 \mu\text{m}$ ). The powder compositions thus obtained were used for the painting tests.

10 The powder compositions were applied on steel panels by electrostatic spraying with a corona gun. Curing was performed in a convection oven at 200 °C for 20–30 min. The results are compiled in the following Table 1.

Table 1

| Test No.      | Flow <sup>(1)</sup> | Weathering Resistance <sup>(2)</sup> | Acetone resistance <sup>(3)</sup> |
|---------------|---------------------|--------------------------------------|-----------------------------------|
| 0 (Reference) | 2                   | 2                                    | 3                                 |
| 1             | 2-3                 | 2                                    | 3                                 |
| 2             | 2-3                 | 2                                    | 3                                 |
| 3             | 3                   | 2                                    | 3                                 |
| 4             | 2-3                 | 2                                    | 3                                 |
| 5             | 3-4                 | 2                                    | 3                                 |
| 6             | 2-3                 | 2                                    | 3                                 |
| 7             | 2-3                 | 2                                    | 3                                 |
| 8             | 2-3                 | 2                                    | 3                                 |
| 9             | 3-4                 | 2                                    | 3                                 |

Evaluation: 1: excellent, 2: good, 3: sufficient, 4: poor, 5: inadequate

<sup>(1)</sup> smoothness of the painted surface, visually determined

5 <sup>(2)</sup> accelerated weathering test according to ASTM G 53

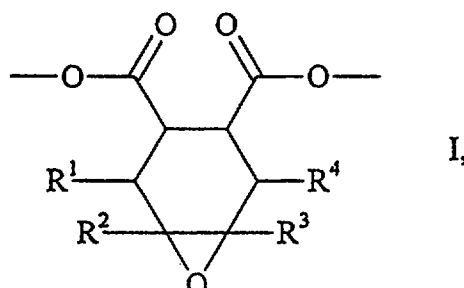
<sup>(3)</sup> acetone rub test, visually determined

## Claims



1. A solid epoxidized polyester resin comprising at least one epoxidized ester containing, per molecule, two or more cycloaliphatic moieties of the general formula

5



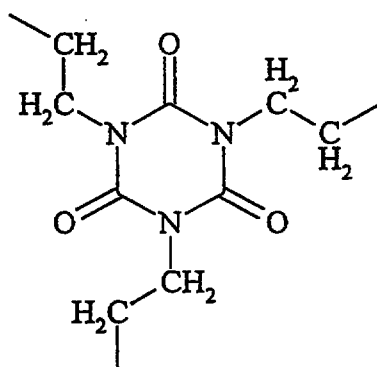
wherein

- 10  $R^1$  and  $R^4$  are independently selected from the group consisting of hydrogen and methyl or  $R^1$  and  $R^4$  together are methylene,
- $R^2$  and  $R^3$  are independently selected from the group consisting of hydrogen and methyl, said two or more cycloaliphatic groups being bonded by their open valencies to moieties independently selected from the group consisting of hydrogen, linear or branched  $C_{1-8}$  alkyls, linear or branched linking  $C_{2-8}$  alkanediyls, linear or branched (cross-) linking  $C_{3-8}$  alkanetriyls, linear or branched (cross-) linking  $C_{4-8}$  alkanetetrayls and
- 15 linking or crosslinking moieties of the general formula  $X(Y-)_n$  wherein  $n$  is an integer from 2 to 4,  $X$  is a di-, tri- or tetravalent group containing at least one isocyclic or heterocyclic ring and  $Y$  is a direct bond or a  $-(CH_2)_m-$  group wherein  $m$  is an integer from 1 to 4,
- 20 characterized in that it is essentially free of monomeric products.

2. A solid epoxidized polyester resin according to claim 1, wherein one of  $R^1$  to  $R^4$  is hydrogen or methyl and the remaining of  $R^1$  to  $R^4$  are hydrogens.
- 25 3. A solid epoxidized polyester resin according to claim 1, wherein  $R^1$  and  $R^4$  together are methylene, one of  $R^2$  and  $R^3$  is hydrogen or methyl and the other one is hydrogen.

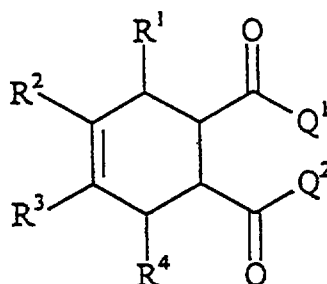
4. A solid epoxidized polyester resin according to any one of claims 1 to 3, wherein the  $C_{1-8}$  alkyls are selected from the group consisting of methyl, ethyl, propyl, isopropyl, butyl, isobutyl and 2-ethylhexyl, the linking  $C_{2-8}$  alkanediyls are selected from the group consisting of 1,2-ethanediyl, 1,2-propanediyl, 1,3-propanediyl, 1,2-butanediyl, 1,3-butanediyl, 1,4-butanediyl, 2,3-butanediyl, 3-methyl-1,3-butanediyl, 1,2-hexanediyl, 1,6-hexanediyl and 2,2-dimethyl-1,3-propanediyl, the (cross-) linking  $C_{3-8}$  alkanetriyls are selected from the group consisting of 1,2,3-propanetriyl and 2,2-dimethylbutane-1,1',1''-triyl and the (cross-) linking  $C_{4-8}$  alkanetetrayls are selected from the group consisting of 1,2,3,4-butanetetrayl and 2,2-dimethylpropane-1,1',1'',3-tetrayl.

5. A solid epoxidized polyester resin according to any one of claims 1 to 3, wherein the linking or crosslinking moieties of the general formula  $X(Y-)_n$  are isocyanurate groups of the formula



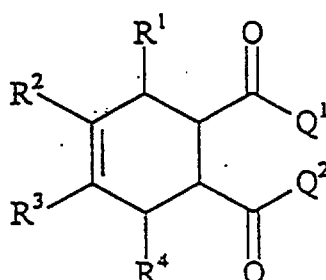
6. A solid epoxidized polyester resin according to any one of claims 1 to 5, characterized in that it has an acid number of not more than 2 mg KOH/g, preferably not more than 1 mg KOH/g.

7. Process for preparing a solid epoxidized polyester resin according to any one of claims 1 to 6, comprising the steps of
- i) reacting an unsaturated dicarboxylic acid or acid derivative of the general formula



II,

- wherein  $R^1$  to  $R^4$  are as defined in claim 1 and  $Q^1$  and  $Q^2$  are independently selected from the group consisting of hydroxy and  $C_{1-8}$  alkoxy or  $Q^1$  and  $Q^2$  together are  $-O-$ ,  
 5 with at least one hydroxy compound selected from the group consisting of linear or branched  $C_{2-8}$  alkanediols, linear or branched  $C_{3-8}$  alkanetriols, linear or branched  $C_{4-8}$  alkanetetraols and hydroxycompounds of the general formula  $X(Y-OH)_n$  wherein  $n$  is an integer from 2 to 4,  $X$  is a di-, tri- or tetravalent group containing at least one isocyclic or heterocyclic ring and each  $Y$  is a direct bond or a  $-(CH_2)_m-$  group wherein  $m$  is  
 10 an integer from 1 to 4;  
 and a linear or branched  $C_{1-8}$  alkanol,  
 ii) removing essentially all monomeric byproducts, and  
 iii) epoxidizing the resulting unsaturated polyester.
- 15 8. Process for preparing a solid epoxidized polyester resin according to any one of claims 1 to 6, comprising the steps of  
 i) reacting an unsaturated dicarboxylic acid ester of the general formula



II,

20

wherein  $R^1$  to  $R^4$  are as defined in claim 1 and  $Q^1$  and  $Q^2$  are  $C_{1-8}$  alkoxy groups, with at least one hydroxy compound selected from the group consisting of linear or branched



34

- 5  $C_{2-8}$  alkanediols, linear or branched  $C_{3-8}$  alkanetriols, linear or branched  $C_{4-8}$  alkane-tetraols and hydroxy compounds of the general formula  $X(Y-OH)_n$  wherein  $n$  is an integer from 2 to 4,  $X$  is a di-, tri- or tetravalent group containing at least one isocyclic or heterocyclic ring and each  $Y$  is a direct bond or a  $-(CH_2)_m-$  group wherein  $m$  is an integer from 1 to 4,
- ii) removing essentially all monomeric byproducts, and
- iii) epoxidizing the resulting unsaturated polyester by reacting it with a peroxy compound.
- 10 9. Process according to claim 7 or 8, wherein the monomeric byproducts are removed by vacuum distillation.
10. Process according to any one of claims 7 to 9, wherein the peroxy compound is a peroxycarboxylic acid.
- 15 11. Process according to any one of claims 7 to 9, wherein the peroxy compound is hydrogen peroxide.
12. A composition comprising at least one solid epoxidized polyester resin according to any one of claims 1 to 6 and, optionally, at least one catalyst.
- 20 13. A composition according to claim 12 which further comprises at least one polymer capable of reacting with epoxy groups.
- 25 14. A composition according to 13, wherein the polymer capable of reacting with epoxy groups is selected from the group consisting of polymers containing carboxy groups, polymers containing anhydride groups, polymers containing hydroxy groups, polymers containing amido and/or amino groups and polymers containing epoxy groups.
- 30 15. A composition according to claim 14, wherein the polymer capable of reacting with epoxy groups is selected from the group consisting of modified polyesters, modified poly-

acrylates and modified polyethers.



16. A composition according to claim 15, wherein the polymer capable of reacting with epoxy groups is a carboxylated polyester with an acid number of 10 to 70 and a glass transition temperature of 50 to 70 °C.
17. A composition according to any one of claims 13 to 16, wherein there is no substantial crosslinking between the epoxidized polyester resin and the polymer capable of reacting with epoxy groups.
18. A composition according to any one of claims 13 to 16, wherein the epoxidized polyester resin and the polymer capable of reacting with epoxy groups are partially crosslinked.
19. Process for preparing a composition according to claim 17, comprising the steps of melting the epoxidized polyester resin and the polymer capable of reacting with epoxy groups, thoroughly mixing at a temperature at which no substantial crosslinking occurs, solidifying and comminuting.
20. Process for preparing a composition according to claim 18, comprising the steps of melting the epoxidized polyester resin and the polymer capable of reacting with epoxy groups, thoroughly mixing, keeping at an elevated temperature for a time sufficient to achieve partial crosslinking, solidifying and comminuting.
21. A thermosetting one-component binder composition suitable for powder coating, comprising at least one solid epoxidized polyester resin according to any one of claims 1 to 6 or a composition according to any one of claims 12 to 18.
22. A thermosetting two-component binder composition suitable for powder coating, comprising a hardener and a reactive polymer and, optionally, a catalyst, wherein the hardener comprises at least one solid epoxidized polyester resin according to any one of



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claims 1 to 6 or a composition according to any one of claims 13 to 18 and the reactive polymer comprises at least one polymer capable of reacting with epoxy groups.

23. A thermosetting two-component binder composition according to claim 22, wherein the polymer capable of reacting with epoxy groups is selected from the group consisting of polymers containing carboxy groups, polymers containing anhydride groups, polymers containing hydroxy groups, polymers containing amido and/or amino groups and polymers containing epoxy groups.
24. A thermosetting two-component binder composition according to claim 23, wherein the polymer capable of reacting with epoxy groups is selected from the group consisting of modified polyesters, modified polyacrylates and modified polyethers.
25. A thermosetting two-component binder composition according to claim 24, wherein the polymer capable of reacting with epoxy groups is a carboxylated polyester with an acid number of 10 to 70 and a glass transition temperature of 50 to 70 °C.
26. A powder coating composition comprising a thermosetting binder composition and one or more substances selected from the group consisting of pigments, catalysts, curing agents, fillers and auxiliary materials, wherein the thermosetting binder composition is a composition according to any one of claims 21 to 25.
27. Process for preparing a wholly or partially coated substrate by applying a powder coating composition according to claim 26 on a substrate and curing the coating by subjecting it to heat for a sufficient time at a suitable temperature to obtain a completely cured coating.
28. Wholly or partially coated substrate, wherein the coating is obtained from a binder composition according to any one of claims 12 to 18 and 21 to 25 or by a process according to claim 27.