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Unsaturated, amorphous polyesters based on certain
dicidol isomers

5 The invention relates to unsaturated, amorphous
polyesters based on certain dicidol isomers and acids.

Unsaturated polyester resins (UP resins) are well
known. They are prepared by condensing saturated and
unsaturated dicarboxylic acids or their anhydrides with
10 diols. Their properties depend substantially on the
type and ratio of the starting materials.

The bearers of the polymerizable double bonds used are
usually α,β -unsaturated acids, primarily maleic acid
15 and its anhydride or fumaric acid; unsaturated diols
are of minor importance. The higher the content of
double bonds, i.e. the smaller the separation of the
double bonds in the chain molecules, the more reactive
the polyester resin. It polymerizes very rapidly with
20 intense development of heat and extensive contraction
to give a highly crosslinked and therefore
comparatively brittle end product. For this reason, the
reactive double bonds in the polyester molecule are
"diluted" by co-condensing saturated aliphatic or
25 aromatic dicarboxylic acids. The alcohol components
used are straight-chain and branched diols. The
individual UP resin types differ not only in the
components used to prepare them but also in the ratio
of saturated to unsaturated acids which determines the
30 crosslinking density in the polymerization, the degree
of condensation, i.e. the molar mass, the acid number
and the OH number, i.e. the type of end groups in the
chain molecules, the monomer content and the type of
additives (Ullmann's Encyclopedia of Industrial
35 Chemistry, VOL A21, p. 217ff, 1992).

UP resins based on dicidol as the diol component are
known, for example, from DE 924 889, DE 953 117,
DE 22 45 110, DE 27 21 989, EP 114 208, EP 934 988.

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It is an object of the present invention to provide novel unsaturated and amorphous polyester resins from the multiplicity of possibilities and diversity of the prior art which are also readily soluble without cloudiness in many solvents and are transparent as solids. This object is achieved as will be illustrated henceforth.

10 The invention provides unsaturated, amorphous polyesters substantially comprising at least one α,β -unsaturated dicarboxylic acid component and one alcohol component,

wherein

15 the alcohol component comprises a dicidol mixture of the isomeric compounds 3,8-bis(hydroxymethyl)tricyclo [5.2.1.0^{2,6}]decane, 4,8-bis(hydroxymethyl)tricyclo [5.2.1.0^{2,6}]decane and 5,8-bis(hydroxymethyl)tricyclo [5.2.1.0^{2,6}]decane,

20 where each isomer may be present in the mixture in a proportion of from 20 to 40% and the sum of the three isomers is from 90 to 100%,

and at least 5% of the mixture is present in the alcohol component of the polyester.

25

The invention also provides a process for preparing unsaturated, amorphous polyesters substantially comprising at least one α,β -unsaturated dicarboxylic acid component and one alcohol component,

30 wherein

the alcohol component comprises a dicidol mixture of the isomeric compounds 3,8-bis(hydroxymethyl)tricyclo [5.2.1.0^{2,6}]decane, 4,8-bis(hydroxymethyl)tricyclo [5.2.1.0^{2,6}]decane and 5,8-bis(hydroxymethyl)tricyclo

35 [5.2.1.0^{2,6}]decane,

each isomer may be present in the mixture in a proportion of from 20 to 40% and the sum of the three isomers is from 90 to 100%,

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and at least 5% of the mixture is present in the alcohol component of the polyester, by reacting the starting components at a temperature of from 150 to 270°C, preferably in an inert gas atmosphere, where the inert gas has an oxygen content of less than 50 ppm.

The unsaturated, amorphous polyester resins according to the invention are obtained by reacting the alcohol component with the acid component.

According to the invention, the alcohol component used is a didicol mixture of the isomeric compounds 3,8-bis(hydroxymethyl)tricyclo [5.2.1.0^{2,6}]decane, 4,8-bis(hydroxymethyl)tricyclo [5.2.1.0^{2,6}]decane and 5,8-bis(hydroxymethyl)tricyclo [5.2.1.0^{2,6}]decane, where each isomer may be present in the mixture in a proportion of from 20 to 40% and the sum of the three isomers is from 90 to 100%, preferably from 95 to 100%, and at least 5% of the mixture is present in the alcohol component of the polyester. The isomer content of the didicol mixture may be determined qualitatively and quantitatively, for example by GC analysis, or quantitatively by separating by means of preparative GC or HPLC and subsequent NMR spectroscopy. All corresponding isomers of didicol in the 9-position are equally suitable but, owing to the mirror symmetry of the abovementioned isomers, like the cis- and trans-isomers, cannot be differentiated under normal, practical conditions.

The didicol mixture may further comprise up to 10% of further isomers of didicol and/or trimeric and/or higher isomeric diols of the Diels-Alder reaction product of cyclopentadiene. The alcohol component preferably consists of 20%, of 50%, preferably of 90%, more preferably of 100%, of didicol mixture which more preferably comprises from 95 to 100% of the abovementioned three isomeric compounds.

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In addition to the dicidol mixture, the alcohol component may comprise further linear and/or branched, aliphatic and/or cycloaliphatic and/or aromatic diols and/or polyols. The additional alcohols used are preferably ethylene glycol, 1,2- and/or 1,3-propanediol glycol, diethylene glycol, dipropylene glycol, triethylene glycol or tetraethylene glycol, 1,2- and/or 1,4-butanediol, 1,3-butylethylpropanediol, 1,3-methylpropanediol, 1,5-pentanediol, cyclohexanedimethanol, glycerol, hexanediol, neopentyl glycol, trimethylolethane, trimethylolpropane and/or pentaerythritol.

The starting acid component present in the unsaturated, amorphous polyester resins according to the invention comprises at least one α,β -unsaturated dicarboxylic acid. The unsaturated polyester resins preferably comprise citraconic acid, fumaric acid, itaconic acid, maleic acid and/or mesaconic acid.

In addition, aromatic and/or aliphatic and/or cycloaliphatic monocarboxylic acids and/or dicarboxylic acids and/or polycarboxylic acids may also be present, for example phthalic acid, isophthalic acid, terephthalic acid, 1,4-cyclohexanedicarboxylic acid, succinic acid, sebacic acid, methyltetrahydrophthalic acid, methylhexahydrophthalic acid, hexahydrophthalic acid, tetrahydrophthalic acid, dodecanedicarboxylic acid, adipic acid, azelaic acid, isononanoic acid, 2-ethylhexanoic acid, pyromellitic acid and/or trimellitic acid. Preference is given to phthalic acid, hexahydrophthalic acid, tetrahydrophthalic acid, 1,4-cyclohexanedicarboxylic acid, adipic acid and/or azelaic acid.

The acid component may partly or entirely consist of anhydrides and/or alkyl esters, preferably methyl esters.

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In general, the alcohol component is present in a molar ratio of from 0.5:1 to 2.0:1 to the acid component, preferably from 0.8:1 to 1.5:1. The reaction of the alcohol component more preferably takes place in a
5 molar ratio of from 1.0:1 to 1.1:1 to the acid component.

The unsaturated, amorphous polyesters according to the invention may have an acid number of from 1 to 200 mg
10 KOH/g, preferably from 1 to 100 mg KOH/g, more preferably from 1 to 50 mg KOH/g, and an OH number of from 1 to 200 mg KOH/g, preferably from 1 to 100 mg KOH/g, more preferably from 1 to 50 mg KOH/g.

15 The Tg of the unsaturated, amorphous polyesters according to the invention varies from -30 to +80°C, preferably from -20 to +50°C, more preferably from -10 to +40°C.

20 In one preferred embodiment I, the saturated polyesters (UP resins) according to the invention consist of an alcohol component comprising at least 90%, preferably 95%, more preferably 100%, of the dicidol mixture of the isomeric compounds 3,8-bis-(hydroxymethyl)tricyclo
25 [5.2.1.0^{2,6}]decane, 4,8-bis(hydroxymethyl)tricyclo [5.2.1.0^{2,6}]decane and 5,8-bis(hydroxymethyl)tricyclo [5.2.1.0^{2,6}]decane, and of fumaric acid and/or maleic acid/anhydride. In a further preferred embodiment II, the polyesters comprise the abovementioned starting
30 components as under I, but additionally a further acid selected from adipic acid and phthalic acid/anhydride, where the ratio of α,β -unsaturated acid to the additional acid may vary from 2:1 to 1:4. Preference is given to ratios of approx. 1:1 to 1:2. These polyesters
35 generally have acid numbers of from 1 to 200 mg KOH/g, preferably 1-100 mg KOH/g, more preferably 1-50 mg KOH/g, OH numbers of from 1 to 200 mg KOH/g, preferably 1-100 mg KOH/g, more preferably 1-50 mg KOH/g, and a Tg

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of from -30 to +80°C, preferably from -20 to +50°C, more preferably from -10 to +40°C.

- 5 The polyesters according to the invention may also comprise assistants and additives which are selected from inhibitors, water and/or solvents, neutralizing agents, surface-active substances, oxygen scavengers and/or radical scavengers, catalysts, light stabilizers, color brighteners, photosensitizers,
- 10 thixotropic agents, antiskinning agents, defoamers, antistats, thickening agents, thermoplastic additives, dyes, pigments, flame retardants, internal release agents, fillers and/or blowing agents are.
- 15 The polyesters according to the invention are prepared by (semi)continuous or batchwise esterification of the starting acids and alcohols in a one-stage or two-stage procedure.
- 20 The process according to the invention, as described above, is preferably operated in an inert gas atmosphere at from 150 to 270°C, preferably from 160 to 230°C, more preferably from 160 to 200°C. The inert gas used may be nitrogen or a noble gas, in particular
- 25 nitrogen. The inert gas has an oxygen content of less than 50 ppm, in particular less than 20 ppm.

The polyester resins according to the invention are further illustrated by the examples which follow:

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Examples

Starting component: dicitol mixture (claim 1) in an isomeric ratio of approximately 1:1:1

5 **Example 1**

Dodecanedioic acid and fumaric acid (ratio 0.6:0.4) are reacted with dicitol in a ratio of 1:1.05 at 180°C in a nitrogen atmosphere until an acid number of 24 mg KOH/g and an OH number of 34 mg KOH/g are attained. To this
10 end, the fumaric acid is initially esterified with dicitol over the course of one hour and then the adipic acid is added. $M_n = 2200$ g/mol, $M_w = 5500$ g/mol, glass transition temperature 4°C.

15 **Example 2**

Adipic acid and maleic acid (ratio 1:1) are reacted with dicitol in a ratio of 1:1.05 at 180°C in a nitrogen atmosphere until an acid number of 26 mg KOH/g and an OH number of 37 mg KOH/g are attained. To this
20 end, the maleic acid is initially esterified with dicitol over the course of one hour and then the adipic acid is added. $M_n = 1800$ g/mol, $M_w = 4300$ g/mol, glass transition temperature 12°C.

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Claims: Amended

1. An unsaturated, amorphous polyester comprising at least one α,β -unsaturated dicarboxylic acid component and one alcohol component,
5 wherein
the alcohol component comprises a dicidol mixture of the isomeric compounds 3,8-bis(hydroxymethyl)-tricyclo[5.2.1.0^{2,6}]decane, 4,8-bis(hydroxymethyl)-tricyclo[5.2.1.0^{2,6}]decane and 5,8-bis-
10 (hydroxymethyl)tricyclo[5.2.1.0^{2,6}]decane,
where each isomer may be present in the mixture in a proportion of from 20 to 40% and the sum of the three isomers is from 90 to 100%,
15 and at least 5% of the mixture is present in the alcohol component of the polyester.
2. The unsaturated, amorphous polyester as claimed in claim 1,
20 wherein
up to 10% of further isomers of dicidol and/or trimeric and/or higher isomeric diols of the Diels-Alder reaction product of cyclopentadiene are present.
- 25 3. The unsaturated, amorphous polyester as claimed in any of the preceding claims,
wherein
the acid component additionally comprises aromatic
30 and/or aliphatic and/or cycloaliphatic monocarboxylic acids and/or dicarboxylic acids and/or polycarboxylic acids.
- 35 4. The unsaturated, amorphous polyester as claimed in any of the preceding claims,
wherein
the acid component consists partly or entirely of anhydrides and/or alkyl esters.

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5. The unsaturated, amorphous polyester as claimed in any of the preceding claims, wherein

