Title: PROCESS FOR MANUFACTURE OF A CARBOXY TERMINATED DENDRITIC POLYESTER

Abstract: A method for production of a carboxy terminated dendritic polyester is disclosed. Said process comprises ring opening addition of at least one anhydride of a di, tri or polyfunctional aromatic and/or cycloaliphatic carboxylic acid to at least one hydroxy functional dendritic polyester having a hydroxyl value of at least 50 mg KOH/g. Said ring opening addition is performed at a molar ratio said anhydride to hydroxyl groups of between 0.2 to 1 and 1 to 1 and at a reaction temperature of 130-150 °C. Yielded carboxy terminated dendritic polyester has a glass transition temperature of at least 35 °C. The invention relates in further aspects to a powder coating composition comprising the carboxy terminated dendritic polyester obtainable by said process and the use of said carboxy terminated dendritic polyester in a resin composition.
PROCESS FOR MANUFACTURE OF A CARBOXY TERMINATED DENDRITIC POLYESTER

The present invention relates to a process for manufacture of a carboxy terminated dendritic polyester. Said process comprises ring opening addition of at least one anhydride of a di, tri or polyfunctional carboxylic acid to at least one sur katalysator functional dendritic polyester. In further aspects the present invention relates to a powder coating composition comprising a carboxy terminated dendritic polyester obtainable by said process and the use of said carboxy terminated dendritic polyester in a resin composition.

Carboxy functional polyesters are a type of polyesters, which in recent years have expanded rapidly in powder coating applications. They are today typically used as main resins for many powder coatings and are cured with either epoxy resins, low molecular epoxy compounds, such as triglycidyl isocyanurate (TGIC) or alkanol adipates and amides of for instance the PRIMID® (EMS Chemie, Switzerland) type. Carboxy functional polyesters used today offer good chemical resistance, good outdoor durability and good surface finish. They do not contain solvents, thus offering environmentally friendly coatings and are furthermore comparatively inexpensive. Hence, carboxy functional polyesters are attractive in a large number of coating applications.

Carboxy functional polyesters currently used in powder coatings suffer, however, from being highly viscous and having fairly low carboxy functionality. This in turn means high curing temperatures and long curing times to obtain coatings with high surface finish (good flow) and sufficient chemical resistance (chemical conversion). The high curing temperatures limit the type of substrates possible to coat with carboxy functional polyesters and the long curing times limit the productivity rate since line speeds have to be kept low.

It is with state of the art technology difficult to develop products offering both improved flow and higher reactivity. Products having such a behavior must exhibit a lower molecular weight and a lower glass transition temperature (Tg) to yield reduced viscosity, and hence improved flow, and must have a higher carboxy functionality. A lowering of the Tg is normally not possible for products used in powder coatings, which products must be solid at lower temperatures and must be possible to dry mix with curatives, pigments and the like prior to being processed in an extruder and milled to fine particles. Typical carboxy functional polyesters accordingly and normally have a Tg in the range of 45-60°C.
It is due to above of interest to develop carboxy functional products offering good product characteristics, that is a high Tg, yet a low viscosity when molten. The products should furthermore have a high carboxy functionality to allow a high curing speed and hence improved productivity.

It has been found that sur katalysator functional dendritic polyesters built up from an alcohol, epoxide, acid or anhydride core and AB₂ monomers, such as di, tri or polyhydroxy acids, can when being converted to carboxy functionality with aromatic or hydrogenated aromatic (cycloaliphatic) anhydrides yield products which combine desired properties as disclosed above. Sur katalysator functional dendritic polyesters built up from alcohol or epoxide cores are disclosed in Swedish patents nos. 468 771 and 503 342 and hydroxy functional dendritic polyesters built up from acid or anhydride cores are disclosed in for instance the published international patent application WO 93/18079. By incorporation of carboxy functionality based on inherently rigid anhydrides, it is now possible to prepare carboxy functional dendritic polyesters combining a high Tg with excellent flow properties and exceptional carboxy functionality.

The ring opening of anhydrides with terminal alcohols to yield an ester and a terminal carboxylic acid group is a well known technique to provide carboxylic acid functionality to a polyester backbone. Ring opening of aromatic and hydrogenated aromatic (cycloaliphatic) anhydrides are usually performed at relatively high temperatures, such as 150-175°C or even higher as disclosed in for instance "Alkyd Resin Technology" chapter "Temperature of Reaction" T.C. Patton, Interscience Publishers, 1962. It is not, using conventional reaction conditions for ring opening of said anhydrides, possible to yield a carboxy functional dendritic polyester of the type herein disclosed. Since the functionality of a dendritic polyester is exceptionally high, it is of the utmost importance to avoid any chance of cross linking of the formed carboxylic acid functional species. When using reaction conditions typical for ring opening of said anhydrides with conventional polyesters, it is not possible to yield a carboxy functional dendritic polyester, due to the fact that the resin will gel in a very short period of time.

A process for production of a carboxy functional dendritic polyester has quite surprisingly been obtained, which due to precise temperature control allows incorporation of carboxy functionality based on inherently rigid anhydrides. By using a reaction temperature close to the melting point of the aromatic anhydride and being in the interval of 130-145°C, it has surprisingly been possible in high yields to produce sur katalysator terminated dendritic polyesters. A carboxy terminated dendritic polyester obtained according to the invention have
a Tg significantly above the hydroxy functional dendritic polyester, onto which the aromatic acid is grafted.

The present invention accordingly refers to a process for production of a carboxy terminated dendritic polyester. Said process comprises ring opening addition of at least one anhydride of a di, tri or polyfunctional aromatic and/or cycloaliphatic carboxylic acid to at least one hydroxy functional dendritic polyester having a hydroxyl value of at least 50 mg KOH/g. The ring opening addition is performed at a molar ratio anhydride to hydroxyl groups of between 0.2, such as 0.3 or 0.5, to 1 and 1 to 1 and at a reaction temperature of 130-150°C. The thus yielded carboxy terminated dendritic polyester may accordingly have one or more residual hydroxyl groups. Yielded carboxy terminated dendritic polyester has, furthermore, a softening point of at least 20°C, such as 20-60°C and/or a glass transition temperature of at least 35°C, such as 40-80°C or preferably 45-65°C, and a preferred acid value of at least 50, such as 80-250, mg KOH/g.

Said at least one anhydride is in preferred embodiments an anhydride selected from the group consisting of o-phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, trimellitic anhydride and/or hexachloroendomethylene tetrahydrophthalic anhydride.

The process of the present invention may comprise an additional ring opening addition, whereby an obtained carboxy terminated polyester, having at least one residual hydroxyl group, in addition to said at least one aromatic or cycloaliphatic anhydride, is terminated by reaction with at least one anhydride of an aliphatic saturated or unsaturated di, tri or polyfunctional carboxylic acid. Said at least one anhydride of said aliphatic saturated or unsaturated di, tri or polyfunctional carboxylic acid is in the most preferred embodiments for instance maleic anhydride and/or succinic anhydride and said additional ring opening addition is most suitably performed at a temperature of 90-110°C.

The hydroxy functional dendritic polyester subjected to said ring opening addition of at least one anhydride of a di, tri or polyfunctional aromatic and/or cycloaliphatic carboxylic acid, has a preferred glass transition temperature of at least 20°C, preferably at least 30°C, and is built up from ester or polyester units optionally in combination with ether or polyether units. Especially preferred embodiments of said at least one hydroxy functional dendritic polyester include dendritic polymers built up from a monomeric or polymeric core, having at least one reactive hydroxyl or epoxide group, to which core are added 1-20, preferably 2-8, branching generations built up from at least one monomeric or polymeric branching chain extender having at least three reactive groups of which at least two are hydroxyl groups and at least one
is a carboxyl or anhydride group, and optionally at least one spacing generation being built up from at least one spacing chain extender, which spacing chain extender has two reactive groups of which one is a hydroxyl group and one is a carboxyl or anhydride group or which spacing chain extender is an inner ether, such as a lactone, thereof.

The hydroxy functional dendritic polyester may furthermore be partially chain stopped and/or functionalised by means of reaction between said polyester and a compound preferably selected from the group consisting of aliphatic or cycloaliphatic saturated or unsaturated monofunctional carboxylic acids or anhydrides thereof, aromatic monofunctional carboxylic acids or anhydrides thereof, diisocyanates, oligomers and adducts of diisocyanates, glycidyl esters of monofunctional carboxylic acids or anhydrides, glycidyl ethers of monofunctional alcohols, adducts of aliphatic or cycloaliphatic saturated or unsaturated mono, di, tri or polyfunctional carboxylic acids or adducts of corresponding anhydrides, adducts of aromatic mono, di, tri or polyfunctional carboxylic acids or adducts of corresponding anhydrides, epoxides of unsaturated monocarboxylic acids or corresponding triglycerides, carboxy functional adducts of aliphatic or cycloaliphatic saturated or unsaturated mono, di, tri or polyfunctional alcohols and carboxy functional adducts of aromatic mono, di, tri or polyfunctional alcohols. Suitable compounds used for said chain stopping or said functionalisation are advantageously exemplified by compounds such as formic acid, acetic acid, propionic acid, butanoic acid, hexanoic acid, acrylic acid, methacrylic acid, crotonic acid, lauric acid, linseed fatty acid, soybean fatty acid, tall oil fatty acid, dehydrated castor fatty acid, capric acid, caprylic acid, benzoic acid, behenic acid, montanoic acid, \( p\)-tert.butylbenzoic acid, abietic acid, sorbic acid, 1-chloro-2,3-epoxypropane, 1,4-dichloro-2,3-epoxybutane, epoxidised soybean fatty acid, phenyl isocyanate, toluene-2,4-diisocyanate, toluene-2,6-diisocyanate, hexamethylene diisocyanate, isophorone diisocyanate, ethylene oxide, propylene oxide and butylene oxide. Further suitable compounds used for said chain stopping or functionalisation are found among for instance compounds such as maleates or succinates of glycerol monoallylether, trimethylolmethane monoallylether, trimethylolpropane monoallyl ether, glycerol diallyl ether, trimethylolmethane diallyl ether, trimethylolpropane diallyl ether, pentaerythritol diallylether or pentaerythritol triallyl ether.

Said hydroxy functional dendritic polyester may, furthermore be partially functionalised by means of reaction between said polyester and at least one epihaloxydrine or allylhalide, such as epichlorohydrine and allylchloride and/or allylbromide.

Embodiments of said monomeric or polymeric core, having said at least one hydroxyl or epoxide group, include mono, di, tri or polyfunctional alcohols or ether alcohols, such as adducts between at least one mono, di, tri or polyfunctional alcohol and at least one alkylene oxide, such as ethylene, propylene and/or butylene oxide, and mono, di, tri or polyfunctional...
epoxides, such as glycidyl esters of monofunctional carboxylic acids, glycidyl ethera of mono, di, tri or polyfunctional alcohols, mono, di or triglycidyl substituted isocyanurates and glycidyl ethers of condensation products between at least one phenol and at least one aldehyde or ketone. Said core is in said preferred embodiments of said hydroxy functional dendritic polyester suitably and preferably selected among 5-ethyl-5-hydroxymethyl-1,3-dioxane, 5,5-dihydroxymethyl-1,3-dioxane, ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, pentanediol, neopentyl glycol, 1,3-propanediol, 2-methyl-2-propyl-1,3-propanediol, 2-ethyl-2-butyl-1,3-propanediol, cyclohexanediethanol, trimethylolpropane, trimethylolethane, glycerol, erythritol, anhydroennea-heptitol, ditrimethylolpropane, ditrimethylolethane, pentaerythritol, methylglucoside, dipentaerythritol, tripentaerythritol, glucose, sorbitol, ethoxylated trimethylolethane, propoxylated trimethylolethane, ethoxylated trimethylolpropane, propoxylated trimethylolpropane, ethoxylated pentaerythritol, propoxylated pentaerythritol, 1-glycidyloxy-2-ethylhexane, bisphenol A or F diglycidylether and diglycidylterephthalate.

Embodiments of said at least one monomeric or polymeric branching chain extender is preferably selected from the group consisting of 2,2-dimethylpropanoic acid, α,α-bis-(hydroxymethyl)butyric acid, α,α,α-tris(hydroxymethyl)acetic acid, α,α-bis(hydroxy-methyl)valeric acid, α,α-bis(hydroxy)propionic acid, 3,5-dihydroxybenzoic acid, α,β-dihydroxypropionic acid, heptonic acid, citric acid, d- or l-tartaric acid, dihydroxymalonic acid and d-gluconic acid.

Said at least one optional spacing chain extender is preferably an aliphatic, cycloaliphatic or aromatic monohydroxyfunctional monocarboxylic acid or anhydride or is an inner ether, such as a lactone, of such an acid. Preferred species of said optional spacing chain extender include hydroxyacetic acid, hydroxyvaleric acid, hydroxypropionic acid, hydroxypivalic acid, glycolide, δ-valerolactone, β-propiolactone and ε-caprolactone.

In a further aspect, the present invention refers to a powder coating composition comprising an intimate blend of

(i) at least one binder composition comprising (a) at least one carboxy terminated dendritic polyester obtainable by the process disclosed above and (b) at least one aliphatic, cycloaliphatic or aromatic polymer, such as a polymer selected from the group consisting of an epoxy, a polyester, an acrylic and/or a blocked urethane polymer, and
(ii) at least one co-reactant preferably selected from the group consisting of for instance monomeric or polymeric bisphenol A or F type glycidyl ethers, glycidyl ethers of the Novolac (thermoplastic resins obtained from acidic condensation of phenols and formaldehyde) type,
triglycidyl isocyanurates, other monomeric or polymeric glycidyl ethers and esters and alkanol amides of the PRIMID® (EMS Chemie, Switzerland) type, and optionally (iii) at least one flow and/or leveling agent and/or at least one degasser.

Said binder composition is in preferred embodiments present in an amount of 40-95% by weight, whereby said component (i) preferably is present in said binder composition in an amount of 5-100% by weight and said component (ii) preferably in an amount of 1-90% by weight. The optional flow and/or levelling agent and/or the optional degasser are/is suitably each and independently present in an amount of 0-2% by weight.

The powder coating composition may, furthermore additionally comprise at least one catalyst, filler, colouring agent, corrosion inhibitor, biocide, plasticiser, UV stabiliser and/or UV absorber.

In yet a further aspect, the present invention relates to the use of a carboxy terminated dendritic polyester obtainable by disclosed process in resin compositions, such as binder compositions for coatings, including powder coatings, such as low gloss powder coatings, whereby said carboxy terminated dendritic polyester provides and/or aids in matting and/or works as a matting agent.

Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following preferred specific embodiments are, therefore, to be construed as merely illustrative and not limitative of the remainder of the disclosure in any way whatsoever. In the following, Examples 1-8 refer to preparation of carboxy terminated dendritic polyesters. Said polyesters are prepared according to embodiments of the process of the present invention.

**Example 1**

A hydroxy functional dendritic polyester (Boltorn® H20, Perstorp Chemicals AB, Sweden), nominally having 16 hydroxyl groups, a nominal molecular weight of 1750 and a tetrafunctional core, was partially end capped with propionic acid at a molar ratio said hydroxyl groups to acid groups of 1:0.25 and at a temperature of 130°C. Obtained intermediate product was subsequently subjected to ring opening addition of phthalic anhydride at a molar ratio said hydroxyl groups to anhydride groups of 1:0.75. Phthalic anhydride was charged at 130°C. A weak exotherm was observed and the reaction temperature was kept at 135-140°C
until the ring opening addition was completed. Obtained product was now cooled to room temperature.

Obtained properties are given in Table 1 below.

Example 2

The same hydroxy functional dendritic polyester as in Example 1 (Boltron® H20, Perstorp Chemicals AB, Sweden) was subjected to ring opening addition of phthalic anhydride at a molar ratio hydroxyl groups to anhydride groups of 1:0.6. The polyester was heated to 130°C and phthalic anhydride was charged at said temperature. A weak exotherm was observed and the reaction temperature was kept at 135-140°C until the ring opening addition was completed. Obtained product was now cooled to room temperature.

Obtained properties are given in Table 1 below.

Example 3

A hydroxy functional dendritic polyester (Boltron® H30, Perstorp Chemicals AB, Sweden), nominally having 32 hydroxyl groups, a nominal molecular weight of 3607 and a tetrafunctional core, was partially end capped with propionic acid at a molar ratio said hydroxyl groups to acid groups of 1:0.25 and at a temperature of 130°C. Obtained intermediate product was subsequently subjected to ring opening addition of phthalic anhydride at a molar ratio said hydroxyl groups to anhydride groups of 1:0.6. Phthalic anhydride was charged at 130°C. A weak exotherm was observed and the reaction temperature was kept at 135-140°C until the ring opening addition was completed. Obtained product was now cooled to room temperature.

Obtained properties are given in Table 1 below.

Example 4

The same hydroxy functional dendritic polyester as in Example 3 (Boltron® H30, Perstorp Chemicals AB, Sweden) was subjected to ring opening addition of phthalic anhydride at a molar ratio hydroxyl groups to anhydride groups of 1:1. The polyester was heated to 130°C and phthalic anhydride was charged at said temperature. A weak exotherm was observed and
the reaction temperature was kept at 135-140°C until the ring opening addition was completed. Obtained product was now cooled to room temperature.

Obtained properties are given i Table 1 below.

**Example 5**

A hydroxy functional dendritic polyester (Bolton® range, Perstorp Chemicals AB, Sweden), nominally having 32 hydroxyl groups, a nominal molecular weight of 4048 and a flexible tetrafunctional core, was partially end capped with propionic acid at a molar ratio said hydroxyl groups to acid groups of 1:0.25 and at a temperature of 130°C. Obtained intermediate product was subsequently subjected to ring opening addition of phthalic anhydride at a molar ratio said hydroxyl groups to anhydride groups of 1:0.75. Phthalic anhydride was charged at 130°C. A weak exotherm was observed and the reaction temperature was kept at 135-140°C until the ring opening addition was completed. Obtained product was now cooled to room temperature.

Obtained properties are given i Table 1 below.

**Example 6**

The same hydroxy functional dendritic polyester as in Example 5 (Bolton® range, Perstorp Chemicals AB, Sweden) was subjected to ring opening addition of phthalic anhydride at a molar ratio hydroxyl groups to anhydride groups of 1:0.6. The polyester was heated to 130°C and phthalic anhydride was charged at said temperature. A weak exotherm was observed and the reaction temperature was kept at 135-140°C until the ring opening addition was completed. Obtained product was now cooled to room temperature.

Obtained properties are given i Table 1 below.

**Example 7**

A hydroxy functional dendritic polyester (Bolton® range, Perstorp Chemicals AB, Sweden) nominally having 16 hydroxyl groups, a nominal molecular weight of 2190 and a flexible tetrafunctional core, was partially end capped with propionic acid at a molar ratio said hydroxyl groups to acid groups of 1:0.25 and at a temperature of 130°C. Obtained intermediate product was subsequently subjected to ring opening addition of phthalic anhydride at a molar
ratio said hydroxyl groups to anhydride groups of 1:0.6. Phthalic anhydride was charged at 130°C. A weak exotherm was observed and the reaction temperature was kept at 135-140°C until the ring opening addition was completed. Obtained product was now cooled to room temperature.

Obtained properties are given in Table 1 below.

Example 8

The same hydroxy functional dendritic polyester as in Example 7 (Boltron® range, Perstorp Chemicals AB, Sweden) was subjected to ring opening addition of phthalic anhydride at a molar ratio hydroxyl groups to anhydride groups of 1:1. The polyester was heated to 130°C and phthalic anhydride was charged at said temperature. A weak exotherm was observed and the reaction temperature was kept at 135-140°C until the ring opening addition was completed. Obtained product was now cooled to room temperature.

Obtained properties are given in Table 1 below.

Table 1

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CLAIMS

1. A method for production of a carboxy terminated dendritic polyester characterised in, that said process comprises ring opening addition of at least one anhydride of a di, tri or polyfunctional aromatic and/or cycloaliphatic carboxylic acid to at least one hydroxy functional dendritic polyester having a hydroxyl value of at least 50 mg KOH/g, said ring opening addition being performed at a molar ratio anhydride to hydroxyl groups of between 0.2 to 1 and 1 to 1 and at a reaction temperature of 130-150°C, and that yielded carboxy terminated dendritic polyester has a softening point of at least 20°C and/or a glass transition temperature of at least 35°C.

2. A method according to Claim 1 characterised in, that yielded carboxy terminated dendritic polyester has a softening point of 20-60°C and/or a glass transition temperature of 40-80°C, preferably 45-65°C.

3. A method according to Claim 1 or 2 characterised in, that yielded carboxy terminated dendritic polyester has an acid value of at least 50 mg KOH/g.

4. A method according to any of the Claims 1-3 characterised in, that yielded carboxy terminated dendritic polyester has an acid value of 80-250 mg KOH/g.

5. A method according to any of the Claims 1-4 characterised in, that said at least one anhydride is selected from the group consisting of o-phthalic anhydride, tetrahydropthalic anhydride, hexahydropthalic anhydride, trimelletic anhydride and/or hexachloroendomethylene tetrahydropthalic anhydride.

6. A method according to any of the Claims 1-5 characterised in, that said carboxy terminated polyester in addition to said at least one aromatic or cycloaliphatic anhydride is additionally terminated by an additional ring opening addition of at least one anhydride of a di, tri or polyfunctional aliphatic saturated or unsaturated carboxylic acid.

7. A method according to Claim 6 characterised in, that said at least one anhydride of a di, tri or polyfunctional aliphatic saturated or unsaturated carboxylic acid is maleic anhydride and/or succinic anhydride.
8. A method according to Claim 6 or 7 characterised in, that said additional ring opening addition is performed at a temperature of 90-110°C.

9. A method according to any of the Claims 1-8 characterised in, that said at least one hydroxy functional dendritic polyester has a glass transition temperature of at least 20°C, preferably at least 30°C.

10. A method according to any of the Claims 1-9 characterised in, that said at least one hydroxy functional dendritic polyester is built up from ester or polyester units optionally in combination with ether or polyether units.

11. A method according to any of the Claims 1-10 characterised in, that said at least one hydroxy functional dendritic polyester is built up from a monomeric or polymeric core, having at least one reactive hydroxyl or epoxide group, to which core are added 1-20, preferably 2-8, branching generations being built up from at least one monomeric or polymeric branching chain extender having at least three reactive groups of which at least two are hydroxyl groups and at least one is a carboxyl or anhydride group, and optionally at least one spacing generation being built up from at least one spacing chain extender, which spacing chain extender has two reactive groups of which one is a hydroxyl group and one is a carboxyl or anhydride group or which spacing chain extender is an inner ether, such as a lactone, of a said spacing chain extender.

12. A method according to any of the Claims 1-11 characterised in, that said monomeric or polymeric core is a mono, di, tri or polyfunctional alcohol or ether alcohol.

13. A method according to Claim 12 characterised in, that said di, tri or polyfunctional alcohol or ether alcohol is selected from the group consisting of 5-ethyl-5-hydroxymethyl-1,3-dioxane, 5,5-dihydroxymethyl-1,3-dioxane, ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, pentanediol, neopentyl glycol, 1,3-propanediol, 2-methyl-2-propyl-1,3-propanediol, 2-ethyl-2-butyl-1,3-propanediol, cyclohexanediol, trimethylolpropane, trimethylene, glycerol, erythritol, anhydroxymea-heptitol, ditrimethylolpropane, ditrimethylenelethane, pentaerythritol, methylglucoside, dipentaerythritol, tripentaerythritol, glucose, sorbitol, ethoxylated trimethylolpropane, propoxylated trimethylolpropane, ethoxylated trimethylolpropane,
propoxylated trimethylolpropane, ethoxylated pentaerythritol and propoxylated pentaerythritol.

14. A method according to any of the Claims 1-11 characterized in, that said monomeric or polymeric core is a mono, di, tri or polyfunctional epoxide.

15. A method according to Claim 14 characterized in, that said epoxide is selected from the group consisting of a glycidyl ester of a monofunctional carboxylic acid, a glycidyl ether of a mono, di, tri or polyfunctional alcohol, a mono, di or triglycidyl substituted isocyanurate and a glycidyl ether of a condensation product between at least one phenol and at least one aldehyde or ketone.

16. A method according to Claim 14 or 15 characterized in, that said epoxide is 1-glycidoxy-2-ethylhexane, bisphenol A or F diglycidylether or diglycidylterephthalate.

17. A method according to any of the Claims 1-16 characterized in, that said at least one monomeric or polymeric branching chain extender is selected from the group consisting of 2,2-dimethylolpropionic acid, \(\alpha,\alpha\)-bis(hydroxymethyl)butyric acid, \(\alpha,\alpha,\alpha\)-tris(hydroxymethyl)acetic acid, \(\alpha,\alpha\)-bis-(hydroxymethyl)valeric acid, \(\alpha,\alpha\)-bis(hydroxy)propionic acid, 3,5-dihydroxybenzoic acid, \(\alpha,\beta\)-dihydroxypropionic acid, heptonic acid, citric acid, \(d\)- or \(l\)-tartaric acid, dihydroxymaloic acid and \(d\)-gluconic acid.

18. A method according to any of the Claims 1-17 characterized in, that said at least one optional spacing chain extender is an aliphatic, cycloaliphatic or aromatic monohydroxyfunctional monocarboxylic acid or anhydride or is an inner ether, such as a lactone, of a said karboxylic acid.

19. A method according to Claim 18 characterized in, that said spacing chain extender is hydroxyacetic acid, hydroxyvaleric acid, hydroxypropionic acid, hydroxypivalic acid, glycolide, \(\delta\)-valerolactone, \(\beta\)-propiolactone and/or \(\epsilon\)-caprolactone.

20. A method according to any of the Claims 1-19 characterized in, that said at least one hydroxy functional dendritic polyester is partially chain stopped or functionalised by means of reaction between said polyester and a compound selected from the group consisting of
i) an aliphatic or cycloaliphatic saturated or unsaturated monofunctional carboxylic acid or anhydride thereof,
ii) an aromatic monofunctional carboxylic acid or anhydride thereof,
iii) a diisocyanate, an oligomer or an adduct thereof,
iv) a glycidyl ester of a monofunctional carboxylic acid or anhydride,
v) a glycidyl ether of a monofunctional alcohol,
vi) an adduct of an aliphatic or cycloaliphatic saturated or unsaturated mono, di, tri or polyfunctional carboxylic acid or anhydride,
vii) an adduct of an aromatic mono, di, tri or polyfunctional carboxylic acid or anhydride,
viii) an epoxide of an unsaturated monocarboxylic acid or corresponding triglyceride, which acid,
ix) a carboxy functional adduct of an aliphatic or cycloaliphatic saturated or unsaturated mono, di, tri or polyfunctional alcohol, and
x) a carboxy functional adduct of an aromatic mono, di, tri or polyfunctional alcohol.

21. A method according to any of the Claims 1-20 characterised in that said at least one hydroxy functional dendritic polyester is partially chain stopped or functionalised by means of reaction between said polyester and a compound selected from the group consisting of formic acid, acetic acid, propionic acid, butanoic acid, hexanoic acid, acrylic acid, methacrylic acid, crotonic acid, lauric acid, linseed fatty acid, soybean fatty acid, tall oil fatty acid, dehydrated castor fatty acid, crotonic acid, capric acid, caprylic acid, benzoic acid, behenic acid, montanoic acid, p-tert.butylbenzoic acid, abietic acid, sorbic acid, 1-chloro-2,3-epoxypropane, 1,4-dichloro-2,3-epoxybutane, epoxidised soybean fatty acid, phenyl isocyanat toluene-2,4-diisocyanate, toluene-2,6-diisocyanate, hexamethylene diisocyanate or isophorone diisocyanate.

22. A method according to any of the Claims 1-20 characterised in that said at least one hydroxy functional dendritic polyes is partially chain stopped or functionalised by means of reaction between said polyes and at least one maleate or succinate of glycerol monoallylether, trimethylolmethylenononallylether, trimethylolpropane monoallyl ether, glycerol diallyl etl trimethylolethehane diallyl ether, trimethylolpropane diallyl ether, pentaerythry diallylether or pentaerythritol triallyl ether.
23. A method according to any of the Claims 1-19
   characterised in, that said at least one hydroxy functional dendritic polyester
   is partially functionalised by means of reaction between said polyester and at least one
   epihalohydre or allylhalid.

24. A method according to Claims 23
   characterised in, that said at least one epihalohydre is epichlorohydre.

25. A method according to Claims 23
   characterised in, that said at least one allylhalide is allylchloride and/or
   allylbromide.

26. A powder coating composition
   characterised in, that it comprises
   i) a binder composition comprising
      a) a carboxy terminated dendritic polyester obtainable by the process of
         any of the Claims 1-25, and
      b) an aliphatic, cycloaliphatic or aromatic polymer, and
   ii) a co-reactant, and
   iii) optionally at least one flow and/or leveling agent and/or at least one degasser.

27. A powder coating composition according to Claim 26
   characterised in, that said aliphatic, cycloaliphatic or aromatic polymer is
   selected from the group consisting of an epoxy, a polyester, an acrylic and/or a blocked
   urethane polymer.

28. A powder coating composition according to Claim 26 or 27
   characterised in, that said co-reactant is a monomeric or polymeric glycidyl
   ether or ester.

29. A powder coating composition according to Claim 26 or 27
   characterised in, that said co-reactant is selected from the group consisting of
   a monomeric or polymeric bisphenol A or F glycidyl ether, a glycidyl ether of a Novolac,
   a triglycidyl isocyanurate and an alkanol adipate and/or amide.

30. A powder coating composition according to any of the Claims 26-29
   characterised in, that said binder composition is present in an amount of
   40-95% by weight.
31. A powder coating composition according to any of the Claims 26-30
characterised in, that component (a) is present in said binder composition in
an amount of 5-100% by weight.

32. A powder coating composition according to any of the Claims 26-31
characterised in, that component (b) is present in said binder composition in
an amount of 1-90% by weight.

33. A powder coating composition according to any of the Claims 26-32
characterised in, that said optional flow and/or levelling agent is present in an
amount of 0-2% by weight.

34. A powder coating composition according to any of the Claims 26-33
characterised in, that said optional degasser is present in an amount of 0-2%
by weight.

35. A powder coating composition according to any of the Claims 26-34
characterised in, that it additionally comprises at least one catalyst, filler,
colouring agent, corrosion inhibitor, biocide, plasticiser, light stabiliser and/or UV
absorber.

36. Use of a carboxy terminated dendritic polyester obtainable by the process of any of the
Claims 1-25 in a resin composition.

37. Use according to Claim 36, said resin composition being included in a coating
composition.

38. Use according to Claim 37, said coating composition being a powder coating
composition.

39. Use according to Claim 38, said powder coating being a low gloss powder coating.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C08G 83/00, C08G 63/20, C09D 201/00, C09D 167/00, C09D 5/03
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C08G, C08L, C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE, DK, FI, NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<th>Relevant to claim No.</th>
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<td>WO 9612754 A (PERSTROP AB), 2 May 1996 (02.05.96)</td>
<td>1-39</td>
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<td>P,X</td>
<td>WO 0146296 A1 (BASF CORP), 28 June 2001 (28.06.01), page 10, line 21, exemple 1</td>
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<td>A</td>
<td>EP 1070748 A1 (E.I. DU PONT DE NEMOURS AND COMPANY), 24 January 2001 (24.01.01)</td>
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Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:
  "A" document defining the general state of the art which is not considered to be of particular relevance
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  "O" document referring to an oral disclosure, use, exhibition or other means
  "P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search: 24 June 2002

Date of mailing of the international search report: 25-06-2002

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