

## A process for the preparation of a condensation polymer

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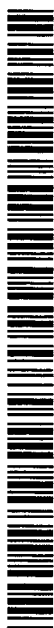


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- (71) Applicant (for all designated States except US): DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): GRISNICH, Willem [NL/NL]; Herxen 49, NL-8131 PD Wijhe (NL). MUSCAT, Dirk [DE/DE]; Fassanenstrasse 18, D-52538 Gangelt-Birgden (DE). HENDRIKS, Patrick, Herman, Marie [NL/NL]; Dr. Schaepmanlaan 73, NL-6191 BP Beek (NL). MAK, Hendrika, Annette, Petronella [NL/NL]; Ambyerstraat Noord 147, NL-6225 ED Maastricht (NL). VAN BENTHEM, Rudolfus, Antonius,
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(54) Title: A PROCESS FOR THE PREPARATION OF A CONDENSATION POLYMER

(57) Abstract: The invention relates to a process to prepare a condensation polymer containing ester groups and at least one amide group in the backbone, having at least one  $\beta$ -alkyl-substituted  $\beta$ -hydroxyalkylamide end group and having a hydroxy alkylamide functionality between 2 and 250. A polyvalent carboxylic acid reacts with an alkanolamine to form a hydroxy-alkylamide from which a polyesteramide is obtained through polycondensation. The obtained polymer may, for example, be used in a thermosetting powder paint composition or in a toner composition.

A PROCESS FOR THE PREPARATION OF A CONDENSATION POLYMER

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The invention relates to a process for the preparation of a condensation polymer containing ester groups and at least one amide group in the backbone, having at least one  $\beta$ -substituted  $\beta$ -hydroxyalkylamide end group and having a hydroxy alkylamide functionality between 2 and 250.

This polymer is disclosed in WO-A-99/16810. WO-A-99/16810 also describes a process for producing this polymer from an alkanolamines and a cycloanhydride or an activated acid, and the use in the technical field of powder paints. It is a disadvantage of this process that curing of the obtained condensation polymers with an acid functional polyester at a temperature of about 200°C may result in the emission of a small amount (generally less than 1,0 % by weight relative to the binder) of volatile organic compounds, for example, cyclic carboxylic anhydrides and/or their derivatives.

It is the object of the present invention to provide a process which does not result in the emission of volatile organic compounds derived from cyclic carboxylic anhydride. The process also must result in the required powder paint properties and powder coating properties.

The process according to the invention is characterized in that a polyvalent carboxylic acid reacts with a alkanolamine to form a hydroxyalkylamide from which a polyesteramide is obtained through polycondensation.

The process according to the invention results in a product which has a broader molecular weight distribution and a broader range of melting points and/or glass transition temperatures and the process does not result in the emission of volatile organic compounds derived from cyclic anhydrides. The obtained polymer results in the required powder paint properties and in the required powder coating properties.

10 Preferably the carboxylic acid is not capable of forming a cyclic anhydride.

Preferably the polyvalent carboxylic acid is a dicarboxylic acid.

Suitable dicarboxylic acids include for example isophthalic acid, terephthalic acid, cis- and trans hexahydroterephthalic acid, 2,6-naphthalene dicarboxylic acid, 4,4-oxybisbenzoic acid, 3,6-dichlorophthalic acid, tetrachlorophthalic acid, tetrabromophthalic acid, tetrahydrophthalic acid, hexachloroendomethylene tetrahydrophthalic acid, phthalic acid, azelaic acid, sebacic acid, decanedicarboxylic acid, adipic acid, diglycolic acid, succinic acid, fumaric acid, glutaric acid, malonic acid, dodecanyl succinic acid, 1,9 nonaic dicarboxylic acid and maleic acid or their mixtures.

More preferably a mixture containing terephthalic acid, isophthalic acid and/or adipic acid is applied. In this mixture the amount of adipic acid generally ranges between 10 and 90% by weight (relative to the total amount of acids in the polymer composition). Preferably this amount ranges between 15 and 50% by weight.

It is also possible to apply minor amounts, for example, less than 20% by weight, relative to the total amount of acids, of tri- or higher functional carboxylic acids in combination with a dialkanolamine. It is also possible to apply, for example, more than

20% by weight of the total amount tri- and higher acids in combination with at least 20% by weight (relative to the total amount of alkanolamines) monoalkanolamine. Suitable tricarboxylic acids include for example  
 5 trimellitic acid, citric acid and 1,3,5-benzene tricarboxylic acid.

Preferably the alkanolamine is a  $\beta$ -substituted alkanolamine.

10 Preferably the  $\beta$ -substituted alkanolamine is a  $\beta$ -alkyl-substituted alkanolamine.

Suitable  $\beta$ -alkyl-substituted  $\beta$ -alkanolamines are for example diisopropanolamine, cyclohexyl isopropanolamine, N-(m)ethyl isopropanolamine, diisobutanolamine, di- $\beta$ -  
 15 cyclohexanolamine and/or n-butyl isopropanolamine.

Preferably a dialkanolamine is applied.

Most preferable diisopropanolamine and/or diisobutanolamine are applied.

20 The equivalent ratio dicarboxylic acid: alkanolamine generally ranges between 1 : 1,3 and 1 : 2.

Preferably, this ratio ranges between 1 : 1,3 and 1 : 1,6.

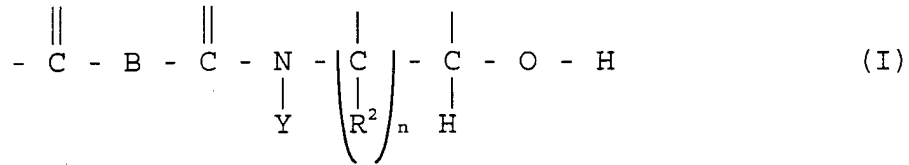
25 Generally, the process according to the invention is applied at a temperature between 120°C and 200°C and preferably the temperature is between 140°C and 180°C.

Generally, the pressure is between 0 and 5.10<sup>5</sup> Pa, and preferably between 0 and 10<sup>5</sup> Pa.

30 The process may be applied in water and/or an organic solvent.

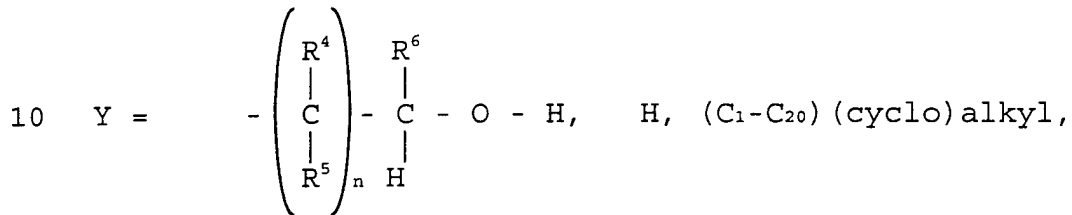
Preferably, the polymer obtained contains at least two groups according to formula (I)





5

in which



15 or (C<sub>6</sub>-C<sub>10</sub>) aryl,

B = (C<sub>2</sub>-C<sub>24</sub>), optionally substituted, aryl or (cyclo)alkyl aliphatic diradical,

R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> may, independently of one another, be the same or different, H, (C<sub>6</sub>-C<sub>10</sub>) aryl or (C<sub>1</sub>-C<sub>8</sub>) (cyclo)alkyl radical and

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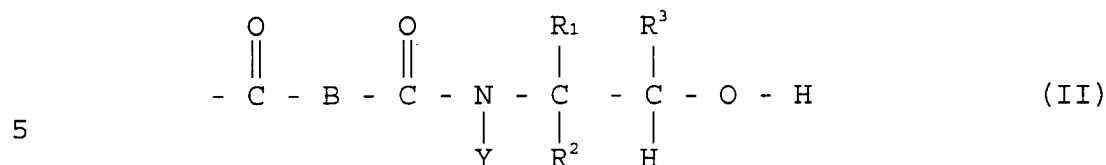
n = 1-4.

Preferably n = 1.

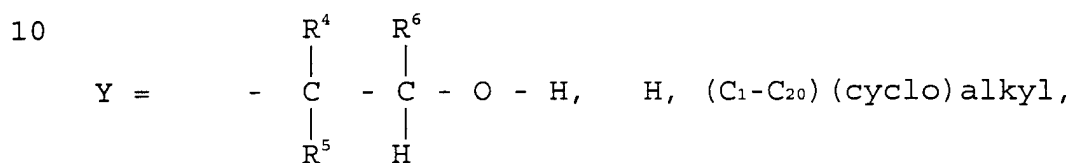
According to a preferred embodiment of the invention B = (C<sub>4</sub>-C<sub>24</sub>) aryl or (cyclo)alkyl aliphatic diradical.

25

More preferably the polymer contains at least two groups according to formula (II):



in which



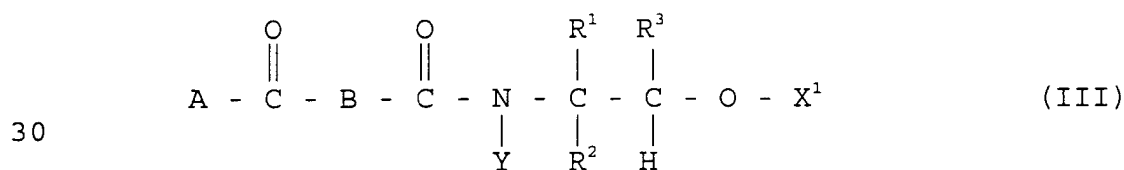
or (C<sub>6</sub>-C<sub>10</sub>) aryl,

B = (C<sub>4</sub>-C<sub>24</sub>), optionally substituted, aryl or (cyclo)alkyl aliphatic diradical, and

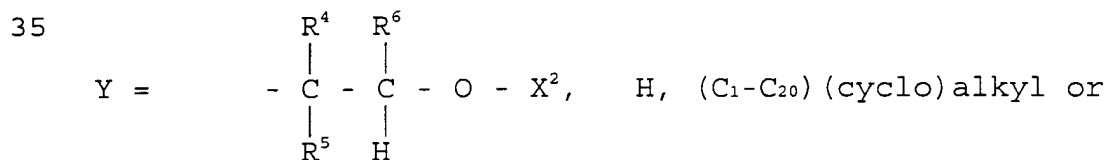
20 R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> may, independently of one another, be the same or different, H, (C<sub>6</sub>-C<sub>10</sub>) aryl or (C<sub>1</sub>-C<sub>3</sub>) (cyclo)alkyl radical.

According to a further preferred embodiment, the polymer containing hydroxyalkylamide groups is a polymer according to formula (III):

25

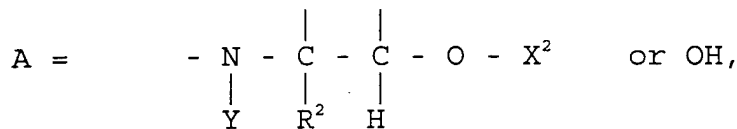


in which:



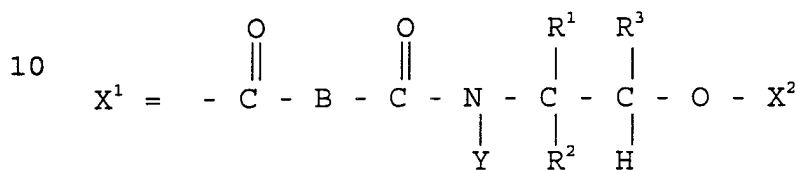
(C<sub>6</sub>-C<sub>10</sub>) aryl

R<sup>1</sup> R<sup>3</sup>



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B = (C<sub>2</sub>-C<sub>24</sub>), optionally substituted, aryl or (cyclo)alkyl aliphatic diradical,

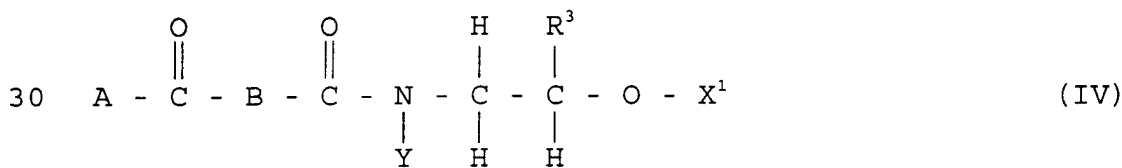


15 X<sup>2</sup> = H or X<sup>1</sup> and

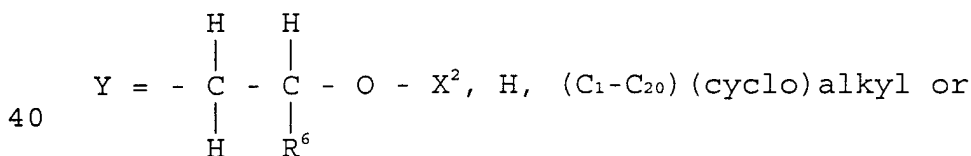
R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> may, independently of one another, be the same or different, H, (C<sub>6</sub>-C<sub>10</sub>) aryl or (C<sub>1</sub>-C<sub>8</sub>) (cyclo)alkyl radical or CH<sub>2</sub>-OX<sup>2</sup>.

20 In formulas (I), (II) and (III) R groups may together or with neighbouring carbon atoms form part of a cycloalkyl group.

According to another preferred embodiment of the invention, the polymer containing β-  
25 hydroxyalkylamide groups is a polymer according to formula (IV):

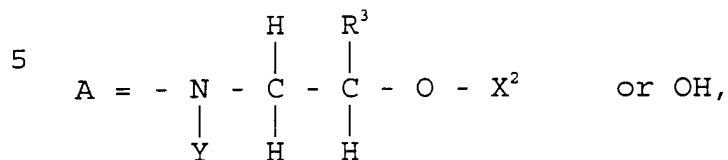


35 in which:

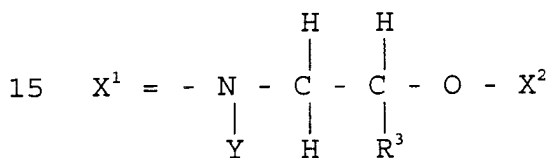




(C<sub>6</sub>-C<sub>10</sub>) aryl,



10 B = (C<sub>4</sub>-C<sub>20</sub>), optionally substituted, aryl or (cyclo)alkyl aliphatic diradical,



20 X<sup>2</sup> = H or X<sup>1</sup>,

R<sup>3</sup> = (C<sub>6</sub>-C<sub>10</sub>) aryl or (C<sub>1</sub>-C<sub>8</sub>)alkyl radical and

R<sup>6</sup> = (C<sub>6</sub>-C<sub>10</sub>) aryl or (C<sub>1</sub>-C<sub>8</sub>)alkyl radical.

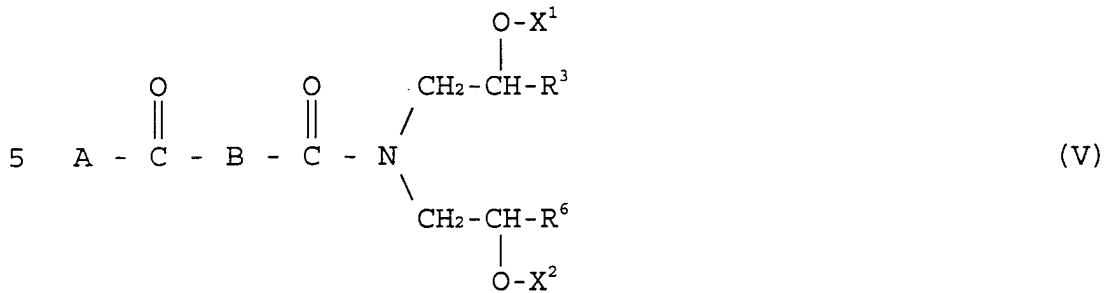
The weight average molecular mass of the polymer obtained with the process according to the invention is generally between 800 and 50,000, and preferably between 1000 g/mol and 25,000 g/mol.

The number average molecular mass of said polymer is generally between 600 and 10,000 and preferably between 700 and 4000.

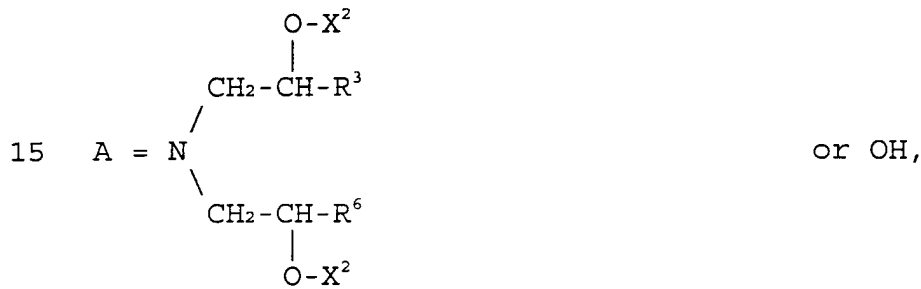
30 The β-hydroxyalkylamide functionality of said polymer is generally between 2 and 250 and preferably between 5 and 50.

The functionality is the average number of reactive groups of the specific type per molecule in the polymer composition.

40 According to another preferred embodiment of the invention the polymer's hydroxyalkylamide functionality of the polymer is ≥ 5 and the polymer containing β-hydroxyalkylamide groups is a polymer represented by formula (V):

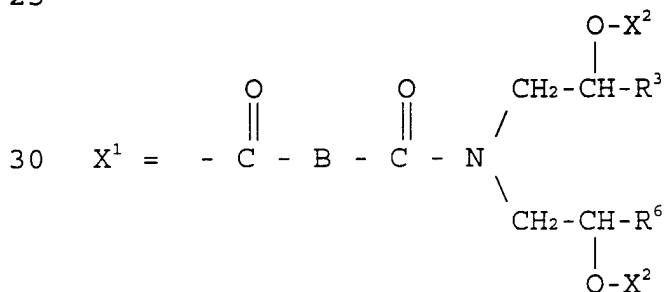


10 in which:



B = (C<sub>2</sub>-C<sub>12</sub>), optionally substituted, aryl or (cyclo)alkyl aliphatic diradical,

25



35 X<sup>2</sup> = H or X<sup>1</sup>,

R<sup>3</sup> = H or (C<sub>6</sub>-C<sub>10</sub>) aryl or (C<sub>1</sub>-C<sub>8</sub>) (cyclo)alkyl radical and

R<sup>6</sup> = H or (C<sub>6</sub>-C<sub>10</sub>) aryl or (C<sub>1</sub>-C<sub>8</sub>) (cyclo)alkyl radical

Preferably R<sup>3</sup> and R<sup>6</sup> are (C<sub>1</sub>-C<sub>4</sub>) alkyl.

40 According to another preferred embodiment of the invention R<sup>3</sup> and R<sup>6</sup> are methyl or ethyl.

B may be saturated or unsaturated.

B may be substituted with for example a (C<sub>1</sub>-C<sub>26</sub>) alkyl group, which may be saturated or unsaturated; preferably C<sub>1</sub> is used.

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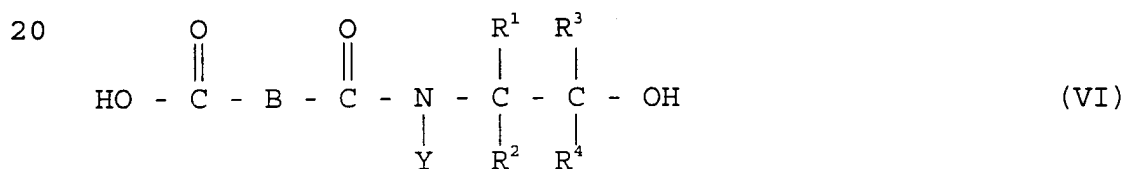
B may be for example a (methyl-)1,2-ethylene, (methyl-)1,2-ethylidene, 1,3-propylene, 1,4

butylene, 1,5 pentylene, 1,6 hexylene, 1,8 octylene,  
 1,10 decylene, cis/trans 1,3-cyclohexylene, cis/trans  
 1,4 cyclohexylene, oxo-bismethylene, (methyl-)1,2-  
 cyclohexyl, (methyl-)1,2-phenylene, 1,3-phenylene, 1,4-  
 5 phenylene, 2,3-norbornyl, 2,3-norbornen-5-yl and/or  
 (methyl-)1,2 cyclohex-4-enyl radical.

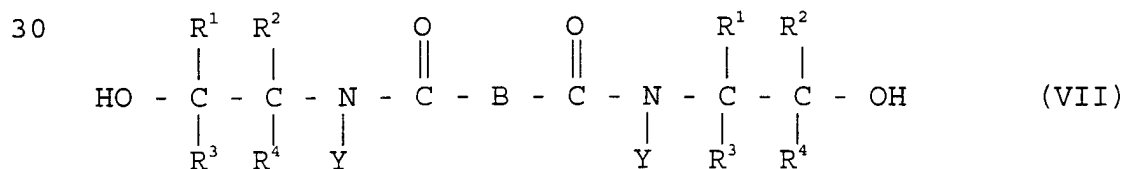
Depending on the starting monomers chosen,  
 the variables B, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> in the molecule  
 or mixture of molecules can be selected to be the same  
 10 or different per variable.

The polymer composition according to the  
 invention is generally a composition comprising higher  
 and lower oligomers, which usually contains less than  
 50 wt.%, preferably less than 30 wt.%, of oligomers  
 15 having a molecular weight smaller than 600.

The monohydroxyalkylamide of a bivalent  
 carboxylic acid generally has the formula (VI):



and the bishydroxyalkylamide of a bivalent carboxylic  
 acid generally can be represented by formula (VII):

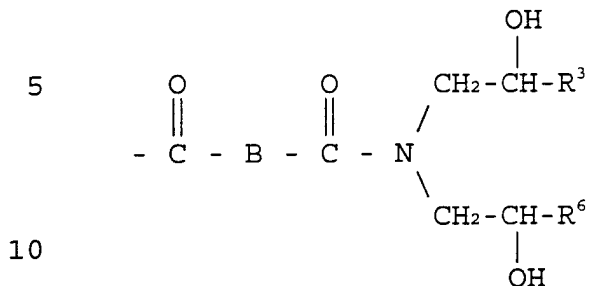


wherein

R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> may, independently of one another, be  
 the same or different, H, (C<sub>6</sub>-C<sub>10</sub>) aryl or  
 40 (C<sub>1</sub>-C<sub>8</sub>) (cyclo)alkyl radical.

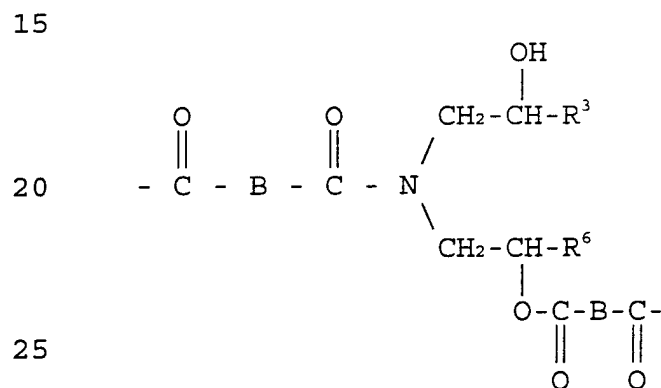
In a branched polymer obtained with the  
 process according to the invention the (β)-

hydroxyalkylamide groups can be present both as an endgroup



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and as a pendant side chain group



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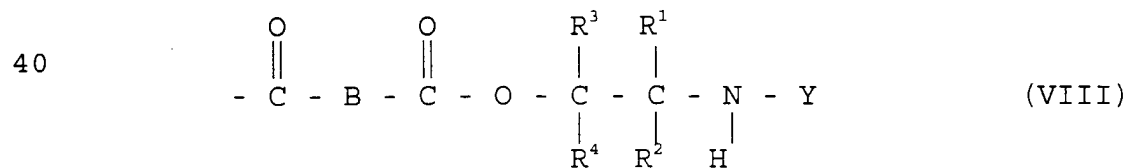
Generally, the molar amount of amide bounds in the chain is higher than the amount of ester bounds.

30

The polymer according to the invention comprises at least 60% by weight of the products represented by the formulas (III)-(V).

35

Due to side reactions during the preparation of the polymer it is possible that the composition according to the invention comprises also for example secondary amine groups having the formula (VIII):



45

wherein:

R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> may, independently of one another, be the same or different, H, (C<sub>6</sub>-C<sub>10</sub>) aryl or (C<sub>1</sub>-C<sub>8</sub>) (cyclo)alkyl radical.

In addition to  $\beta$ -hydroxyalkylamide groups, 5 the polymer may also contain carboxyl groups, in amounts of between 0.01 and 2.0 mg equivalent/gram of polymer. The number of carboxylic acids present in the polymer can be controlled via the anhydride/  
10 alkanolamine ratio and via the degree of conversion. If an alkanolamine excess is used and the polycondensation reaction is (almost) complete, less than 0.2 mg  
15 equivalent acid/gram of polymer is usually present. If carboxyl groups are present, they may in a subsequent step react with compounds containing one or more groups that can react with carboxylic acid, such as for  
20 example epoxy groups or  $\beta$ -hydroxyalkylamide groups. The amount of carboxylic acid is preferably as low as possible, for example between 0.01 and 0.2 mg  
equivalent/gram of polymer.

20 The degree of branching and the functionality of the polymer are dependent on the starting materials and the molecular weight of the polymer. A molecular weight higher than 2000 and the  
25 use of di- and/or trialkanolamines generally lead to highly branched structures with a functionality of  $\geq 10$ .

The present invention also relates to 30 entirely or partly modified polymers. The modification of the polymer may for example take place by the methods as disclosed in WO-A-99/16810 which publication  
is disclosed herein by means of this reference.

The branched polymer obtained with the 35 process according to the invention may also react with a diisocyanate, after which the isocyanate-functional polymer obtained reacts with a compound capable of reacting with isocyanates. As the diisocyanate use may

be made of a compound containing two or more isocyanate groups with different reactivities. This may be an aliphatic diisocyanate with one sterically more accessible isocyanate group bound to a primary carbon atom and one sterically less accessible isocyanate group bound to a tertiary carbon atom.

The modified and the unmodified polymers obtained with the process according to the invention may be very widely used in technically different fields, both in thermosetting and in thermoplastic applications. Examples of applications are powder-paint compositions, coating systems based on water or solvent, can- or coilcoating systems, radiation-curable coating compositions, alkyd resins for coatings, unsaturated resins for construction purposes (for example putties, sealants, castings, compounds and molding compounds), inks, toner compositions, film formers for glass fibre sizings, adhesives, hot melts and in rubber compositions.

Unmodified or partly modified polymers will generally be used in powder-paint systems, in can- or coil-coating systems or in solvent-based coating systems, in air-drying systems, in radiation-curable coatings and construction resins.

Considering the many possibilities of modification of the polymer obtained with the process according to the invention, the modification may be directed at any of a wide range of technical applications.

According to a preferred embodiment the polymers obtained with the process according to the invention are used in thermosetting powder-paint compositions. The polymer may be used in the powder-paint composition as the polymer or as the crosslinker.

Thermosetting powder paints have a better resistance to chemicals than thermoplastic powder paints. As a result of this, intensive efforts have for

a long time been made to develop crosslinkers and polymers for thermosetting powder coatings. Attempts are still being made to find binder compositions for thermosetting powder paints with a good flow behaviour, good storage stability and a good reactivity. A thermosetting powder-paint binder composition generally contains more than 50 wt.% polymer and less than 50 wt.% crosslinker.

The glass transition temperature ( $T_g$ ) of the polymer lies between  $0^\circ\text{C}$  and  $150^\circ\text{C}$ , preferably between  $50^\circ\text{C}$  and  $110^\circ\text{C}$ , depending on the selected starting materials and the molecular weight.

Generally a compound according to any one of formulas (I), (II), (III), (IV) or (V) is used in powder-paint compositions. It is also possible to use a polymer in which up to for example 50 wt.%, preferably less than 30 wt.%, of the hydroxyalkylamide groups are modified.

A coating that ultimately obtained with a powder paint must meet many varying requirements. Various systems are known. Some systems release volatile components during the curing. These systems present the drawback that they form coatings with bubbles and/or that undesirable emissions are released. As far as the latter is concerned, the volatile component, if organic in origin, may cause undesirable environmental or health problems. It has moreover been found that all the desired properties of the powder paint or powder coating are not always realized.

Systems comprising hydroxyalkylamide crosslinkers, such as for example according to EP-A-322834, contain bubbles above a layer thickness limit of about  $100\ \mu\text{m}$  as a result of the reaction water released.

In other systems use is made of polyesters and the usual crosslinkers containing an epoxy group.

No volatile components are generally released from these systems. However, the use of bisphenol-A-epoxy resins in the so-called hybrid systems results in coatings that exhibit a relatively great extent of yellowing and powdering when exposed to UV light, while the frequently used triglycidylisocyanurate (TGIC) crosslinker is toxicologically suspect.

It has been found that use of the polymer obtained with the process according to the invention as the crosslinker in a binder compositions for a powder paint results in a combination of highly desirable properties such as for instance good flow behaviour and good resistance to chemicals, desired gloss without bubble formation at the surface up to and including layer thicknesses of at least 120  $\mu\text{m}$ , a high resistance to scratching, good mechanical properties, good powder stability, good weather resistance and good colour stability of the powder coating.

Depending on the final application desired, the crosslinker according to the invention described above can also be used in combination with another crosslinker, such as for example triglycidyl isocyanurate (TGIC), Araldite GT 7004<sup>TM</sup>, polybisphenol-A-epoxides such as, for instance, the various Epikote<sup>TM</sup> grades, compounds containing (blocked) isocyanate groups, such as for example the caprolactam-blocked isophorone diisocyanate trimer, crosslinkers containing  $\beta$ -hydroxyalkylamide groups such as for example Primid XL 522<sup>TM</sup> (Rohm and Haas) and/or polyfunctional oxazolines. The weight ratio between the crosslinkers may be selected depending on the final application.

The crosslinker obtained with the process according to the invention is preferably combined with a crosslinker comprising at least one linear or branched aliphatic chain with 5-26 carbon atoms and having an epoxy functionality of more than 1, with the



proviso that the epoxy groups are carried on the at least one aliphatic chain. These crosslinkers are described in EP-A-600546 and include, for example, epoxidized oils in which the oil is linseed oil, soybean oil, safflower oil, oiticica oil, carraway seed oil, rapeseed oil, castor oil, dehydrated castor oil, cottonseed oil, wood oil, vernonia oil (a natural oil), sunflower oil, peanut oil, olive oil, soyleaf oil, maize oil, fish oil such as, for instance, herring or sardine oil, and non-cyclic terpene oils.

The epoxidized oil is preferably epoxidized soybean oil and/or epoxidized linseed oil.

As the crosslinker, a powder-paint-binder composition may contain the polymer obtained with the process according to the invention and as the polymer a polymer containing carboxyl groups or containing anhydride groups. The polymer may be selected from the group consisting of a polyester, a polyacrylate, a polyether (such for example a polyether based on bisphenol or a phenol-aldehyde novolak), a polyurethane, a polycarbonate, a trifluoroethylene copolymer or a pentafluoropropylene copolymer, a polybutadiene, a polystyrene or a styrene maleic anhydride copolymer.

Generally, a polymer having an acid value higher than 40 mg KOH/gram resins is applied because a relatively high acid value results in better reactivity with the polymer according to the invention.

The molecular weight (Mn) of this polymer is usually higher than 800, but preferably higher than 1500. The polymer must flow well at temperatures between 100°C and 200°C and therefore has a molecular weight (Mn) that is lower than approximately 10,000, preferably lower than approximately 7000.

This polymer generally has a viscosity at 158°C that is lower than 8000 dPas. The viscosity will

usually be higher than 100 dPas. The viscosity can advantageously vary from approximately 300 to approximately 5000 dPas. The viscosity used here was measured according to the Emila method described by  
5 Misev in Powder Coatings; Chemistry and Technology, pages 287-288 (1991).

The Tg of this polymer is generally higher than approximately 20°C, preferably higher than 30°C, and may be higher than 40°C. The polymer's Tg is usually  
10 lower than 120°C because otherwise the binder composition may become somewhat difficult to prepare. As already indicated above, the choice of the polymer's Tg can be based on the Tg recommended for the binder composition.

15 If use is made of polymers having only terminal groups that can react with a hydroxyalkylamide functionality, the polymer has an average functionality (capable of reacting with the hydroxyalkylamide groups) of more than 1.6, preferably more than 2. The polymer  
20 generally has an average functionality of less than 10, preferably less than approximately 6. If use is made of polymers - such as polyacrylates - with appended functional groups, the average functionality will be higher than approximately 1.6, and preferably higher  
25 than 2. Such a polymer generally has an average functionality of less than 8, preferably less than 4.

Most preferable of the suitable polymers are polyesters and polyacrylates.

30 With the polymers described various properties can be obtained in the binder and in the powder coating itself. Polyacrylates are highly resistant to yellowing and to weather influences.

The polyacrylates may be obtained via known processes. In these processes use can be made of  
35 comonomers such as for instance styrene, maleic acid or maleic anhydride and of small amounts of ethylene, pro-

pylene and acrylonitrile. Other vinyl or alkyl monomers, such as octene, triallyl isocyanurate and diallyl phthalate, can be added in small amounts.

5 A polyacrylate containing acid groups is generally obtained through copolymerization of the desired amount of acid, such as for example (meth)acrylic acid, maleic acid or fumaric acid.

The polyacrylate's viscosity usually lies between 100 and 8000 dPas (measured at 158°C; Emila).

10 The selection of the polymer : crosslinker weight ratio depends on the desired final application and this ratio will generally be between 60:40 and 90:10, preferably between 75:25 and 85:15.

15 If the polymer obtained with the process according to the invention is used as a resin in powder-paint compositions, compounds containing two or more functional groups that can react with  $\beta$ -hydroxyamide groups can be used as the crosslinker. Examples of such groups are anhydrides, carboxylic  
20 acids, carboxylic esters, epoxides, isocyanates and alkoxy silanes. Preferably anhydride groups, carboxylic acids and blocked isocyanates are used. Examples are adipic acid, decanedicarboxylic acid, trimellitic anhydride, phthalic acid or phthalic anhydride,  
25 tetrahydrophthalic acid or tetrahydro-phthalic anhydride, hexahydrophthalic acid or hexahydrophthalic anhydride and IPDI-trimer or HDI-trimer, optionally blocked with caprolactam or triazole.

30 The preparation of thermosetting powder coatings in general and the chemical reactions for curing powder paints to form powder coatings are described by Misev in Powder Coatings, Chemistry and Technology (1991, John Wiley) on pp. 42-54, pp. 148 and 224-226. A thermosetting binder composition is  
35 generally defined as the resinous part of the powder paint consisting of polymer and crosslinker.

If so desired, the usual additives can be used in the binder composition and in the powder-paint system according to the invention, such as for example pigments, fillers, degassing agents, flow agents and stabilizers. Suitable pigments are for example inorganic pigments, such as for example titanium dioxide, zinc sulphide, iron oxide and chromium oxide, and also organic pigments such as for example azo compounds. Suitable fillers are for example metal oxides, silicates, carbonates and sulphates.

Primary and/or secondary antioxidants, UV stabilizers such as quinones, (sterically hindered) phenolic compounds, phosphonites, phosphites, thioethers and HALS compounds (hindered amine light stabilizers) can for example be used as stabilizers.

Examples of degassing agents are benzoin and cyclohexane dimethanol bisbenzoate. The flow agents include for example polyalkylacrylates, fluorohydrocarbons and silicone fluids. Other suitable additives are for example additives for improving tribocharging, such as sterically hindered tertiary amines that are described in EP-B-371528.

Powder paints according to the invention can be applied in the usual manner, for example by electrostatically spraying the powder onto an earthed substrate and curing the coating by exposing it to heat at a suitable temperature for a sufficient length of time. The applied powder can for example be heated in a gas oven, an electric oven or with the aid of infrared radiation.

Thermosetting coatings of powder-paint (coating) compositions intended for industrial applications are described further in a general sense in Powder Coatings, Chemistry and Technology, Misev, pages 141-173 (1991).

Compositions according to the present invention can be used in powder paints for use on, for

example, metal, wooden and plastic substrates. Examples are industrial coatings, coatings for machines and tools, household applications and parts of buildings. The coatings are also suitable for use in the  
5 automotive industry for coating parts and accessories.

According to a further preferred embodiment the condensation polymer obtained with the process according to the present invention is used in a toner composition. A toner composition may comprise a resin,  
10 a colorant, a charge control agent, magnetic material and/or additives. The polymer may be applied, depending on the desired use, in amounts between 0,1 and 100 % by weight relative to the toner binder resin. The polymer may be applied in the toner composition, for example,  
15 as the resin, as the charge control agent, as the release agent to prevent hot-roll offset, as the compatibiliser for pigments and as the agent which causes chain extension and/or partial crosslinking.

Suitable resins include for example  
20 polyesters, polyamides, polyolefins, styrene (meth)acrylates, styrene butadienes, crosslinked styrene polymers, epoxies, polyurethanes, vinyl resins and/or polyester imides.

Preferably, the resin is a polyester and/or  
25 a styrene acrylate.

Suitable charge control agents include for example a positive-charge control agent or negative-charge control agent.

Examples of the positive-charge control  
30 agent include nigrosine dyes, triphenylmethane dyes containing a tertiary amine as a pendant group, quaternary ammonium salt compounds, cetyltrimethylammonium bromide, polyamine resins, imidazole derivatives.

35 Examples of the negative-charge control agent include metal-containing azo dyes, copper phthalocyanine dyes, metal complexes of salicylic alkyl

derivatives and quaternary ammonium salts. The charge control agent may be incorporated in the toner in an amount from 0.1 to 8.0% by weight, preferably from 0.2 to 5.0% by weight, based on the amount of the binder resin.

The invention will be elucidated with reference to the following, non-limiting examples.

#### Example I

##### 10 Preparation of a highly branched polymer comprising units of terephthalic acid and diisopropanolamine

318 g of terephthalic acid, 382 g of diisopropanolamine and 175 g of demi-water were introduced in a double-walled glass reactor, which could be heated by means of thermal oil, fitted with a mechanical stirrer, a distillation head and nitrogen and vacuum connections. The reaction mixture was gradually heated, with stirring, to approx. 70°C and then more slowly to 160°C. Water was distilled-off during the heating. After a total reaction time of 1½ hours vacuum was applied. After 2½ hours of vacuum (< 0.1 bar) the acid value was 41.0 mg KOH/g of resin. The viscosity at 160°C is 40 Pas and the Tg is 73°C. After cooling, the polymer was obtained as a pale yellow glassy mass.

#### Example II

##### A powder paint composition

A powder paint composition according to Table 1 was prepared by mixing and extrusion (PRISM extruder, 110°C). The polyester (Uralac P 4040™ from DSM Resins) comprises units of isophthalic acid, terephthalic acid, adipic acid, neopentyl glycol, ethane diol and trimethylol propane. The composition was in the usual manner ground, sieved and

electrostatically sprayed (Corona) onto steel test panels. After a cure cycle of 10 minutes at 200°C in a circulation oven, the panels were tested to determine their appearance (visually), flexibility (penetration  
5 in mm according to Erichson ISO 1520/DIN 53156), reverse impact resistance (ASTM-2794/69 in inch-pound), adhesion (cross hatch adhesion test) and hardness (König, seconds).

The test results (the table below) show  
10 that the polymer obtained with the process according to the invention results in a coating having good mechanical properties and a high blister limit (visually). No VOC derived from cyclic carboxylic anhydrides were detectable with Thermal Desorption Mass  
15 Spectrometry from Tenax™ tubes subject to the oven air in which the coatings were cured.

Table 1

Polyester resin: Uralac P 4040™	176 g
Crosslinker according to Example I	24 g
Additives:	
TiO <sub>2</sub> Kronos 2310	100 g
Resiflow PV5	3.0 g
Benzoin	1.5 g
Cure cycle	10' 200°C
Hardness	209 s
Impact resistance <sup>1</sup>	130 IP
ESP <sup>2</sup>	> 8 mm
Adhesion <sup>3</sup>	Gt0
Gel time <sup>4</sup>	69 s
Flow behaviour	moderate
Blister limit	> 140 μm

1) Reverse impact test; on steel ASTM-2794/69.

5 The impact is usually given in inch.pound (IP). If no cracks are visible in the coating at 160 IP, 160 IP is quoted as the result. An impact resistance of 160 IP stands for 1.84 m.kg.

2) Erichson Slow Penetration; ISO 1520/DIN 53156.

10 3) Cross-hatch adhesion; ISO 2409/DIN 5315

4) Gel time; DIN 55990, part B.



CLAIMS

1. A process to prepare a condensation polymer  
5 containing ester groups and at least one amide  
group in the backbone, having at least one  $\beta$ -  
substituted  $\beta$ -hydroxyalkylamide end group and  
having a hydroxyalkylamide functionality between  
2 and 250, characterized in that a polyvalent  
10 carboxylic acid reacts with an alkanolamine to  
form a hydroxyalkylamide from which a  
polyesteramide is obtained through  
polycondensation.
2. A process according to Claim 1 characterized in  
15 that the polyvalent carboxylic acid is a  
dicarboxylic acid.
3. A process according to Claim 2, characterized in  
that the dicarboxylic acid is isophthalic acid,  
terephthalic acid, cis- and trans  
20 hexahydroterephthalic acid, 2,6-naphthalene  
dicarboxylic acid, 4,4'-oxybisbenzoic acid, 3,6'-  
dichlorophthalic acid, tetrachlorophthalic  
acid, tetrabromophthalic acid, tetrahydrophthalic  
acid, hexachloroendomethylene tetrahydrophthalic  
25 acid, phthalic acid, azelaic acid, sebacic acid,  
decanedicarboxylic acid, adipic acid, diglycolic  
acid, succinic acid, fumaric acid, glutaric acid,  
malonic acid, dodecyl succinic acid, 1,9 nona-  
dicarboxylic acid and maleic acid or their  
30 mixtures.
4. A process according to any one of Claims 1-3  
characterized in that the alkanolamine is a  $\beta$ -  
substituted alkanolamine.
5. A process according to Claim 4, characterized in  
35 that the  $\beta$ -substituted alkanolamine is a  $\beta$ -alkyl-  
substituted alkanolamine.

6. A process according to Claim 5, characterized in that the alkanolamine is diisopropanolamine, N-(m)ethylisopropanolamine, diisobutanolamine, cyclohexylisopropanolamine, di- $\beta$ -  
5 cyclohexanolamine and/or n-butylisopropanolamine.
7. A process according to any one of Claims 1-6, characterized in that the equivalent ratio dicarboxylic acid: alkanolamine ranges between 1 : 1,3 and 1 : 2.
- 10 8. A powder paint binder composition comprising a polymer obtained with the process according to any one of Claims 1-7.
9. A powder paint composition comprising a binder composition according to Claim 8.
- 15 10. A powder coating obtained by curing of a powder paint according to Claim 9.
11. An entirely or partly coated substrate, characterized in that a powder coating according to Claim 10 is used as the coating.
- 20 12. A toner composition comprising a polymer obtained with a process according to any one of Claims 1-7.

# INTERNATIONAL SEARCH REPORT

Inter. Application No  
PCT/NL 00/00526

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 7 C08G69/44 C09D177/12 C09D5/03 C08G63/685

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)  
IPC 7 C08G C09D

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

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

EPO-Internal

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 99 16810 A (STANSSENS DIRK ARMAND WIM ;DSM NV (NL); RIETBERG JOHAN (NL); BENTH) 8 April 1999 (1999-04-08) cited in the application ---	
A	US 3 709 858 A (BLOOD A ET AL) 9 January 1973 (1973-01-09) -----	

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
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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

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*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
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Leroy, A

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No  
PCT/NL 00/00526

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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