

## Powder paint composition

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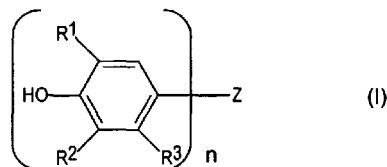
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(54) Title: POWDER PAINT COMPOSITION



(57) Abstract: The invention relates to a powder paint composition comprising: a) a compound comprising hydroxyalkylamide units, b) a stabilizer, and c) a compound capable of reacting with hydroxyalkylamide units, whereby said compound a) comprising hydroxyalkylamide units is a branched condensation polymer containing ester groups, having at least one amide group in the backbone, having at least one hydroxyalkylamide end group and having a weight average molecular mass of at least 800 g/mol and, whereby said stabilizer b) is at least one phenolic anti-oxidant according to Formula (I) wherein R<sup>1</sup> is an, optionally substituted, alkyl or cycloalkyl with at least 4 C-atoms, R<sup>2</sup> and R<sup>3</sup> are identical or different, and can independently of each other be H, or (C<sub>1</sub>-C<sub>18</sub>) (cyclo)alkyl radicals, Z is an mono-, bis- or multifunctional organic group, and n=1-4, whereby when n=1, Z contains at least 3 C-atoms or heteroatoms. The invention also relates to the powder coating obtained after curing of the powder paint composition and to wholly and partly coated substrates.



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POWDER PAINT COMPOSITION

5                   The invention relates to a powder paint composition comprising a compound comprising hydroxyalkylamide units, a stabilizer and a compound capable of reacting with hydroxyalkylamide units. The invention also relates to the coating obtained after curing of the powder paint composition and to wholly and partly coated substrates.

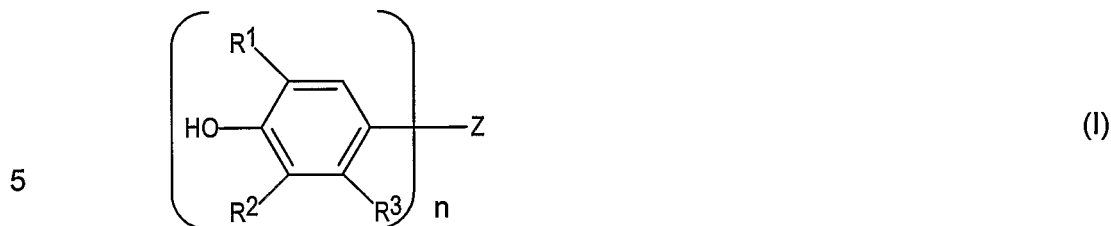
10                   Powder paint compositions are subject to discolouration during curing of the composition. The colour characteristics of the coating after curing, especially in a directly fired gas oven, have to be improved. For example, it is known that although some epoxy-polyester hybrid powder coatings have relatively good colour characteristics after curing in an electrical oven, the colour properties after curing in a  
15 directly fired gas oven need to be improved.

                  A powder paint composition with colour and heat stability is known from WO01/68781, wherein the composition contains a compound comprising carboxylic acid units, a compound comprising hydroxyalkylamide units and a stabilizer combination of at least one phosphite and either a) one or more aromatic amine(s) or  
20 b) one or more phosphinic acid(s), optionally combined with one or more phenolic anti-oxidant(s). However, for some applications the colour properties of the coating have to be improved, especially when the powder paint composition is cured in a directly fired gas oven. Furthermore, WO 01/68781 discloses that for curing in a directly fired gas oven, the use of a combination of a phenolic anti-oxidant and a phosphite further  
25 combined with either an aromatic amine or an phosphinic acid is not desired.

                  The object of the invention is to provide a powder paint composition resulting in a coating with improved colour characteristics after curing, especially after cure in a directly fired gas oven.

                  This object is reached by the invention with a powder paint  
30 composition comprising:  
a) a compound comprising hydroxyalkylamide units  
b) a stabilizer and  
c) a compound capable of reacting with hydroxyalkylamide units  
whereby compound a) comprising hydroxyalkylamide units is a branched condensation  
35 polymer containing ester groups, having at least one amide group in the backbone, having at least one hydroxyalkylamide end group and having a weight average molecular mass of at least 800 g/mol and,

whereby stabilizer b) is at least one phenolic anti-oxidant according to formula (I)



wherein

R<sup>1</sup> is an, optionally substituted, alkyl or cycloalkyl with at least 4 C-atoms;

10 R<sup>2</sup> and R<sup>3</sup> are identical or different, and can independently of each other be H, or (C<sub>1</sub>-C<sub>18</sub>) (cyclo)alkyl radicals;

Z is an mono-, bis- or multifunctional organic group;

and n=1-4, whereby when n=1, Z contains at least 3 C-atoms or heteroatoms.

The powder paint composition according to the invention after curing results in a coating having improved colour properties.

15 An additional advantage of the powder paint composition according to the invention is that these improved colour properties are reached after curing in an electrical oven as well as in a directly or indirectly fired gas oven. Furthermore, other desirable properties, for example impact resistance, heat stability, chemical resistance and flow, are obtained.

20 Preferably the powder paint composition does not contain a combination of a phosphite with an aromatic amine or a combination of a phosphite with a phosphinic acid. It has been found that when the powder paint composition according to the invention is void of phosphite in combination with an aromatic amine or in combination with a phosphinic acid, the colour properties after cure are better, especially when cured in a directly fired gas oven. In the most preferred embodiment of the invention the powder paint composition does not contain a phosphite.

30 A powder paint composition generally comprises a binder composition and additives. The binder composition generally comprises a resin and a crosslinker, which have complementary functional groups to form a network. The difference between the resin and the crosslinker is the relative amount in which they are present in the binder composition. Usually the resin is present in an amount of equal to or more than 50 wt % relative to the weight of the binder composition, whilst the crosslinker is present in an amount of less than 50 wt % relative to the weight of the binder composition. In the powder paint composition according to the invention, the binder composition comprises the compounds a) and c).

35

In one embodiment of the invention the powder paint binder

composition comprises compound a) as crosslinker and compound c) as resin. In this case the weight ratio between the compound a) and the compound c) may for example range between 30 : 70 and 3 : 97, and is preferably between 20 : 80 and 5 : 95. The selection of this ratio may be governed by the envisaged application.

5                   According to another embodiment of the invention the powder paint binder composition comprises a binder composition which contains compound a) as resin, and compound c), being preferably a polymer, as crosslinker.

                  The compound a) is a branched condensation polymer containing ester groups, at least one amide group in the backbone and having at least one  
10 hydroxyalkylamide end group and having a weight average molecular mass of at least 800 g/mol. A polymer generally comprises a backbone, at least two end groups, and optionally side chains. Examples of suitable branched condensation polymers, which may be applied as the crosslinker or as the resin in the powder paint composition according to the invention, are disclosed in WO-A-99/16810, which content is  
15 incorporated herein by reference.

                  In WO 99/16810 it is disclosed that it would be possible to use stabilizers in a powder paint composition such as for example (sterically hindered) phenolic compounds. However, WO 99/16810 does not disclose the specific stabilizer  
20 b) according to the invention, nor discloses that the use of the specific stabilizer b) would result in improved colour characteristics of the resulting coating, or any of the other advantages that can be reached with the powder composition according to the invention. The branched condensation polymer may contain hydroxyalkyl amide groups having a weight average molecular mass of between 800 and 50,000 g/mol, a number average molecular mass ( $M_n$ ) of between 600 and 10,000 and a hydroxyalkylamide  
25 functionality of between 2 and 250.

                  According to WO 99/16810 it is also possible to obtain these condensation polymers by reacting a cyclic anhydride with an alkanolamine, resulting in a hydroxylamide that is converted into a polymer by polycondensation. Preferably the molar ratio between anhydride and the alkanolamine is between 1:1 and 1:2. The  
30 use of a higher molar ratio results in a crosslinked product with less desirable properties due to the presence of too many amine groups in the crosslinker. Using a lower molar ratio results in a low amount of crosslinks in the crosslinked product. Preferably the molar ratio between anhydride and alkanolamine is between 1:1.1 and 1:1.5.

35                   According to a preferred embodiment of the invention the anhydride is succinic acid anhydride, hexahydrophthalic acid anhydride and/or phthalic acid

anhydride and the preferred alkanolamine is di-isopropanol amine, which results in good reactivity and good colour properties of the crosslinked product.

Even more preferred is the hydroxylalkylamide unit comprising compound prepared by the reaction between phthalic acid anhydride with di-  
 5 isopropanol amine. An advantage of this preference is the high hardness of the crosslinked product. Most preferred is a molar ratio of phthalic acid anhydride to di-isopropanol amine of between 1:1.1 and 1:1.4.

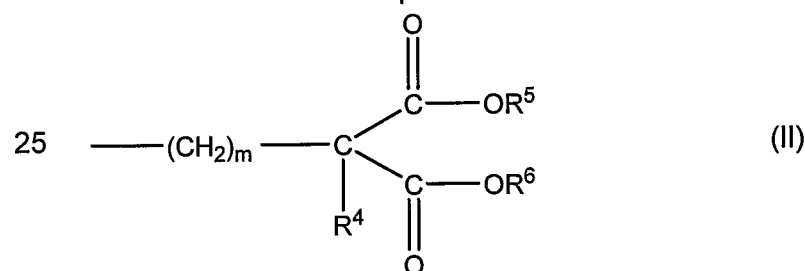
The stabilizer b) is at least one phenolic anti-oxidant according to formula (I).

10 Examples of suitable groups for R<sup>1</sup> in formula (I) are tertiary butyl, methylcyclohexyl, tertiary pentyl, 1-methyl pentadecyl and isopentane. Most preferably R<sup>1</sup> is a tertiary butyl group.

Examples of suitable groups for R<sup>2</sup> and R<sup>3</sup> in formula (I) are methyl, ethyl, n-propyl, isopropyl, isobutyl, butyl, tert-butyl, isopentyl, pentyl, neopentyl, tert-  
 15 pentyl, isohexyl, hexyl and/or cyclohexyl. Preferably one of the groups R<sup>2</sup> and R<sup>3</sup> is H when the other group is something else than hydrogen. Preferably R<sup>2</sup> is a methyl group and R<sup>3</sup> is hydrogen. Another preference is when R<sup>3</sup> is a tertiary butyl group and R<sup>2</sup> is hydrogen.

20 Examples of suitable groups for Z in formula (I) are mono-, bis- or multifunctional alkyl groups, esters, ethers or amides. They can also contain other heteroatoms, for example Si and S.

Examples of suitable monofunctional groups for Z are:



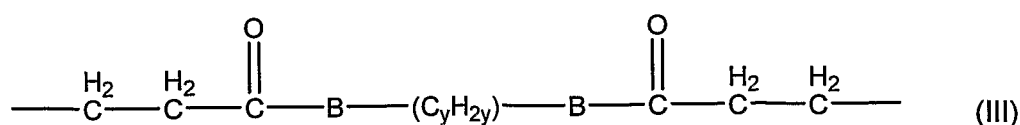
wherein:

R<sup>4</sup> = H or C<sub>1</sub>-C<sub>6</sub> alkyl;

30 m = 0 - 4;

and R<sup>5</sup> and R<sup>6</sup> are independently of each other a C<sub>6</sub>-C<sub>24</sub> alkyl.

An example of a suitable bifunctional group for Z in formula (I) is:





methyl-phenyl)-propionate, 1,6-hexane-diol-bis-3-(3,5-di-t-butyl-4-hydroxyphenyl)-propionate, 2,6-di-t-butyl-4-sec-butyl-phenol, N,N'-1,3-propanediylbis(3,5-di-t-butyl-4-hydroxyhydrocinnamamide).

According to a preferred embodiment of the invention compound b) is  
5 tetrakis [methylene (3,5-di-t-butyl-4-hydroxyhydrocinnamate)] methane or 4,4'-butylidenebis (6-t-butyl-3-methyl-phenol). It was found that these phenolic anti-oxidants yield the best results. The colour properties of coatings comprising these anti-oxidants are surprisingly good. Further more the mechanical properties of the cured coating are good.

10 The phenolic anti-oxidant according to the invention may be present in a concentration, relative to the weight of the binder composition of at least 0.01 wt%. In an amount of less than 0.01 wt% no effect of the presence of the phenolic anti-oxidant was observed. Preferably the phenolic anti-oxidant is present in an amount equal to or less than 5 wt%, more preferably in an amount from 0.25 to 2.5 wt%, even  
15 more preferably in an amount from 0.4 to 2.0 wt% and most preferably in an amount from 0.4 to 1.5 wt %. For some compositions the presence of an amount of phenolic-antioxidant higher than 5 wt% may lead to a deterioration of the desired colour properties.

The stabilizer b), optionally together with other additives, may be  
20 added to the resin, to the crosslinker, to the binder composition consisting of the resin and the crosslinker, and/or to the powder paint composition. It is also possible to add the stabilizer b) to the resin or the crosslinker during the synthesis of the resin and/or the crosslinker. In other words, stabilizer b) may be mixed with compounds a) or to compound c) during their respective synthesis.

25 According to a preferred embodiment of the invention stabilizer b) is mixed with compound c) during the synthesis of compound c).

According to another preferred embodiment of the invention the stabilizer b) comprising at least one phenolic anti-oxidant according to formula (I), is added to the resin during the resin synthesis. This results in a better mixing of the  
30 components and consequently a lower amount of phenolic anti-oxidant according to formula (I) needed to obtain the same results in comparison to adding the anti-oxidant in another stage of the preparation of the powder paint composition.

The compound capable of reacting with hydroxyalkylamide units is for example a compound comprising carboxylic acid units, isocyanate units, amino units or  
35 a combination of any of them. The wording 'units' is intended to refer to both the structural group itself as its derivatives. Also compounds functionalized with carboxylic



acid units, isocyanate units, amino units or a combination of any of them, may be suitable for the invention. Compound c) preferably is a compound comprising carboxylic acid units. Compound c) is even more preferably a polymer containing carboxyl groups or containing anhydride groups. Suitable polymers containing carboxyl groups or containing anhydride groups may include for example a polyester, a polyacrylate, a polyether (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 and/or a styrene maleic anhydride copolymer.

10 According to a preferred embodiment of the invention the polymer is a polyester.

Polyesters are generally based on the residues of aliphatic polyalcohols and polycarboxylic acids.

The polyester may comprise units of for example isophthalic acid, terephthalic acid, 2,6-naphthalene dicarboxylic acid and 4,4'-oxybisbenzoic acid.

15 Other suitable aromatic, cycloaliphatic and/or acyclic polycarboxylic acids useful herein include, for example, 3,6-dichloro phthalic acid, tetrachloro phthalic acid, tetrahydro phthalic acid, hexahydro terephthalic acid, hexachloro endomethylene tetrahydro phthalic acid, phthalic acid, azelaic acid, sebacic acid, decane dicarboxylic acid, adipic acid, succinic acid and maleic acid. These other carboxylic acids can be used in amounts of up to for example 25 mol% of the total amount of carboxylic acids. These acids may be used as such, or, in so far as available as their anhydrides, acid chlorides or lower alkyl esters. Small amounts of trifunctional acids for example trimellitic acid may be applied to obtain branched polyesters.

25 Hydroxy carboxylic acids and/or optionally lactones can also be used, for example, 12-hydroxy stearic acid, hydroxy pivalic acid and  $\epsilon$ -caprolactone. Monocarboxylic acids may, if desired, be used in minor amounts. Examples of these acids are benzoic acid, tert.-butyl benzoic acid, hexahydro benzoic acid and saturated aliphatic monocarboxylic acids.

30 Useful polyalcohols, in particular diols, reactable with the carboxylic acids to obtain the polyester include aliphatic diols. Examples are ethylene glycol, propane-1,2-diol, propane-1,3-diol, butane-1,2-diol, butane-1,4-diol, butane-1,3-diol, 2,2-dimethylpropanediol-1,3 (= neopentyl glycol), hexane-2,5-diol, hexane-1,6-diol, 2,2-bis-(4-hydroxy-cyclohexyl)-propane (hydrogenated bisphenol-A),  
35 1,4-dimethylolcyclohexane, diethylene glycol, dipropylene glycol, 2,2-bis[4-(2-hydroxy

ethoxy)-phenyl] propane, the hydroxy pivalic ester of neopentyl glycol, butylethylpropane diol and ethylmethylpropane diol.

Small amounts, for example less than about 20 wt % and preferably less than 15 wt %, of trifunctional alcohols may be used in order to obtain branched  
5 polyesters. Examples of suitable polyols include glycerol, hexanetriol, trimethylol ethane, trimethylol propane and tris-(2-hydroxyethyl)- isocyanurate. Examples of suitable polyfunctional alcohols and acids are sorbitol, pentaerythritol and pyromellitic acid.

The polyester may be prepared according to conventional methods  
10 by esterification or transesterification, optionally in the presence of customary esterification catalysts for example dibutyltin oxide or tetrabutyl titanate. Preparation conditions and the COOH/OH ratio can be selected by person skilled in the art in order to obtain end products that have an acid number and/or a hydroxyl number within the targeted range of values.

15 Generally, the polymer has an acid value between 20 and 120 mg KOH/gram resin and more preferably between 20 and 80 mg KOH/gram resin.

The number average molecular weight (Mn) of the polymer may be for example between 2000 and 6000.

The polymer preferably has a viscosity at 158°C that is lower than  
20 150 Pa.s. The glass temperature, Tg, of the polymer preferably ranges between 20°C and 80°C.

The preparation of thermosetting powder coatings in general and the chemical curing reactions of powder paints to cured coatings are described by Misev in Powder Coatings, Chemistry and Technology (1991, John Wiley) on pp. 42-54, pp. 148  
25 and 224-226.

Curing of the composition may take place in an electrical oven, a directly fired gasoven, an indirectly fired gasoven or by IR-radiation.

The colour properties of the powder coating can be expressed in a b\*-value, measured with a Dr Lange Micro Color Meter measured at a layer thickness of  
30 60 µm according to ISO 7724.

Preferably the b\* is as low as possible. The b\*-value may differ with the cure conditions, such as cure method, cure temperature and cure time.

Furthermore the b\*-value is dependent on the hiding power of the used pigment.

Preferably, the b\* of a powder coating pigmented with TiO<sub>2</sub> (for example Kronos<sup>TM</sup>

2160 or 2310) after a ten minute cure in a gas oven (NOx) at 215 °C is equal to or lower than 5.

For an electrical oven, the  $b^*$  of a powder coating pigmented with TiO<sub>2</sub> after a ten minute cure at 180 °C is preferably equal to or lower than 1.

5 It is also possible to add additional stabilizers to the powder paint binder composition according to the invention. Suitable additional stabilizers include for example: hindered amine light stabilizers (HALS), lactones, hydroxylamines and UV-absorbers for example hydroxybenzophenones, hydroxybenzotriazoles, triazines for example 2-[4,6-diphenyl-1,3,5-triazin-2-yl]-5-(hexyl)oxy-phenol (Tinuvin™ 1577, Ciba  
10 Specialty Chemicals) or 2,4-bis (2,4-dimethylphenyl)-6-(2-hydroxy-4-n-octyloxyphenol)-1,3,5-triazine (Cyasorb™ UV1164, Cytec).

If desired, the usual additives, for example pigments, fillers, degassing agents, catalysts, flow-promoting agents can be incorporated into the binder composition and the powder paint composition.

15 The powder paint composition according to the invention can be used together with or without pigments. If pigments are used those that have no interaction with the selected catalyst are preferred. If pigments are used both inorganic and organic pigments are suitable for example, titanium dioxide, zinc sulphide, iron oxide and chromium oxide, and as organic pigments, for example azo compounds.

20 Suitable fillers include for example metal oxides, silicates, carbonates and sulphates.

Examples of degassing agents are benzoin and cyclohexane dimethanol bisbenzoate. The range of flow-promoting agents includes for instance polyalkyl acrylates, fluorocarbons and silicon oils. Other suitable additives are for  
25 example additives for improvement of the triboelectric chargeability, for example sterically hindered tertiary amines which are described in EP 0 371 528.

The present invention further relates to the use of powder paint compositions according to the present invention for coating a substrate. Powder paint compositions according to the invention may be applied in the customary manner, for  
30 example by electrostatic spraying of the powder onto an earthed substrate and by curing the paint by exposing it to heat at a suitable temperature and for a sufficiently long time. The applied powder can be heated and cured, for example, in a directly or indirectly fired gas oven or in an electric oven or by means of infrared irradiation.

Thermosetting coatings based on powder paint compositions for  
35 industrial applications are further described in a general sense in Powder Coatings, Chemistry and Technology, Misev, pp. 141-173 (1991).

The invention also relates to a substrate coated with a coating obtained after curing of the powder paint composition according to the present invention. The powder paint compositions according to the invention may be applied on, for example, metal, wood and plastic substrates. Examples are industrial coatings, coatings for machines and tools, domestic applications and component parts of buildings. The powder paint compositions according to the invention are further suitable for use in the automotive industry for coating of parts and accessories. The powder paint composition according to the invention may also be used for example in other technical fields of the coating industry, in toner compositions, in printing ink applications and in the technical field of adhesives applications.

Preferably the powder paint composition according to the invention results in a coating having a  $b^*$  value according to ISO 7724 of lower than or equal to 5 obtained after curing of the powder paint composition in a directly fired gas oven for ten minutes at 215 °C. According to another embodiment of the invention the powder paint composition results in a coating having a  $b^*$  value according to ISO 7724 of lower than or equal to 1 obtained after curing of the powder paint composition in an electrical oven for ten minutes at 180 °C. Most preferably the powder paint composition according to the invention is such that when it would be cured in a directly fired gas oven or in an electrical oven under the respective circumstances as mentioned above it would result in respectively a coating having a  $b^*$  value according to ISO7724 of lower than or equal to 5 after curing in the directly fired gas oven and lower than or equal to 1 after curing in an electrical oven.

The invention further relates to a coating having a  $b^*$  value according to ISO 7724 of lower than or equal to 5 obtained after curing of a powder paint composition according the invention in a gas oven for ten minutes at 215 °C.

The invention further relates to a coating having a  $b^*$  value according to ISO 7724 of lower than or equal to 1 obtained after curing of a powder paint composition according the invention in an electrical oven for ten minutes at 180 °C.

Hereafter the invention is further elucidated with some non-limiting examples.

Examples I and II and Comparative Experiments A and B.

Coating compositions were prepared in the amounts as shown in table 1.

Table 1. Amounts (wt. parts) of compounds in the coating compositions.

	Example I	Example II	Comparative Experiment A	Comparative Experiment B
Hydroxylalkylamide units				
Containing compound a)				
-Reaction product of a condensation reaction between diisopropanol amine and phthalic anhydride with an acid value of	16,6	15		
- PRIMID XL-552 <sup>TM</sup> (EMS)			10	
Phenolic anti-oxidant b)				
- 4,4'-butylidenebis (6-t-butyl-3-methyl-phenol)	1,0	1,0	1,0	1,0
Compound c)				
Polyester (compound c)				
- Uralac <sup>TM</sup> P873 (DSM)	83,4		90	
- Uralac <sup>TM</sup> P5212 (DSM)		85		
- Uralac <sup>TM</sup> P5127 (DSM)				50
Epoxy type Crosslinker				
- Araldite <sup>TM</sup> GT7004 (Vantico AG)				50

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To all compositions 50 wt parts TiO<sub>2</sub> was added as a pigment. The compounds as described in the table and the pigment were weighed and premixed in a Kinematica Mixotron MB550. The premix was extruded at 110°C in a PR15M extruder. The extrudate was cooled down to room temperature and grinded with a Retsch2M100 centrifugal mill at 18000 rpm. The grinded composition was sieved at 90µm with a Retsch AS200 digit sieve to yield a powder coating composition. The obtained powder coating compositions were sprayed on non pre-treated steel plates with a Gema

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Corona PGI Powdergun followed by baking them in a Heraeus hot air electrical oven UT6120 or in a directly fired gas oven at the conditions as shown in the table with results below. The  $b^*$  values were measured with a Dr. Lange Micro Colour meter at a layer thickness of 60  $\mu\text{m}$ , according to ISO7724. The results of these measurements are shown in table 2.

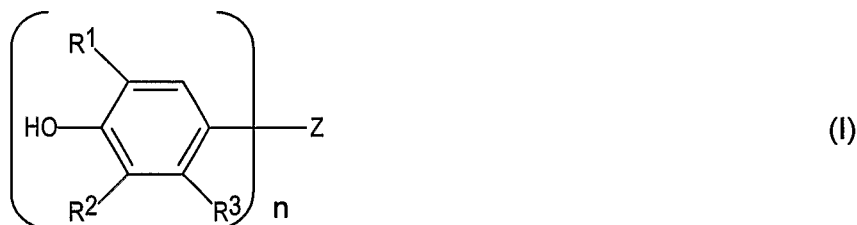
Table 2. Results of the measurements of  $b^*$ .

Cure conditions			$b^*$ - value of			
Oven type	Time (min)	Temperature ( $^{\circ}\text{C}$ )	Example I	Example II	Comparative Experiment A	Comparative Experiment B
Electrical oven	15	180	0.8	0.9	1.8	0.7
Electrical Oven	60 overbake	200	2.1	1.5	3.7	1.8
Gas oven	10	215	5.0	3.9	6.6	6.4

CLAIMS

1. A powder paint composition comprising:

- 5 a) a compound comprising hydroxyalkylamide units  
 b) a stabilizer and  
 c) a compound capable of reacting with hydroxyalkylamide units,  
 whereby compound a) comprising hydroxyalkylamide units is a branched  
 condensation polymer containing ester groups, at least one amide group in the  
 backbone and having at least one hydroxyalkylamide end group and having a  
 10 weight average molecular mass of at least 800 g/mol and whereby stabilizer b)  
 is at least one phenolic anti-oxidant according to formula (I)



wherein

- R<sup>1</sup> is an, optionally substituted, alkyl or cycloalkyl with at least 4 C-atoms  
 R<sup>2</sup> and R<sup>3</sup> are identical or different, and can independently of each other be H,  
 20 or (C<sub>1</sub>-C<sub>18</sub>) (cyclo)alkyl radicals,  
 Z is an mono-, bis- or multifunctional organic group,  
 and n=1-4,  
 whereby when n=1, Z contains at least 3 C-atoms or heteroatoms.

2. A composition according claim 1, wherein the composition does not contain a  
 25 phosphite.  
 3. A composition according to any one of claims 1-2, wherein the compound a) is  
 prepared by the reaction between succinic acid anhydride, hexahydrophthalic  
 acid anhydride and/or phthalic acid anhydride with di-isopropanol amine.  
 4. A composition according to any one of claims 1-3, wherein the compound c) is  
 30 a compound containing carboxylic acid units.  
 5. A composition according to any one of claims 1-4, whereby the stabilizer b) is  
 mixed with compound c) during the synthesis of compound c).  
 6. A composition according to any one of claims 1-5, wherein the stabilizer b) is  
 35 tetrakis [methylene (3,5-di-t-butyl-4-hydroxyhydrocinnamate)] methane or 4,4'-  
 butylidenebis (6-t-butyl-3-methyl-phenol).

7. Use of a powder coating composition according to any one of claims 1-6 for coating a substrate.
8. A coating having a b\* value according to ISO 7724 of lower than or equal to 5 obtained after curing of a powder paint composition according to any one of claims 1-6 in a gas oven for ten minutes at 215 °C.
9. A coating having a b\* value according to ISO 7724 of lower than or equal to 1 obtained after curing of a powder paint composition according to any one of claims 1-6 in an electrical oven for ten minutes at 180 °C.
10. A substrate coated with a coating obtained after curing of the powder paint composition according to any one of claims 1-6 or with a coating according to any one of claims 8-9.



INTERNATIONAL SEARCH REPORT

In  national Application No  
PCT/NL 03/00397

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C09D5/03 C09D7/12

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 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)

WPI Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99 16810 A (STANSSENS DIRK ARMAND WIM ;DSM NV (NL); RIETBERG JOHAN (NL); BENTH) 8 April 1999 (1999-04-08)	1-3,7,10
Y	claims 1,17,18 page 28, line 13 - line 17 page 29, line 3 - line 9 example V	1-10
Y	WO 01 68781 A (DSM NV ;GIJSMAN PIETER (NL); GRISNICH WILLEM (NL); BENTHEM RUDOLFU) 20 September 2001 (2001-09-20) cited in the application claims 1,7,11 page 3, line 19 -page 4, line 26	1-10
A	EP 0 857 765 A (CIBA GEIGY AG) 12 August 1998 (1998-08-12) claims 1,5-8	1
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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
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- \*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
- \*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

Date of the actual completion of the international search

8 July 2003

Date of mailing of the international search report

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## INTERNATIONAL SEARCH REPORT

Int. Patent Application No

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	EP 1 127 931 A (DSM NV) 29 August 2001 (2001-08-29) claims 1,11 page 6, line 9, paragraph 55 - line 11 -----	1

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