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(71) Applicant (for all designated States except US): **DSM IP ASSETS B.V.** [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **JANSEN, Johan Franz Gradus Antonius** [NL/NL]; Marisstraat 11, NL-6165 AP Geleen (NL). **DRIJFHOUT, Jan Pieter** [NL/NL]; Oostercluft 117, NL-8332 DC Steenwijk (NL).

(74) Agents: **HEIJMAN, Renske** et al.; P.O. Box 9, NL-6160 MA Geleen (NL).

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(54) Title: TWO COMPONENT HEAT-CURABLE POWDER COATING COMPOSITION

(57) Abstract: The invention relates to a powder coating composition comprising a physical mixture of a powder (A) and a powder (B), wherein the powder (A) comprises a thermal radical initiator selected from the group of peroxyesters, monoperoxy carbonates and mixtures thereof, wherein the powder (B) comprises a catalyst for the thermal radical initiator, selected from the group of salts or complexes of Mn, Fe, Cu and mixtures thereof, wherein powder (A) does not comprise a catalyst for the thermal radical initiator and wherein powder (B) does not comprise a thermal radical initiator, wherein a resin containing reactive unsaturations is present in powder (A) and/or powder (B), wherein in case the reactive unsaturations in the resin are not able to react with each other after thermal radical initiation, a co-crosslinker selected from the group of vinyl ethers, methacrylates, acrylates, vinylamides, itaconates, vinyl esters, enamines, thiols and mixtures thereof, is present in powder (A) and/or in powder (B).



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TWO COMPONENT HEAT-CURABLE POWDER COATING COMPOSITION

The invention relates to a two component heat-curable powder coating composition, a process for the preparation thereof, use of the powder coating composition to coat a substrate therewith, a substrate coated with the powder coating composition and a process for coating a substrate using the powder coating composition.

As shown by the article "Overview of the powder coatings market worldwide" by G. Maggiore in Pitture e Vernice Europe 1/92, pp. 15-22 and by the lecture by D. Richart "Powder Coating: Current Developments, Future Trends" (Waterborne, High-Solids and Powder Coatings Symposium, February 22-24, 1995), the search is still continuing for powder coating compositions which can be cured with little thermal stress of the substrate and which consequently are suitable for use on heat-sensitive substrates such as, for example, wood and plastic.

Therefore, there is a need for a powder coating composition that balances the ability to be cured at a low temperature of for example 60 to 130°C.

Furthermore, it is also important that these powder coating compositions are chemically storage stable. With 'chemically storage stable' is meant that a powder coating composition retains its curing characteristics, including flow, after storage, for example, after storage at 20°C for 2 months. In order to obtain a chemically storage stable composition, a two component powder coating composition may be used.

Flow characteristics (flow) of the powder coating compositions on the substrate can be determined by comparing the flow of the coating with PCI Powder Coating Flow panels (ACT Test Panels Inc.) at a coating thickness of approximately 60 µm. The rating of flow is from 1 to 10, with 1 representing the roughest coating and 10 representing the coating with the best flow.

A two-component heat curable powder coating composition is known from EP 0 957 141 A1 which describes a low-temperature mixture of a powder (A) and a powder (B) in which at least the powder (A) includes an unsaturated polyester resin and a free radical initiator for initiating polymerization of unsaturated polyester resins in the powder coating composition and the powder (B) includes a polymerization promoter.

A disadvantage of this two-component heat curable powder coating composition is that the cure at low temperatures of below 100°C is still insufficient.

Therefore, it is the object of the invention to provide a two-component heat curable powder coating composition which can be cured to a sufficient degree at temperatures of below 100°C.

This object is achieved by a powder coating composition comprising a
5 physical mixture of a powder (A) and a powder (B),
wherein the powder (A) comprises

- a thermal radical initiator selected from the group of peroxyesters, monoperoxycarbonates and mixtures thereof

wherein the powder (B) comprises
10 - a catalyst for the thermal radical initiator, selected from the group of salts or complexes of Mn, Fe, Cu and mixtures thereof

wherein powder (A) does not comprise a catalyst for the thermal radical initiator and wherein powder (B) does not comprise a thermal radical initiator

wherein a resin containing reactive unsaturations is present in powder (A) and/or
15 powder (B)

wherein in case the reactive unsaturations in the resin are not able to react with each other after thermal radical initiation, a co-crosslinker selected from the group of vinyl ethers, methacrylates, acrylates, vinylamides, itaconates, vinyl esters, enamines, thiols and mixtures thereof, is present in powder (A) and/or in powder (B),

20 This powder coating composition provides powder coating which is cured to an acceptable degree at temperatures of below 100°C.

With 'cure to an acceptable degree' is meant that the powder coating when cured at at most 100°C for at most 10 minutes is able to resist at least 40 acetone double rubs (ADR).

25 As an additional advantage, the powder coating composition of the invention may be advantageous from an environmental perspective.

For the purpose of the invention with one acetone double rub (ADR) is meant one back and forward movement over the surface of a coating having a thickness of approximately 60 µm using a cotton cloth drenched in acetone, which
30 cotton cloth covers a hammer head having a weight of 980 gram and a contact surface area with the coating of 2 cm². Every 20 rubs the cloth is drenched in acetone. The measurement is continued until the coating is removed (and the obtained ADR number is noted down) or until 100 ADR are reached.

With heat curable is meant within the framework of the current
35 invention that curing of the powder coating composition can be effected by using heat.

A thermal initiation system is present in the composition of the present invention to make this heat curing possible. Heat curing has the advantage that in a one step process of heating a powder coating composition without the use of additional equipment, for instance equipment that generates UV light or accelerated electrons, the powder coating can be melted and cured onto a substrate, whereas with radiation curing of a powder coating composition on a substrate two steps are needed to melt and cure a powder coating on a substrate. In such a two step of radiation curing, first the powder coating composition is melted onto the substrate using heat, after which it is cured using UV or electron beam irradiation. Heat curing is especially desirable for coating 3D objects.

Preferably, the powder coating composition of the present invention is cured at a temperature of from 60 to 130°C. More preferably, the curing temperature is at least 65°C, even more preferably at least 70°C, for example at least 75°C, for example at least 80°C. More preferably, the curing temperature is at most 125°C, even more preferably at most 120°C, in particular at most 115°C, in particular at most 110°C, for example at most 105°C or for example at most 100°C. In special cases, for example for substrates that are more heat-sensitive, it may be of advantage to cure the powder coating composition at an even lower temperature, for example at a temperature lower than 100°C, lower than 95°C, lower than 90°C or even lower than 85°C.

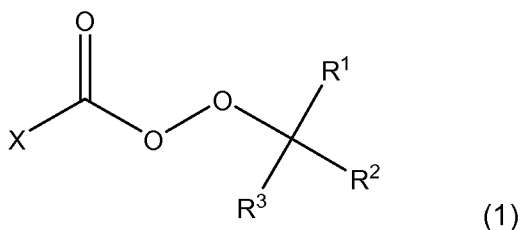
With 'powder coating composition' is meant a composition that can be applied to a substrate as a dry (without solvent or other carrier) finely divided solid, which when melted and fused, forms a continuous film that adheres to the substrate.

With a 'one component system', also called a 1K system, is meant that all (reactive) components of the powder coating composition form part of one powder. This as opposed to a two component system as used herein, also called 2K system, wherein the powder coating composition is composed of at least two different powders with different chemical compositions, which keeps the reactive components physically separated. The at least two different powders may be mixed in a physical blend before the powder coating composition is put in the storage container or may be mixed just before applying the 2K system to a substrate to let a curing reaction take place. The compositions of the at least two different powders in the 2K system are usually selected such that each powder contains an ingredient which is needed for curing but is absent from the other powder(s). This separation allows preparation of the individual powder composition in a heated state (such as by melt mixing) without the initiation of the cure reaction.

The curing of the powder coating composition according to the invention takes place by means of heat; that is the powder coating composition is heat curable. The thermal radical initiator with the help of the catalyst for the thermal radical initiator upon heating generates (free) radicals able to initiate polymerization of the reactive unsaturations in the resin in combination with the unsaturated groups in the co-crosslinker or the polymerization of the reactive unsaturations in the resins.

The amounts of catalyst for the thermal radical initiator and the thermal radical initiator are calculated based on the amount of resin and co-crosslinker (the resin system) in the powder coating composition. In other words, for purpose of determining the amount of catalyst for the thermal radical initiator and the thermal radical initiator, the resin system is defined as the resin containing the reactive unsaturations plus the co-crosslinker, excluding the usual powder coating composition additives like pigments, fillers etc.

The thermal radical initiator in the powder coating composition is selected from the group of peroxyesters, monoperoxycarbonates and mixtures thereof. Preferably, the peroxide is a peroxyester or monoperoxycarbonate of formula (1)



wherein R^1 , R^2 and R^3 each independently stand for an alkyl, and wherein X stands for R^4 or for OR^4 , wherein R^4 stands for an alkyl, an aryl or for an oligomer or polymer.

Preferably, R^1 , R^2 and R^3 each independently stand for an alkyl of 1 to 6 C-atoms, more preferably for methyl or ethyl. Most preferably, the peroxide is a compound of formula (1), wherein R^1 stands for methyl, R^2 stands for methyl and R^3 stands for ethyl or methyl. Preferably, the peroxide is t-butyl peroxybenzoate, t-butyl peroxy-2-ethyl hexanoate, t-amyl peroxy (2-ethyl) hexanoate or t-butyl peroxy-2-ethylhexyl carbonate.

Preferably R^4 stands for an aryl of 6 to 20 C-atoms, preferably R^4 stands for phenyl, or R^4 stands for an alkyl of 1 to 20 C-atoms, more preferably for an alkyl of 6 to 12 C-atoms.

The peroxyesters and/or monoperoxycarbonates according to formula (1) suitable for use in the composition of the present invention are peroxides that are

capable of initiating a radical crosslinking reaction with the reactive unsaturations in the resin that is present in the powder coating composition.

It is of course also possible to use mixtures of peroxides of formula (1) in the powder coating composition of the invention.

5 The optimal amount of peroxide of formula (1) is dependent on the choice of transition metal and of the peroxyester or monoperoxycarbonate, but can easily be determined by the person skilled in the art through routine experimentation. Usually, the amount of peroxide of formula (1) is at least 1 mmol peroxide/kg resin, preferably at least 10, more preferably at least 25 mmol peroxide/kg resin. Usually, the
10 amount of peroxide of formula (1) is at most 1000, preferably at most 500, for example at most 250 or at most 200 mmol peroxide/kg resin system.

 Examples of peresters include tert-butyl peroxybenzoate (Trigonox C), tert-butyl peroxyacetate (Trigonox F-C50), tert-amyl peroxybenzoate (Trigonox 127), tert-amyl peroxyacetate (Trigonox 133-CK60), tert-butyl-2-ethylhexanoate
15 (Trigonox 21S), tert-butylperoxydiethylacetate (Trigonox 27), di-tert-butylperoxypivalate (Trigonox 25-C75), tert-butyl peroxyneohexanoate (Trigonox 257-C75) and cumylperoxyneodecanoate (Trigonox 99-C75). Examples of monopercarbonates include tert-butyl peroxy-2-ethylhexylcarbonate (Trigonox 117), tert-butyl peroxyisopropylcarbonate (Trigonox BPIC75), and tert-amylperoxy-2-
20 ethylhexylcarbonate (Trigonox 131). It should be noted that Trigonox is a trademark from Akzo Nobel.

 The catalyst for the thermal radical initiator is chosen from the group of salts and complexes of Mn, Fe, Cu and mixtures thereof. These catalysts are advantageous from an environmental perspective. Most preferably, the catalyst for the
25 thermal radical initiator is a salt or complex of Cu.

 The salt or complex part of the transition metal catalysts is preferably organic, for example organic acid transition metal salts or derivatives thereof, for example transition metal carboxylates or transition metal acetoacetates, for example transition metal ethylhexanoate may be used. If a copper compound is used, it may for
30 example be in the form of a copper⁺ salt or a copper²⁺ salt. If a manganese compound is used, it may for example be in the form of a manganese²⁺ salt or a manganese³⁺ salt.

 The optimal amount of catalyst for the thermal radical initiator is dependent on the choice of catalyst for the thermal radical initiator and of the thermal radical initiator, but can easily be determined by the person skilled in the art through
35 routine experimentation. Generally, the amount of catalyst for the thermal radical

initiator may be chosen in the range of from 0.00001 to 25 mmol catalyst for the thermal radical initiator/kg resin system.

Depending on the combined reactivity of the thermal radical initiator and the catalyst for the thermal radical initiator, one or more inhibitors may optionally be present in powder (A) and/or powder (B) if the reactivity is too high. The inhibitor may be added to the resin, for example before, during or just after the resin synthesis. Alternatively, the inhibitor may be directly added to the powder.

Examples of inhibitors are preferably chosen from the group of phenolic compounds, stable radicals, catechols, phenothiazines, hydroquinones, benzoquinones and mixtures thereof, more preferably from the group of stable radicals, catechols, phenothiazines, hydroquinones, benzoquinones and mixtures thereof.

Examples of phenolic compounds include 2-methoxyphenol, 4-methoxyphenol, 2,6-di-t-butyl-4-methylphenol, 2,6-di-t-butylphenol, 2,6-di-6-butyl-4-ethyl phenol, 2,4,6-trimethyl-phenol, 2,4,6-tris-dimethylaminomethyl phenol, 4,4'-thio-bis(3-methyl-6-t-butylphenol), 4,4'-isopropylidene diphenol, 2,4-di-t-butylphenol and 6,6'-di-t-butyl-2,2'-methylene di-p-cresol.

Examples of stable radicals include 1-oxyl-2,2,6,6-tetramethylpiperidine, 1-oxyl-2,2,6,6-tetramethylpiperidine-4-ol (a compound also referred to as TEMPOL), 1-oxyl-2,2,6,6-tetramethylpiperidine-4-one (a compound also referred to as TEMPON), 1-oxyl-2,2,6,6-tetramethyl-4-carboxyl-piperidine (a compound also referred to as 4-carboxy-TEMPO), 1-oxyl-2,2,5,5-tetramethylpyrrolidine, 1-oxyl-2,2,5,5-tetramethyl-3-carboxylpyrrolidine (also called 3-carboxy-PROXYL and galvinoxyl (2,6-di-tert-butyl- α -(3,5-di-tert-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-p-tolyloxy).

Examples of catechols include catechol, 4-t-butylcatechol, and 3,5-di-t-butylcatechol.

Examples of hydroquinones include hydroquinone, 2-methylhydroquinone, 2-t-butylhydroquinone, 2,5-di-t-butylhydroquinone, 2,6-di-t-butylhydroquinone, 2,6-dimethylhydroquinone and 2,3,5-trimethylhydroquinone.

Examples of benzoquinones include benzoquinone, 2,3,5,6-tetrachloro-1,4-benzoquinone, methylbenzoquinone, 2,6-dimethylbenzoquinone, and naphthoquinone.

Other suitable inhibitors may for example be chosen from the group of an aluminium-N-nitrosophenyl hydroxylamine, a diethylhydroxylamine and a phenothiazine.

It is also possible to use a mixture of (the above mentioned) inhibitors. Preferably as an inhibitor hydroquinones are used. Examples of hydroquinone inhibitors (hydroquinones) include hydroquinone, 2-methylhydroquinone, 2-t-butylhydroquinone, 2,5-di-t-butylhydroquinone, 2,6-di-t-butylhydroquinone,
5 2,6-dimethylhydroquinone and 2,3,5-trimethylhydroquinone.

Preferably a methylhydroquinone, more preferably 2-methylhydroquinone or a t-butylhydroquinone, more preferably 2-t-butylhydroquinone is used.

The resin contains reactive unsaturations in which the reactive
10 unsaturations are carbon carbon double bonds connected directly to an electron withdrawing group. With reactive unsaturations is meant that the carbon carbon double bonds connected directly to an electron withdrawing group are reactive towards radicals generated by a thermal radical initiator. For the avoidance of doubt, reactive unsaturations do not include aromatic rings.

15 In the two-component powder coating composition, a resin containing reactive unsaturations is present in powder (A) and/or powder (B). It is of course also possible to use more than one resin in the two-component powder coating composition.

The WPU can for example be determined using ¹H-NMR, for example as described in Journal of Applied Polymer Science, Vol. 23, 1979, pp 25-38, the
20 complete disclosure of which is hereby incorporated by reference, or by the method as described herein in the experimental section. In the method of the experimental section, the weight per unsaturation (WPU) was determined via ¹H-NMR on a 300 MHz Varian NMR-spectrometer using pyrazine as internal standard.

Alternatively, the WPU may be determined theoretically by dividing
25 the Mn by the amount of unsaturations as added during the synthesis of the resin and/or the co-crosslinker.

Examples of suitable resins include polyesters, polyacrylates (= acrylic resins), polyurethanes, epoxy resins, polyamides, polyesteramides, polycarbonates, polyureas etc., as well as mixtures thereof. Preferably the resin is a
30 polyester.

The reactive unsaturations (the carbon carbon double bonds connected directly to an electron withdrawing group) may be present in the backbone of the resin, pendant on the (backbone of the) resin, at the terminus of the resin or at a combination of these locations. Preferably resins having reactive unsaturations based
35 on fumaric acid, maleic acid and/or itaconic acid, more preferably resins having

reactive unsaturations based on fumaric acid and/or maleic acid are used in the powder coating composition of the present invention.

Examples of how to introduce the reactive unsaturation in the resin are described below.

5 Polyesters are generally polycondensation products of polyalcohols and polycarboxylic acids.

 Examples of polycarboxylic acids which may be used in the preparation of a polyester include isophthalic acid, terephthalic acid, hexahydroterephthalic acid, 2,6-naphthalenedicarboxylic acid and 4,4'-oxybisbenzoic
10 acid, 3,6-dichlorophthalic acid, tetrachlorophthalic acid, tetrahydrophthalic acid, hexahydroterephthalic acid, hexachloroendomethylenetetrahydrophthalic acid, endomethylenetetrahydrophthalic acid, phthalic acid, azelaic acid, sebacic acid, decanedicarboxylic acid, adipic acid, succinic acid and trimellitic acid. These illustrative acids can be used in their acid form or where available, in the form of their anhydrides,
15 acyl chlorides or lower alkyl esters. Mixtures of acids can also be used. In addition hydroxycarboxylic acids and lactones can be used. Examples include hydroxypivalic acid and ϵ -caprolactone.

 Polyalcohols, in particular diols, can be reacted with the carboxylic acids or their analogues as described above to prepare the polyester. Examples of
20 polyalcohols include aliphatic diols, for example, ethylene glycol, propane-1,2-diol, propane-1,3-diol, butane-1,2-diol, butane-1,4-diol, butane- 1,3-diol, 2,2-dimethylpropane-1,3-diol (neopentyl glycol), hexane-2,5-diol, hexane-1,6-diol, 2,2-bis- (4-hydroxycyclohexyl)-propane (hydrogenated bisphenol-A), 1,4-dimethylolcyclohexane, diethylene glycol, dipropylene glycol and
25 2,2-bis[4-(2-hydroxyethoxy)- phenyl]propane, the hydroxypivalic ester of neopentylglycol and 4,8-bis-(hydroxymethyl)tricyclo[5,2,1,0]decane (= tricyclodecane dimethylol) and 2,3-butenediol.

 Trifunctional or more functional alcohols (together: polyols) or acids can be used to obtain branched polyesters. Examples of suitable polyols and polyacids
30 are glycerol, hexanetriol, trimethylolethane, trimethylolpropane, pentaerythritol and trimellitic acid.

 Monofunctional acids, for example para-tert-butyl benzoic acid, benzoic acid, metha-toluic acid, cinnamic acid, crotonic acid may be used to block the polymer chain.

Preferably, the resin in the powder coating composition of the present invention is a polyester prepared from at least the following monomers: terephthalic acid, neopentylglycol and/or propylene glycol. For branching trimethylolpropane may be present in the polyester.

5 The polyesters can be prepared via customary, generally known polymerization methods by esterification and/or transesterification or by esterification and/or transesterification via the use of an enzyme. For example, if needed, customary esterification catalysts such as, for example, butylchlorotindihydroxide, dibutyltin oxide, tetrabutyl titanate or butyl stannic acid can be used. Examples of amounts of these
10 esterification catalysts used are usually around 0.1 wt% based on the total weight of the polyester.

The conditions of preparation of the polyester and the COOH/OH ratio can be chosen such that end products are obtained which have an acid value or hydroxyl value which is within the intended range of values.

15 Preferably, the viscosity of the polyester resin is in the range of from 2 to 30 Pa.s as measured at 160°C using the method as described herein.

The resin can also be a polyacrylate, also known as acrylic resin. Generally, an acrylic resin is based on alkyl esters of (meth)acrylic acid optionally in combination with styrene. These alkyl esters of (meth)acrylic acid may be replaced by
20 hydroxyl or glycidyl functional (meth)acrylic acids. Examples of alkyl esters of (meth)acrylic acid include, for example ethyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, n-propyl (meth)acrylate, isobutyl (meth)acrylate, ethylhexyl acrylate, cyclohexyl (meth)acrylate and mixtures thereof.

To obtain an acrylic resin having a hydroxyl functionality, the acrylic
25 resin contains a hydroxyl functional (meth)acrylic acid, preferably in combination with alkyl esters of (meth)acrylic acid. Examples of hydroxyl functional (meth)acrylic acid esters include hydroxyethyl (meth)acrylate, and hydroxypropyl (meth)acrylate etc..

To obtain an acrylic resin having a glycidyl functionality, the acrylic resin contains a glycidyl functional (meth)acrylic acid esters, preferably in combination
30 with alkyl esters of (meth)acrylic acid. Examples of glycidyl functional (meth)acrylic acid esters include glycidyl methacrylate, etc..

Clearly, it is also possible to synthesize acrylic resins with both hydroxyl and glycidyl functionality.

Polyurethanes can for example be prepared using customary, generally known polyaddition reaction of a (poly)isocyanate with a (poly)alcohol in the presence of, if needed a catalyst and other additives.

For example, if needed, customary catalysts such as, for example
5 tertiary amines or organometallic compounds, such as for example monobutyltin tris(2-ethylhexanoate), tetrabutyl titanate or dibutyl tin dilaurate can be used. Examples of amounts of these catalysts used are usually around 0.01 wt% based on the total weight of the resin.

Examples of the (poly)alcohols that may be used in the preparation of
10 polyurethanes are the same as those that can be used in the preparation of a polyester.

Examples of isocyanates that may be used in the preparation of polyurethanes include but are not limited to diisocyanates, for example toluene 2,4-diisocyanate, toluene 2,6-diisocyanate, 4,4'-diphenyl methane diisocyanate,
15 2,4'-diphenyl methane diisocyanate, 2,2'-diphenyl methane diisocyanate, hexamethylene diisocyanate, 5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethylcyclohexane (isophorone diisocyanate), m-tetramethylxylene diisocyanate, dicyclohexylmethane 4,4'-diisocyanate, naphthalene 1,5-diisocyanate or 1,4-diisocyanatobenzene; and triisocyanates, for example triphenylmethane-4,4',4''-
20 triisocyanate.

The resin may also be a polyepoxide, also known as epoxy resin. Epoxy resins may for example be prepared from phenolic compounds in combination with epichlorohydrins resulting in epoxy resins like for example a bisphenol A diglycidyl ether such as is commercially available as EpicoteTM1001 or a Novolac epoxide.

25 Polyamides can for example be prepared by a polycondensation reaction of a diamine and a dicarboxylic acid.

The dicarboxylic acids may be branched, non-linear or linear. Examples of suitable dicarboxylic acids are for example phthalic acid, isophthalic acid, terephthalic acid, 1,4-cyclohexanedicarboxylic acid, naphthalene-2,6-dicarboxylic acid,
30 cyclohexanediic acid, diphenyl-4,4'-dicarboxylic acid, phenylenedi (oxyacetic acid), sebacic acid, succinic acid, adipic acid, glutaric acid and/or azelaic acid.

Examples of suitable aliphatic diamines include for example isophorondiamine, 1,2-ethylenediamine, 1,3-propylenediamine, 1,6-hexamethylenediamine, 1,12-dodecylenediamine, 1,4 cyclohexanebismethylamine,
35 piperazine, p-xylylenediamine and/or m-xylylenediamine. The polyamide may also be

branched using branching components. Suitable examples of branching components include amines, for example di-alkylene-triamines, such as for example di-ethylene-triamine or di-hexamethylene-triamine; di-alkylene-tetramines or di-alkylene-pentamines; acids, for example 1,3,5-benzene tricarboxylic acid, trimellitic anhydride or pyromellitic anhydride; and poly-functional amino acids, such as for
5 example aspartic acid or glutamic acid.

Polyester amides are resins containing both ester bonds (as in a polyester) and amide bonds (as in a polyamide) and may for example be prepared from mono-, di-, tri- or polyfunctional monomers, such as monomers with carboxylic acid
10 functionality, monomers with hydroxyl functionality, monomers with amine functionality and/or monomers having a combination of any of these functionalities.

In principle any solid hydroxyl functional polycarbonate may be used. Hydroxyfunctional polycarbonates are commercially available from various sources.

Polyureas can for example be prepared using customary, generally
15 known polyaddition reactions of a (poly)isocyanate with a (poly)amine in the presence of, if needed a catalyst and other additives similar to what is described above for polyurethanes. Suitable (poly)amines for the preparation of polyureas include those as are exemplified above for the polyamides. Suitable (poly)isocyanates for the preparation of polyureas include those as are exemplified above for the polyurethanes.

20 The reactive unsaturation may be built into the resin backbone, for instance by reacting a hydroxyl functional monomer (such as the polyalcohols mentioned before) with an unsaturated carboxylic acid or anhydride, such as for example fumaric acid, maleic acid, citraconic acid, itaconic acid or mesaconic acid. Resins where it is possible to build reactive unsaturation into the backbone by reacting
25 a hydroxyl functional monomer with an unsaturated carboxylic acid are for example polyesters.

Also, the reactive unsaturation may be connected to a side-group on the resin, by reacting an epoxide functional pendant group in the resin, for example a glycidyl functional acrylate, with an unsaturated carboxylic acid, such as for example
30 methacrylic acid or acrylic acid or the monoesters of fumaric acid, maleic acid, citraconic acid, itaconic acid or mesaconic acid.

Also, the reactive unsaturation may be connected to a side-group on the resin, by reacting a hydroxyl functional pendant group in the resin, for example a hydroxyl functional acrylate, with an unsaturated carboxylic acid, such as for example

methacrylic acid or acrylic acid or an unsaturated carboxylic anhydride, such as for example the anhydrides of itaconic acid, maleic acid or citraconic acid.

It is also possible to connect the reactive unsaturation to the terminus (or termini) of the resin, for example by reacting a hydroxyl functional, epoxide
5 functional or amine functional terminal group with an unsaturated carboxylic acid, such as for example fumaric acid, maleic acid, citraconic acid, itaconic acid, mesaconic acid or the monoesters thereof, methacrylic acid or acrylic acid. So, a resin having a hydroxyl, amine or glycidyl terminal group may be reacted with such carboxylic acids.

Also, or alternatively, hydroxyl or amine functional resins may be
10 modified with hydroxyl functional compounds containing a reactive unsaturation via reaction with a diisocyanate forming urethane and/or urea bonds. This modification may be done both on pendant hydroxyl groups and on terminal hydroxyl groups.

The weight per unsaturation (WPU) of the resin as determined using ^1H NMR is usually less than 7500, preferably less than 1500, for example less than
15 1150 or less than 1100 or less than 1000 g/mole and/or preferably more than 100, more preferably more than 250 g/mole, for example more than 500 g/mole.

In case of an amorphous resin, the glass transition temperature (T_g) of the resin is preferably at least 20°C , more preferably at least 25°C . Preferably, the resin is a polyester having a T_g of at least 40, preferably at least 45°C and/or a T_g of at
20 most 65°C , preferably at most 60°C , for example at most 55°C , for example at most 50°C .

The amount of acid groups in a resin is determined by the titration of the acid/anhydride groups by KOH. The amount of acid groups is expressed as the acid value (AV) in mg KOH/g resin.

25 The amount of hydroxyl groups in a resin is determined by the titration of the hydroxyl groups with acetic anhydride and the back titration with KOH. The amount of hydroxyl groups is expressed as the hydroxyl value (OH-value or OHV) in mg KOH used per g resin.

A resin is classified as acid functional in case the hydroxyl value is
30 lower than the acid value. In case a carboxylic functional resin is desired, the hydroxyl value of the resin is usually below 10 mg KOH per g resin.

A resin is classified as hydroxyfunctional in case the acid value is lower than the hydroxyl value. In case a hydroxyl functional resin is desired, the acid value of the resin is usually below 10 mg KOH per g resin.

The hydroxyl value of the resin in the powder coating composition of the present invention is usually in the range of from 0 to 70 mg KOH per g resin.

It is desired to have a resin, preferably a polyester, with an acid value of less than 10, preferably less than 5 mg KOH per g resin in case a vinylether or
5 vinylester co-crosslinker is used in the powder coating composition of the present invention. In case a co-crosslinker other than a vinylether or a vinylester is used, the acid value of the resin, preferably a polyester may range from 0 to 250, for example from 0 to 60 mg KOH per g of the resin.

The number average molecular weight (M_n) of the resin is in principle
10 not critical and can for example be from 1,000 to 20,000 Da. Preferably, the M_n of the resin is at least 1,500 Da, for example at least 2,000 Da and/or preferably at most 8,000, for example at most 4,000 Da in case of an amorphous resin and/or preferably at most 15,000 Da in case of a crystalline resin. Preferably, the resin is a polyester having a number average molecular weight (M_n) in the range of from 1,500 to 8,000,
15 for example in the range of from 2,100 and 4,000Da.

In case the reactive unsaturations in the resins are not able to react with each other after radical initiation, a co-crosslinker, which co-crosslinker has the ability to react with the reactive unsaturations in the resin after radical initiation, is present in powder (A) and/or powder (B). The co-crosslinker having the ability to react
20 with the reactive unsaturations in the resin after radical initiation, is a compound having carbon carbon double or triple bonds.

Examples of suitable co-crosslinkers include those selected from the group of acrylates, methacrylates, vinylesters, vinylethers, vinyl amides, itaconates, enamines, thiols and mixtures thereof, preferably the co-crosslinker is chosen from the
25 group of vinylesters, vinylethers and mixtures thereof.

An acrylate is a monomer, oligomer or polymer having an acrylate moiety (see formula (2) in Table 1). A methacrylate is a monomer, oligomer or polymer having a methacrylate moiety (see formula (3) in Table 1). Examples of liquid (meth)acrylates include butanediol dimethacrylate hexanedioldiacrylate and
30 hydroxypropylmethacrylate. Examples of other (meth)acrylates are as given herein (see for example the part on a resin modified with (meth)acrylate). Since resins containing unsaturations based on (meth)acrylic acid can homopolymerize, a resin based on (meth)acrylic acid may be used in combination with an oligomer or polymer containing (meth)acrylic acid based unsaturations as a co-crosslinker.

A vinylester is a monomer, oligomer or polymer having a vinylester moiety (see formula (4) in Table 1). Examples of vinylesters include mono functional vinylesters, for example stearic acid vinylester, palmitic acid vinylester, benzoic acid vinylester, lauric acid vinylester, hexanoic acid vinylester, pivalic acid vinylester, oleic acid vinylester, methacrylic acid vinylester, decanoic acid vinylester, bromo acetic acid vinylester, myristic acid vinylester, valeric acid vinylester, nonanoic acid vinylester, heptanoic acid vinylester, phenyl acetic acid vinylester, maleic acid (di)vinylester, undecanoic acid vinylester, iodo acetic acid vinylester, 2-naphthoic acid vinylester, 3-chloro-butyric acid vinylester, 4-chloro-butyric vinylester and 2-chloro-butyric acid vinylester; di functional vinylesters, such as for example adipic acid divinylester, fumaric acid divinylester, sebacic acid divinylester, phthalic acid divinylester and terephthalic acid divinylester; and polyfunctional vinylesters, for example trimellitic acid trivinylester.

A vinylether is a monomer, oligomer or polymer having a vinylether moiety (see formula (5) in Table 1). The co-crosslinker in the powder coating composition of the present invention is for example a vinylether. Examples of liquid vinylethers include mono (alcohol) functionalized vinylethers, for example ethyl vinylether, 4-hydroxybutyl vinylether, 2-hydroxyethyl vinylether, diethylene glycol monovinyl ether or 4-(hydroxy methyl) cyclohexyl methyl vinyl ether (1,4-cyclohexanedimethanol vinyl ether); di alcohol functionalized vinylethers, such as for example butanediol divinylether, diethyleneglycol divinylether, triethyleneglycol divinylether, tetraethyleneglycol divinylether, poly-THFTM 290-divinylether, hexanediol divinylether, 1,4-cyclohexanedimethanol divinylether; tri alcohol functionalized vinylethers, for example trimethylol propane trivinylether, 1,2,4-trivinylcyclohexane; and mono amino functional vinylethers, for example 3-amino propyl vinyl ether.

For example, a vinylether may be prepared from a dimethylester and a hydroxyfunctional vinylether under formation of a vinyletherester.

Examples of amorphous or semi-crystalline vinyl ethers include vinylether urethanes, vinylether polyester urethanes, vinylether ureas and vinylether polyester ureas. The polyester part of a vinylether polyester urethane is generally a polycondensation product of polyalcohols and polycarboxylic acids and may have the same monomers and may be synthesized analogous to the synthesis of polyesters as described above. The polyester part of vinylether polyester urethane may be saturated or unsaturated and may be similar to the resin.

In order to prepare a vinyl ether urethane, isocyanate may be reacted with a hydroxyfunctional vinyl ether and/or a polyalcohol. To prepare a vinyl ether polyester urethane, an isocyanate may be reacted with a hydroxyfunctional vinyl ether and a hydroxyfunctional polyester (for example a polyester as described above). These reactions are customary, generally known polyaddition reaction of a (poly)isocyanate with a (poly)alcohol in the presence of, if needed, a catalyst and other additives. Some examples of catalysts, other additives, polyalcohols and isocyanates are given herein (see for example the part on polyurethanes).

Examples of vinyl ethers also include vinyl ether polyesters, which for example can be prepared from acid functional polyesters (for example as exemplified herein) with hydroxyfunctional vinyl ethers (for example as exemplified herein). Of course, it is also possible to prepare vinyl ether polyesters via transesterification of hydroxyfunctional or alkylfunctional polyesters with hydroxyfunctional vinyl ethers.

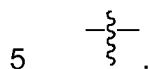
A vinylamide is a monomer, oligomer or polymer having a vinylamide moiety (see formula (6) in Table 1).

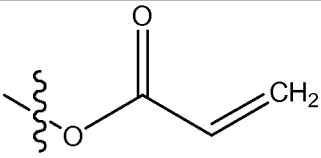
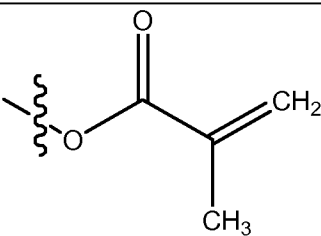
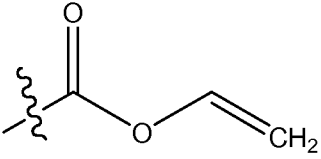
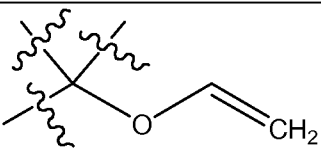
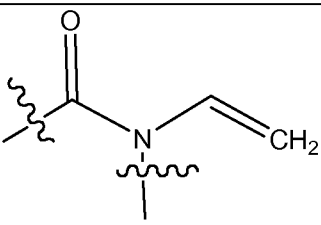
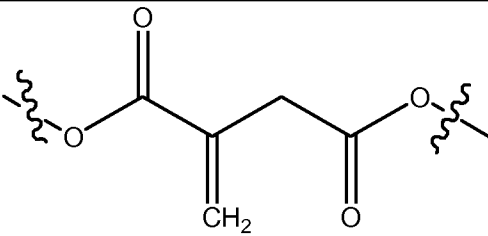
An itaconate is a monomer, oligomer or polymer having an itaconate moiety (see formula (7) in Table 1). Examples of liquid itaconates include diethylitaconate, dibutylitaconate, etc. Examples of solid itaconates include dimethylitaconate. Examples of amorphous itaconates are as given above (see for example the part on a resin modified with monoesters of itaconic acid or itaconic acid). Since resins containing unsaturations based on itaconic acid can homopolymerize, a resin containing itaconic acid based unsaturations may be used in combination with an oligomer or polymer containing itaconic acid based unsaturations as a co-crosslinker.

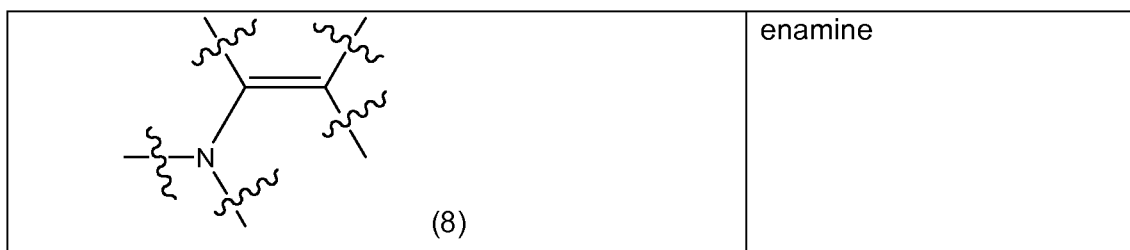
An enamine is a monomer, oligomer or polymer having an enamine moiety (see formula (8) in Table 1).

As defined herein, a monomer has an M_n below 500Da, an oligomer has an M_n below 1,500Da and a polymer has an M_n of at least 1,500Da.

Table 1. The co-crosslinker for use in the composition of the present invention, is chosen from the group of monomers, oligomers or polymers comprising one or more of the following moieties: (meth)acrylate, vinylester, vinylether, vinyl amide, itaconate and/or enamine moieties. The points of attachment of the moieties are indicated with



Structure formula	name
 (2)	acrylates
 (3)	methacrylate
 (4)	vinylester
 (5)	vinylether
 (6)	vinyl amide
 (7)	itaconate



In case the carbon carbon double bonds directly connected to an electron withdrawing group in the resin are capable of reacting with the resin itself (i.e. the resin is homopolymerizable) as may be the case for some resins containing

5 acrylate, methacrylate or itaconate moieties, the resin and the co-crosslinker may contain the same moieties, and in a special embodiment, the presence of a separate co-crosslinker is therefore optional and the resin and the co-crosslinker may be the same.

In case the resin is incapable of homopolymerization, a separate

10 co-crosslinker needs to be present to obtain curing. For the avoidance of doubt, within the framework of the invention, a resin can homopolymerize if the reactive unsaturations in the resins are able to react with each other after radical initiation by the thermal radical initiator.

The separate co-crosslinker may be (semi-)crystalline or amorphous.

15 Also, a liquid co-crosslinker may be used. Preferably, the co-crosslinker is non-volatile at the temperatures and pressures used when processing, applying and storing the powder coating composition.

The weight per unsaturation of the co-crosslinker as determined using ^1H NMR is preferably lower than 870 g/mole, for example lower than 680 g/mole,

20 for example lower than 650 g/mole, for example lower than 630 g/mole and/or preferably higher than 70, more preferably higher than 100, for example higher than 150 g/mole. The M_n of the co-crosslinker is not critical and may vary between wide ranges, for example the M_n may be between 100 and 20,000 Da.

The amount of co-crosslinker used in the powder coating composition

25 is in principle not critical, especially if a homopolymerizable resin is used. In case the resin is not capable of homopolymerization, for example, the molar ratio of the unsaturations in the co-crosslinker and the unsaturations in the resin may be between 9:1 and 1:9, preferably between 2:1 and 1:2. Preferably, in this case, about equimolar amounts of unsaturations in the co-crosslinker and resin are used.

In one embodiment of the invention, the resin containing the reactive unsaturations and the optional co-crosslinker are present in both powder (A) and in powder (B).

In another embodiment of the invention, the hydroquinone inhibitor is
5 present in both powder (A) and in powder (B).

In yet another embodiment of the invention, the resin containing the reactive unsaturations, the optional co-crosslinker and the hydroquinone inhibitor are present in both powder (A) and in powder (B).

The preparation of powder coating compositions is described by
10 Misev in "Powder Coatings, Chemistry and Technology" (pp. 224-300; 1991, John Wiley) hereby incorporated by reference.

A common way to prepare a powder is to mix the separately weighed-out components in a premixer, heat the obtained premix, for example in a kneader, preferably in an extruder to obtain an extrudate, cool down the obtained extrudate until
15 it solidifies and crush it into granules or flakes that are further grinded to reduce the particle size followed by appropriate classification to obtain a powder of the right particle size.

To obtain a two-component powder coating composition, at least two powders are physically mixed.

20 The invention also relates to a process for the preparation of a two component powder coating composition according to the invention comprising the steps of:

- (a) forming the powder (A) using a method as known per se
- (b) forming the powder (B) using a method as known per se
- 25 (c) physically mixing powder (A) and powder (B) to form the two component powder coating composition.

In another aspect, the invention relates to a process for coating a substrate comprising the following steps:

- 1) applying a powder coating composition according to the invention to a
30 substrate such that the substrate is partially or fully coated with a coating.
- 2) heating the obtained partially or fully coated substrate for such time and to such temperature such that the coating is at least partially cured.

The powder coating composition of the present invention may be applied using the techniques known to the person skilled in the art, for example using
35 electrostatic spray or electrostatic fluidized bed.

Heating of the coated substrate may be done using conventional methods, such as with a convection oven and/or with an (N)IR lamp. Even microwave equipment may be used to heat the substrate.

The time during which the coating is at least partially cured is preferably below 60 minutes and usually above 1 minute in case a convection oven is used to heat the coating. More preferably, the curing time is below 40 minutes in case a convection oven is used to heat the coating.

The temperature at which the coating is cured is preferably below 130°C and usually above 60°C. Preferably, the curing temperature is lower than 120°C, more preferably lower than 110°C, most preferably lower than 100°C, most preferably lower than 95°C. Preferably, the curing temperature is at least 65°C, more preferably 70°C, even more preferably at least 75°C.

The powder coating composition of the present invention may optionally contain the usual additives, such as for example fillers/pigments, degassing agents, flow agents, or (light) stabilizers. It should be noted that none of these usual additives are considered to be transition metal compounds. Examples of flow agents include BykTM 361 N. Examples of suitable fillers/pigments include metal oxides, silicates, carbonates or sulphates. Examples of suitable stabilizers include UV stabilizers, such as for example phosphonites, thioethers or HALS (hindered amine light stabilizers). Examples of degassing agents include benzoin and cyclohexane dimethanol bisbenzoate. Other additives, such as additives for improving tribo-chargeability may also be added.

In another aspect, the invention relates to a substrate that is fully or partially coated with a powder coating based on the heat-curable powder coating composition according to the present invention.

In one embodiment of the invention the substrate is a non heat-sensitive substrate, for example glass, ceramic, fibre cement board, or metal, for example aluminum, copper or steel. In another embodiment of the invention, the substrate is a heat-sensitive substrate. Therefore, the invention also relates to use of a powder coating composition of the invention to coat a heat-sensitive substrate, preferably wood.

Heat-sensitive substrates include plastic substrates, wood substrates, for example solid wood, such as for example: hard wood, soft wood, plywood; veneer, particle board, low density fibre board, medium density fibreboard and high density fibreboard, OSB (Oriented Strand Board) wood laminates, chipboard and other

substrate in which wood is a important constituent, such as for example foil covered wooden substrates, engineered wood, plastic modified wood, plastic substrates or wood plastic compounds (WPC); substrates with cellulosic fibres, for example cardboard or paper substrates; textile and leather substrates.

5 Other heat-sensitive substrates include objects that are a combination of a metal substrate with a heat-sensitive part, such as plastic hosing, heavy metal parts, strips, for example aluminium frames with heat strips etc.

Examples of plastic substrates include unsaturated polyester based compositions, ABS (acrylonitril butadiene styrene), melamine-formaldehyde resins,
10 polycarbonate, polyethylene, polypropylene, ethylene-propylene-diene monomer (EPDM), thermoplastic olefin (TPO), polyurethane (PU), polypropylene oxide (PPO), polyethylene oxide (PEO), polyethyleneterephthalate and nylon, for example polyamide 6,6 and combinations thereof, for example polycarbonate-ABS.

Other substrates that are particularly suitable for coating with the
15 powder coating of the invention are those where a low temperature cure is desired for efficient production, such as heavy metal parts.

In another aspect, the invention relates to the use of a composition according to the invention to fully or partially coat a substrate.

Also, the invention relates to the use of a powder coating composition
20 according to the invention as a stain, primer or topcoat layer.

Specific wood coating markets where the powder coating composition of the invention may be used include domestic furniture, such as tables, chairs, cabinets, etc., bedroom and bathroom furniture, office furniture, contract furniture such as school and child furniture, hospital furniture, restaurant and hotel furniture, kitchen
25 cabinets and furniture, (flat) panels for interior design, interior and exterior windows and doors, interior and exterior window frames and door frames, exterior and interior sidings and wooden flooring.

Specific plastic coating markets where the powder coating composition of the invention may be used include automotive applications, such as
30 interior car parts, wheel covers, bumpers, under the hood parts etc, flexible flooring, sporting goods, cosmetics, audio-visual applications, such as TV sets, computer housing, phones, etc., household appliances and satellite dishes.

EXAMPLES

The invention is explained in more detail with reference to the following non-limiting examples.

5 Experimental sectionSynthesis and application of the powder coatingTable 2: Chemicals

Chemical name	Commercial name	Description or use
Neopentyl glycol		Monomer
Trimethylol propane		Monomer
Terephthalic acid		Monomer
Fumaric acid		Monomer
Ethylene carbonate		Monomer
Tert-butyl peroxybenzoate	Trigonox™ C from Akzo Nobel	Initiator
Tert-butyl hydroquinone		Inhibitor
Cobalt bis(2-ethylhexanoate), also known as Cobalt octanoate	COMMET™ Cobalt Octanoate from De Monchy International B.V.	Accelerator
Harcat copper naphthenate		Accelerator
Bis-(4-vinyl oxy butyl) hexamethylenediurethane	URACROSS™ P3307 from DSM	Co-crosslinker
	Byk™ 361-N from Byk	Flow agent

Synthesis of resins : General procedure

10 The chemicals used in the following examples are described in table 2.

Resin synthesis (resin A)

15 A reaction vessel fitted with a thermometer, a stirrer and a distillation device, was filled with a tin catalyst and the monomers for the first step (all the (poly)alcohols and terephthalic acid) as listed in table 3. Stirring was then applied and a light nitrogen flow was passed over the reaction mixture while the temperature was raised to 220°C. Subsequently, for the second step fumaric acid together with a small amount of radical inhibitor was added at a temperature of 180°C followed by
 20 esterification at 220°C. When an acid value of less than approximately 15 mg KOH/g resin was reached, the reaction mixture was cooled to 205°C. The third stage of the polyester preparation was carried out under reduced pressure till an acid value of approximately 5 mg KOH/g resin was reached. The acid value of the resin was brought

below 5 mg KOH/g resin via reaction of the remaining acid-groups of the resin with ethylene carbonate. The used amount was dependent on the acid value before addition.

5 Resin analysis:

Glass transition temperature (T_g) measurements (inflection point) and melting temperature measurements were carried out via differential scanning calorimetry (DSC) on a Mettler Toledo, TA DSC821, in N₂ atmosphere and at a heating rate of 5°C/min. Viscosity measurements were carried out at 160°C, on a Rheometric Scientific CT 5 (Rm 265) apparatus (Mettler Toledo). A 30 mm spindle was used. The applied shear-rate was 70s⁻¹. The acid and hydroxyl values of the resins were determined titrimetrically according to ISO 2114-2000 and ISO 4629-1978, respectively.

The weight per unsaturation (WPU) was determined via ¹H-NMR on a 300 MHz Varian NMR-spectrometer using pyrazine as internal standard. Recorded spectra were analyzed in full with ACD software and peak areas of all peaks were calculated.

The weight resin per mole unsaturation was calculated with the following formula:

$$20 \quad WPU = \left[\frac{W_{pyr}}{W_{resin}} \frac{1}{MW_{pyr}} \frac{A_{C=C} / N_{C=C}}{A_{pyr} / N_{pyr}} \right]^{-1}$$

W_{pyr} and W_{resin} are weights pyrazine (is internal standard) and resin, respectively, expressed in the same units. MW_{pyr} is molecular weight pyrazine (= 80 gr/mole). A_{C=C} is the peak area for hydrogens attached to the carbon carbon double bonds (C=C component) of the reactive unsaturations in the resin; N_{C=C} is the number of hydrogens of that particular C=C component. A_{pyr} is the peak area for pyrazine and N_{pyr} is the number of hydrogens (= 4).

Table 2: Synthesis and properties of the resin used

Resin no.	A
Monomers	Amount (mole %)
Neopentylglycol	47.9
Trimethylol propane	3.7
Terephthalic acid	37.5
Fumaric acid	10.9
Ethylene carbonate	X
Resin characterization	
Weight per unsaturation (WPU) (theoretical)	1028
Weight per unsaturation (WPU) (measured with NMR)	1130
Mn (theoretical)	2723
Hydroxyl value (mg KOH/g)	42.7
Acid value (mg KOH/g)	3.1
Tg (°C)	46.5
Viscosity at 160°C (Pa.s)	21.2

Preparation of the powder coating composition, application and analysis:

- The compositions of the tested powder coating composition are given
- 5 in the tables below. The components were extruded at 60°C using a Prism Twin Screw extruder (200 rpm, torque > 90%). The extrudate was grinded and sieved; the sieving fractions smaller than 90 microns were used as a powder coating composition. Both powders x.1 and x.2 were dry blended in a 1:1 ratio. The dry blended powder coating compositions were applied with a corona powder application spray gun on an
- 10 aluminum ALQ panel and cured at various temperatures for 10 minutes in a convection oven (Heraeus UT 6120). The applied coating layer thickness was approximately 60 µm.

Acetone double rubs

- 15 Acetone double rubs (ADR) were carried out as described herein to determine the curing.

Preparation of the powder coating composition

The ratio resin : co-crosslinker is chosen 1:1 on mole unsaturation. The amount of initiator in the initiation system is based on the total weight of the resin system. (e.g. x mole initiator per kg resin system). The amount of inhibitor in the initiation system is based on the total weight of the resin system. The amount of accelerator in the initiation system is based on the total weight of the resin system (e.g. x mole accelerator per kg resin system). The amount of flow agent is calculated in wt% of the total powder coating composition.

10 Example 1 and comparative experiments A-

2 component powder coatings were prepared employing the compositions described below. The powders x.1 and x.2 were mixed as dry blend and applied as powder.

15 Table 3

	1.1	1.2	A.1	A.2
Resin	A	A	A	A
Co-crosslinker	Uracross™ P 3307	Uracross™ P 3307	Uracross™ P 3307	Uracross™ P 3307
Inhibitor	Tert-butyl hydroquinone 500 ppm	Tert-butyl hydroquinone 500 ppm	Tert-butyl hydroquinone 500 ppm	Tert-butyl hydroquinone 500 ppm
Initiator	Trigonox™ C 155 mmol/kg		Trigonox™ C 155 mmol/kg	
Accelerator Cobalt ethylhexanoate (10%Co)				6 mmol/kg
Accelerator Copper naphthenate (8%Cu)		6 mmol/kg		
Flow agent Byk™ 361-N	0.5 wt%	0.5 wt%	0.5 wt%	0.5 wt%
ADR reached at 80°C	40		20	
ADR reached at 90°C	95		30	

As can be seen from the above table, the composition of the invention comprising a salt or complex of Cu as a catalyst for the radical initiator provides a powder coating having a better cure at low temperatures (as can be seen from the

amount of ADRs reached) as compared to a composition comprising a salt or complex of Co as a catalyst for the radical initiator.

Furthermore, from an environmental perspective, it is desired to use a salt or complex of Cu, Fe or Mn rather than a salt or complex of Co.

CLAIMS

1. Powder coating composition comprising a physical mixture of a powder (A)
and a powder (B), wherein the powder (A) comprises
 - 5 - a thermal radical initiator selected from the group of peroxyesters,
monoperoxyarbonates and mixtures thereofwherein the powder (B) comprises
 - a catalyst for the thermal radical initiator, selected from the group of salts
or complexes of Mn, Fe, Cu and mixtures thereof
- 10 wherein powder (A) does not comprise a catalyst for the thermal radical
initiator and wherein powder (B) does not comprise a thermal radical initiator
wherein a resin containing reactive unsaturations is present in powder (A)
and/or powder (B)
wherein in case the reactive unsaturations in the resin are not able to react
15 with each other after thermal radical initiation, a co-crosslinker selected from
the group of vinylethers, methacrylates, acrylates, vinylamides, itaconates,
vinylesters, enamines, thiols and mixtures thereof, is present in powder (A)
and/or in powder (B),
2. Composition according to claim 1, wherein the catalyst for the radical initiator
20 is a salt or complex of Cu.
3. Composition according to any one of claims 1-3, wherein an inhibitor is
present in powder (A) and/or powder (B).
4. Composition according to claim 3, wherein the inhibitor is a hydroquinone
inhibitor, preferably selected from the group of methylhydroquinones and t-
25 butylhydroquinones.
5. Composition according to any one of claims 1-4, wherein the resin contains
reactive unsaturations based on maleic acid and/or on fumaric acid.
6. Composition according to any one of claims 1-5, wherein the resin is a
polyester prepared from at least the following monomers: terephthalic acid,
30 neopentylglycol and/or propylene glycol.
7. Composition according to any one of claims 1-6, wherein the co-crosslinker is
chosen from the group of vinylethers, vinylesters and mixtures thereof.
8. Composition according to any one of claims 1-7, wherein the resin containing
the reactive unsaturations and the optional co-crosslinker are present in both
35 powder (A) and in powder (B).

9. Composition according to any one of claims 3-8, wherein the inhibitor is present in both powder (A) and in powder (B).
10. Process for the preparation of a two component powder coating composition according to any one of claims 1-9 comprising the steps of
 - 5 (a) forming the powder (A) using a method as known per se
 - (b) forming the powder (B) using a method as known per se
 - (c) physically mixing powder (a) and powder (B) to form the two component powder coating composition.
11. Process for coating a substrate comprising the following steps:
 - 10 1) applying a powder coating composition according to any one of claims 1-9 to a substrate to obtain a coated substrate
 - 2) heating the coated substrate.
12. Substrate that is fully or partially coated with a powder coating composition according to any one of claims 1-9.
- 15 13. Use of a powder coating composition of any one of claims 1-9 to coat a heat-sensitive substrate, preferably wood.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2009/064733

A. CLASSIFICATION OF SUBJECT MATTER

INV. C09D5/03 C08K5/00 C08K5/13

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)

C09D C08K

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, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 957 141 A1 (FERRO CORP [US] ROHM & HAAS DENMARK FINANCE AS [DK]) 17 November 1999 (1999-11-17) cited in the application claims 1-17	1-13
A	EP 0 942 050 A2 (MORTON INT INC [US]) 15 September 1999 (1999-09-15) claims 1-18	1,10-13
A	EP 1 424 142 A1 (MORTON INT INC [US]) 2 June 2004 (2004-06-02) claims 1,11-12	1,10-13



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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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,
Fax: (+31-70) 340-3016

Authorized officer

Miao, Kathryn

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2009/064733

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0957141	A1	17-11-1999	CA 2270852 A1 11-11-1999
			DE 69914967 D1 01-04-2004
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			US 6194525 B1 27-02-2001
EP 0942050	A2	15-09-1999	NONE
EP 1424142	A1	02-06-2004	NONE