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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: ONE COMPONENT HEAT-CURABLE POWDER COATING COMPOSITION

(57) Abstract: The invention relates to a one component heat-curable powder coating composition comprising a resin containing reactive unsaturations and wherein all said reactive unsaturations are carbon carbon double bonds connected directly to an electron withdrawing group, a thermal initiation system comprising a transition metal catalyst and a peroxide, wherein the peroxide is chosen from the group of peroxyesters, mono-peroxycarbonates and mixtures thereof and a co-crosslinker chosen from the group of vinylethers, vinylesters, vinylamides, itaconates, enamines and mixtures thereof.

ONE COMPONENT HEAT-CURABLE POWDER COATING COMPOSITION

The invention relates to a 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.

Besides the desire for a powder coating composition that can be cured at low temperature, it is also desired that such a powder coating composition can still be processed in an extruder.

Therefore, there is a need for a powder coating composition that balances the ability to be cured to an acceptable degree, if cured at a low temperature of for example at most 130°C with a good processability in an extruder. Such powder coating composition would be very suitable for use not only for non heat-sensitive substrates, but in particular also for heat-sensitive substrates.

Furthermore, there is a desire to have a one component powder coating composition as opposed to a two component powder coating composition as one component powder coating compositions may provide coatings having a better properties, such as for example surface appearance, resistance to acetone, impact resistance etc.

It is therefore the object of the present invention to provide a one component heat curable powder coating composition which is easily processable in the extruder and which can be cured to an acceptable degree, if cured at a low temperature of for example at most 130°C.

This object is achieved by a one component heat-curable powder coating composition comprising a resin containing reactive unsaturations and wherein all said reactive unsaturations are carbon carbon double bonds connected directly to an electron withdrawing group, a thermal initiation system comprising a transition metal

catalyst and a peroxide, wherein the peroxide is chosen from the group of peroxyesters, mono-peroxycarbonates and mixtures thereof and a co-crosslinker chosen from the group of vinylethers, vinylesters, vinylamides, itaconates, enamines and mixtures thereof.

An additional advantage of the composition of the present invention may be acceptable flow.

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.

With easily processable in the extruder is meant that the powder coating composition can be extruded to form an extrudate without forming gel particles, preferably without forming a gel.

With 'cure to an acceptable degree' is meant that the powder coating when cured at most 130°C, for example for at most 20, preferably for at most 15 minutes, is able to resist at least 50 acetone double rubs (ADR).

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 cotton cloth covers a hammer head having a weight of 980 gram and a contact surface area with the coating of 2 cm^2. 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.

Preferably, a coating prepared from a powder coating composition of the present invention resists at least 60 ADR, for example at least 70 ADR, at least 80 ADR, at least 90 ADR or at least 100 ADR when the coating composition is applied to a substrate, for example to an aluminum substrate (for example an ALQ panel) when cured for example for at most 20, preferably for at most 15 minutes at a temperature of at most 130°C.

With heat curable is meant within the framework of the current 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.

The amounts of transition metal catalyst and peroxides are calculated based on the amount of resin and co-crosslinker (the resin system) in the powder coating composition. In other words, the resin system is the resin containing the reactive unsaturations plus the co-crosslinker, excluding usual powder coating composition additives like pigments, fillers etc.

The resin contains reactive unsaturations in which the reactive 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 initiator. For the avoidance of doubt, reactive unsaturations do not include aromatic rings.

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 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 on fumaric acid, maleic acid itaconic acid, acrylic acid and/or methacrylic 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.

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 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, 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 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 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

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.

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 stannoic acid can be used. Examples of amounts of these 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.

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 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 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

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 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 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, 2,4'-diphenyl methane diisocyanate, 2,2'-diphenyl methane diisocyanate, hexamethylene diisocyanate, 5-isocyabato-1-(isocyanatomethy)-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"-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 Epicote^{TM}1001 or a Novolac epoxide.

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, cyclohexanediacetic 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, 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 pyromelitic anhydride; and poly-functional amino acids, such as for 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 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. Hydroxyl functional polycarbonates are commercially available from various sources.

Polyureas can for example be prepared using customary, generally 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.

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 a hydroxylfunctional 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 methacrylic acid or acrylic acid or the monoesters of fumaric acid, maleic acid,

citraconic acid, itaconic acid or mesaconic acid, preferably with methacrylate or acrylic 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 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, preferably with methacrylate 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 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.

Sometimes also a small amount of inhibitor is present during the esterification to prevent loss of unsaturations due to the possible presence of peroxides in glycols and instability due to the esterification temperatures.

The weight per unsaturation (WPU) of the resin as determined using ^{1}H NMR is usually less than 7500, preferably less than 1500, for example less than 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.

The WPU can for example be determined using ^{1}H-NMR, for example as described in Journal of Applied Polymer Science, Vol. 23, 1979, pp 25-38, the 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 ^{1}H-NMR on a 300 MHz Varian NMR-spectrometer using pyrazine as internal standard, or the WPU was determined theoretically by dividing the Mn by the amount of unsaturations as added during the synthesis of the resin and/or the co-crosslinker.

In case of an amorphous resin, the glass transition temperature (Tg) of the resin is preferably at least 20°C, more preferably at least 25°C. Preferably, the

resin is a polyester having a Tg of at least 40, preferably at least 45°C and/or a Tg of at 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.

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 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 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 (Mn) of the resin is in principle not critical and can for example be from 1,000 to 20,000 Da. Preferably, the Mn 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 (Mn) in the range of from 1,500 to 8,000, for example in the range of from 2,100 and 4,000Da.

With the term 'thermal initiation system' as used herein is meant the system that triggers radical polymerization.

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

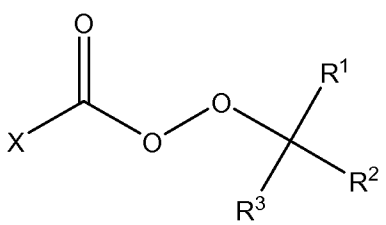
curable. The thermal initiator in the thermal initiation system upon heating generates (free) radicals able to initiate polymerization of the reactive unsaturations in the resin in combination with the unsaturated groups in the co-crosslinker or with the polymerization of the reactive unsaturations in the resins.

The transition metal catalyst may be chosen from the group of transition metal salts, transition metal complexes and mixtures thereof. Transition metals are elements with atomic numbers from/equal to 21 and up to/equal to 79. In chemistry and physics, the atomic number (also known as the proton number) is the number of protons found in the nucleus of an atom. It is traditionally represented by the symbol Z. The atomic number uniquely identifies a chemical element. In an atom of neutral charge, the atomic number is equal to the number of electrons. Examples of suitable transition metal catalysts are those salts and complexes of the following transition metals: V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, W, etc., preferably Mn, Fe, Co or Cu. From an environmental perspective, it is most preferred to use Cu, Fe or Mn.

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 example be in the form of a copper^{+} salt or a copper^{2+} salt. If a manganese compound is used, it may for example be in the form of a manganese^{2+} salt or a manganese^{3+} salt. If a cobalt compound is used, it may for example be in the form of a cobalt^{2+} salt.

The optimal amount of transition metal catalyst 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. Generally, the amount of transition metal catalyst may be chosen in the range of from 0.00001 to 25 mmol transition metal catalyst/kg resin system.

Preferably, the peroxide is a peroxyester or monoperoxycarbonate of formula (1)



(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.

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 (Trigonox 21S), tert-butylperoxydiethylacetate (Trigonox 27), di-tert-butylperoxypivalate (Trigonox 25-C75), tert-butyl peroxyneoheptanoate (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-ethylhexylcarbonate (Trigonox 131). It should be noted that Trigonox is a trademark from Akzo Nobel.

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

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 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.

The amount of thermal initiation system is preferably chosen such that when the powder coating composition is applied to a substrate and cured at a temperature of 130°C for 20 minutes, the resulting coating resists at least 50 acetone

double rubs, preferably at least 70 acetone double rubs. A method for measuring the acetone double rubs is described herein.

The composition of the invention comprises a co-crosslinker chosen from the group of vinylethers, vinylesters, vinylamides, itaconates, enamines and mixtures thereof, preferably the co-crosslinker is chosen from the group of vinylethers, vinylesters and mixtures thereof.

A vinylether is a monomer, oligomer or polymer having a vinylether moiety (see formula (2) 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-THF^{TM} 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 vinylether urethane, isocyanate may be reacted with a hydroxyfunctional vinylether and/or a polyalcohol. To prepare a vinylether polyester urethane, an isocyanate may be reacted with a hydroxyfunctional vinylether 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 vinylethers also include vinyletherpolyesters, which for example can be prepared from acid functional polyesters (for example as exemplified herein) with hydroxyfunctional vinylethers (for example as exemplified herein). Ofcourse, it is also possible to prepare vinyletherpolyesters via transesterification of hydroxyfunctional or alkylfunctional polyesters with hydroxyfunctional vinylethers.

A vinylester is a monomer, oligomer or polymer having a vinylester moiety (see formula (3) 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.

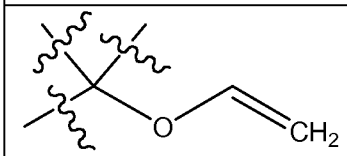
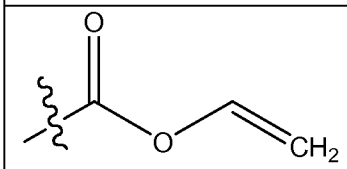
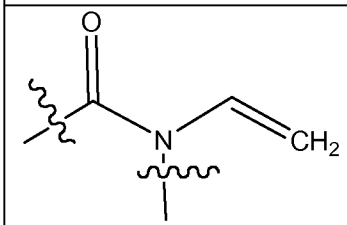
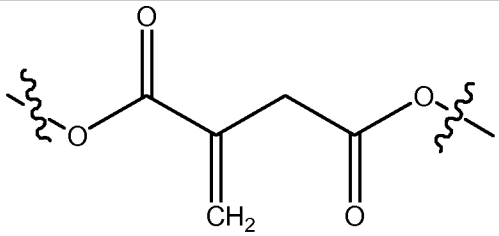
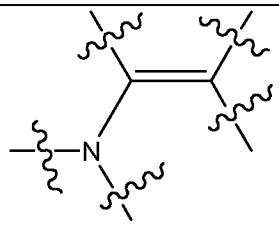
A vinylamide is a monomer, oligomer or polymer having a vinylamide moiety (see formula (4) in Table 1).

An itaconate is a monomer, oligomer or polymer having an itaconate moiety (see formula (5) 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 (6) in Table 1).

As defined herein, a monomer has an Mn below 500Da, an oligomer has an Mn below 1,500Da and a polymer has an Mn 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: vinylether, vinylester, vinyl amide, itaconate and/or enamine moieties. The points of attachment of the moieties are indicated with .

Structure formula	name
 (2)	vinylether
 (3)	vinylester
 (4)	vinyl amide
 (5)	itaconate
 (6)	enamine

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 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 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 radical initiator.

The separate co-crosslinker may be (semi-)crystalline or amorphous. 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 ^{1}H NMR is preferably lower than 870 g/mole, 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 Mn of the co-crosslinker is not critical and may vary between wide ranges, for example the Mn may be between 100 and 20,000 Da.

The amount of co-crosslinker used in the powder coating composition 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. For example, about equimolar amounts of unsaturations in the co-crosslinker and resin may be used.

With a 'one component system' as used herein, 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, 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.

Depending on the reactivity of the initiation system besides the peroxide and the transition metal catalyst, one or more inhibitors and/or one or more co-accelerators may optionally be present in the initiation system. In case the reactivity of the initiation system is too high, one or more inhibitors may be added to the initiation system. Alternatively, the inhibitor may be added to the resin, for example during the resin synthesis. Therefore, the invention also relates to the powder coating composition of the invention further comprising an inhibitor.

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.

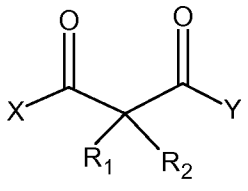
Examples of benzoquinones include benzoquinone, 2,3,5,6-tetrachloro-1,4-benzoquinone, methylbenzoquinone, 2,6-dimethylbenzoquinone, and napthoquinone.

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 or catechols, more preferably hydroquinones, most preferably 2-methylhydroquinone or 2-t-butylhydroquinone are used, depending on the choice of (type and amount of) transition metal compound.

Examples of suitable co-accelerators include 1,3-dioxocompounds, bases and thiol containing compounds.

The 1,3-dioxo compound is preferably a 1,3-dioxo compound having the following formula:



(A)

wherein X,Y = H, C_1-C_{20} alkyl, C_6-C_{20} aryl, alkylaryl, arylalkyl, part of a resin chain, OR_3, NR_3R_4; R_1, R_2, R_3, and R_4 each individually may represent hydrogen (H), or a C_1-C_{20} alkyl, aryl, alkylaryl or arylalkyl group, that each optionally may contain one or more hetero-atoms (e.g. oxygen, phosphor, nitrogen or sulphur atoms) and/or substituents; a ring may be present between R_1 and R_2, R_1 and R_3, and/or between R_2 and R_4; R_3 and/or R_4 may be part of a polymer chain, may be attached to a polymer chain or may contain a polymerizable group. Preferably, X and/or Y are/is C_1-C_{20} alkyl and/or C_6-C_{20} aryl. More preferably, X and/or Y are/is a methyl group. Preferably, the 1,3-dioxo compound is acetylacetone. The 1,3-dioxo compound may be a resin or may be polymerizable.

Other examples of 1,3-dioxo compounds include 1,3-diketones, 1,3-dialdehydes, 1,3-ketoaldehydes, 1,3-ketoesters, and 1,3-ketoamides.

Examples of suitable base co-accelerators are organic bases or inorganic bases. Inorganic bases are for example alkali metal or earth alkali metal compounds. The organic base is preferably a nitrogen containing compound, preferably an amine.

Examples of suitable thiol-containing compounds that may be used as a co-accelerator include aliphatic thiols, more preferably primary aliphatic thiols. The aliphatic thiol is preferably an α-mercapto acetate, a ß-mercapto propionate, a

dodecylmercaptane or a mixture thereof. The thiol-functionality of the thiol-containing compound in the powder coating composition is preferably ≥ 2, more preferably ≥ 3.

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

A common way to prepare a powder coating composition 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 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 coating composition of the right particle size. Therefore, the invention also relates to a process for the preparation of a powder coating composition according to the invention comprising the steps of:

a. mixing the components of the powder coating composition to obtain a premix
b. heating the obtained premix, preferably in an extruder, to obtain an extrudate
c. cooling down the obtained extrudate to obtain a solidified extrudate and
d. breaking the obtained solidified extrudate into smaller particles to obtain the powder coating composition.

Preferably, the premix is heated to a temperature at least 5°C, more preferably at least 10°C below the temperature at which it is intended to cure the powder coating composition. If the premix is heated in an extruder, it is preferred to use a temperature control in order to avoid too high temperatures that could lead to curing of the powder coating composition in the extruder.

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 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 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. Examples of flow agents include Byk™ 361 N. Examples of suitable fillers/pigments include metal oxides, silicates, carbonates or sulphates. It should be noted that none of these usual additives are considered to be transition metal catalysts. 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.

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, 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 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 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 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 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.

In a special embodiment, the invention relates to the use of a powder coating composition of the invention to coat a heat-sensitive substrate, preferably wood.

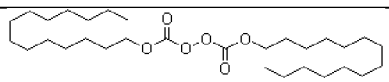
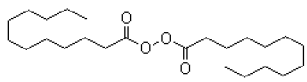
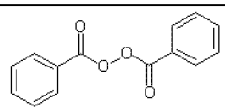
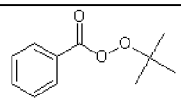
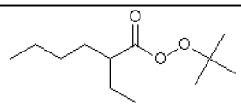
EXAMPLES

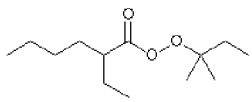
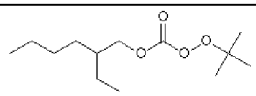
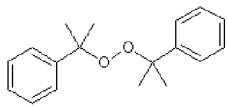
The invention is explained in more detail with reference to the following non-limiting examples.

Examples

Synthesis and application of the powder coating

Table 2: Chemicals

Chemical name	Structure	Commercial name	Description or use
Propylene glycol			Monomer
Neopentyl glycol			Monomer
Trimethylol propane			Monomer
Hydrogenated bis-phenol A			Monomer
Terephthalic acid			Monomer
Isophthalic acid			Monomer
Fumaric acid			Monomer
Hydroxylbutyl vinylether			Monomer
Isophoronediisocyanate			Monomer
Ethylene carbonate			Monomer
2,3-epoxy propyl neodecanoate			Monomer
Dimyristyl peroxy dicarbonate		Perkadox™ 26 from Akzo Nobel	Initiator
Dilauroyl peroxide		Laurox™ S from Akzo Nobel	Initiator
Dibenzoyl peroxide (BPO)		Luperox™ A75 from Arkema	Initiator
Tert-butyl peroxybenzoate		Trigonox™ C from Akzo Nobel	Initiator
Tert-butyl peroxy-2-ethyl hexanoate		Trigonox™ 21-S from AkzoNobel	Initiator

Chemical name	Structure	Commercial name	Description or use
Tert-amyl peroxy (2-ethyl) hexanoate		Trigonox™ 121 from AkzoNobel	Initiator
Tert-butyl peroxy-2-ethylhexyl carbonate		Peroxan™ BEC from Perkan	Initiator
Dicumyl peroxide		Perkadox™ BC-FF from AkzoNobel	Initiator
Tert-butyl hydroquinone			Inhibitor
Cobaltbis(2-ethylhexanoate), also known as Cobalt octanoate		COMMET™ Cobalt Octanoate from De Monchy International B.V.	Accelerator
		Octa Soligen™ Manganese 10 from OMG Borchers	Accelerator
Harcat copper naphthenate			Accelerator
Iron acetate			Accelerator
		Byk™ -361 N from Byk	Flow agent

Synthesis of resins: General procedure

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

Resin synthesis (resin A)

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 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 at 205°C 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 an epoxy or an alkylene carbonate group (see table 3 which chemical is used). The used amount was dependent on the acid value before addition.

Resin synthesis (resin B)

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 esterification at 205°C. When an acid value of less than approximately 30 mg KOH/g resin was reached, the third stage of the polyester preparation was carried out under reduced pressure at 205°C 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 an epoxy (see table 3 which chemical is used). The used amount was dependent on the acid value before addition.

Resin and co-crosslinker analysis:

Glass transition temperature (Tg) measurements (inflection point) and melting temperature measurements were carried out via differential scanning calorimetry (DSC) on a Mettler Toledo, TA DSC821, in N_2 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 ^{1}H-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:

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

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 of the reactive unsaturations (C=C component) 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 3 Synthesis and properties of the resins used

Resin no.	A	B
Monomers	Amount (mole %)	Amount (mole %)
Propylene glycol		34.8
Neopentylglycol	47.9	
Trimethylol propane	3.7	0.5
Terephthalic acid	37.5	44.4
Fumaric acid	10.9	20.2
Ethylene carbonate	X	
2,3-epoxy propyl neodecanoate		X
Resin characterization		
Weight per unsaturation (WPU) (theoretical)	1028	502
Weight per unsaturation (WPU) (measured with NMR)	1130	536
Mn (theoretical)	2723	2612
Hydroxyl value (mg KOH/g)	42.7	43.8
Acid value (mg KOH/g)	3.1	1.3
Tg (°C)	46.5	48.1
Viscosity at 160°C (Pa.s)	21.2	7.6

Synthesis of vinyl ether based co crosslinkers: General procedure

Method to determine presence of free-NCO.

An FT-IR spectra was recorded on a Varian Excalibur apparatus equipped with an ATR (Golden Gate) accessories. A characteristic peak for free NCO

can be found at 2250 cm^{-1}. Presence of a peak at this position refers to free NCO groups.

Co-crosslinker synthesis (I)

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, isophthalic acid) as listed in table 4. 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 a vinylether as listed in table 4 and a tin catalyst were added at a temperature of 120°C. Subsequently, an isocyanate as listed in table 4 was dosed such that the reaction mixture was kept below 120°C during addition. After all isocyanate was dosed, the temperature was kept or set at 120°C and maintained at this temperature for approximately half an hour. Next, n-butanol was added until all free NCO had reacted (measured using FT-IR as described above). The temperature was kept at 120°C and vacuum (0.1 bar) was applied to remove all volatiles. After vacuum the content of the vessel was discharged.

Table 4. Synthesis and properties of the co-crosslinker

Co-crosslinker	I
Type	Vinylether urethane
	Amount (mole %)
Hydroxyl butyl vinyl ether	28.5
Isophorone diisocyanate	28.5
Hydrogenated bisphenol A	14.3
Neopentylglycol	14.3
Isophthalic acid	14.3
Co-crosslinker characterization	
Mn (theoretical)	1152
Weight per unsaturation in g/mole (WPU) (theoretical)	576
Weight per unsaturation in g/mole (WPU) (determined using ^{1}H NMR)	623
Phase	Amorphous
Tm or Tg (°C)	Tg = 41°C
Hydroxyl value (mg KOH/g)	1.0
Acid value (mg KOH/g)	0.5
Viscosity at 160°C (Pa.s)	3.9

Preparation of the powder coating composition, application and analysis:

The compositions of the tested powder coating composition are given 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. The powder coating compositions were applied with a corona powder application spray gun on an aluminum ALQ panel and cured at various temperatures for 15 minutes in a convection oven (Heraeus UT 6120). The applied coating layer thickness was approximately 60 µm.

Acetone double rubs

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

Within the framework of the invention, an acceptable cure is defined as the ability of a powder coating composition cured for 15 minutes to withstand at least 50 acetone double rubs (ADR), more preferably at least 70 acetone double rubs. The cure temperature (in °C) at which the powder coating composition can withstand at least 50 ADR or at least 70 ADR is defined herein as the $T_{>50\ ADR}$, respectively $T_{>70\ ADR}$ for purposes of the invention, this temperature is less than 130°C.

Preparation of the powder coating composition

The ratio resin : co-crosslinker is chosen 3:2 on mole unsaturation. The amount of initiator in the thermal initiation system is based on the total weight of the resin system (e.g. x mole initiator per kg resin system; The resin system is the resin containing the reactive unsaturations plus the co-crosslinker excluding the usual powder coating composition additives, like pigments, fillers etc.). 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. In all powder coating compositions 0.8 wt% flow agent is used, unless indicated differently.

Example 1.

Table 5 Influence of the choice of peroxide on the cure of the powder coating composition.

Exp-#	1.1	1.2	1.3	1.4	comparative example 1.5	comparative example 1.6	comparative example 1.7	comparative example 1.8
Resin	A	A	A	A	A	A	A	A
Co-crosslinker	I	I	I	I	I	I	I	I
Initiation system								
Initiator	Trigonox™ C 92.0 mmol/kg	Trigonox™ 21-S 92.0 mmol/kg	Trigonox™ 121 92.0 mmol/kg	Peroxan™ BEC 92.0 mmol/kg	Perkadox™ 26 92.0 mmol/kg	Laurox™ S 92.0 mmol/kg	Luperox™ A75 92.0 mmol/kg	Perkadox™ BC-FF 92.0 mmol/kg
Chemical name	Tert-butyl peroxybenzoate	Tert-butyl peroxy-2-ethyl hexanoate	Tert-amyl peroxy (2-ethyl) hexanoate	Tert-butyl peroxy-2-ethylhexyl carbonate	Dimyristyl peroxy dicarbonate	Dilauroyl peroxide	Dibenzoyl peroxide	Dicumyl peroxide
Inhibitor	Tert-butyl hydroquinone 500 ppm	Tert-butyl hydroquinone 500 ppm	Tert-butyl hydroquinone 500 ppm	Tert-butyl hydroquinone 500 ppm	Tert-butyl hydroquinone 500 ppm	Tert-butyl hydroquinone 500 ppm	Tert-butyl hydroquinone 500 ppm	Tert-butyl hydroquinone 500 ppm
Accelerator	Co 3.0 mmol/kg	Co 3.0 mmol/kg	Co 3.0 mmol/kg	Co 3.0 mmol/kg	Co 3.0 mmol/kg	Co 3.0 mmol/kg	Co 3.0 mmol/kg	Co 3.0 mmol/kg
Extrusion	Ok	Ok	Ok	Ok	Gel	Ok	Ok	Ok
$T_{> 50 ADR}$ (°C)	100	90	80	120		120°C	120	> 130°C
$T_{> 70 ADR}$ (°C)	100	100	80	120		> 130°C	130	> 130°C

As can be seen from the above table 5, the use of peresters and mono-percarbonates, preferably of peresters results in a coating that can be cured to an acceptable level if cured for 15 minutes at a relatively low temperature (below 130°C), whereas the use of other peroxides results in coatings that cannot be cured to an acceptable level at these low temperatures.

These experiments were conducted with a resin having a WPU of 1130; in case a resin with a lower WPU is used with a similar initiation system (the peroxide + transition metal catalyst and optionally an inhibitor), $T_{>50\ ADR}$ will be lower.

Example 2 Initiation systems without cobalt.

Table 6 Different initiation systems without cobalt.

Exp-#	comparative example 2.1	comparative example 2.2	comparative example 2.3	comparative example 2.4	comparative example 2.5	comparative example 2.6	comparative example 2.7	comparative example 2.8
Resin	A	A	A	A	A	A	A	A
Co-crosslinker	I	I	I	I	I	I	I	I
Initiation system								
Initiator	Trigonox™ C 92.0 mmol/kg	Trigonox™ 21-S 92.0 mmol/kg	Trigonox™ 121 92.0 mmol/kg	Peroxan™ BEC 92.0 mmol/kg	Perkadox™ 26 92.0 mmol/kg	Laurox™ S 92.0 mmol/kg	Luperox™ A75 92.0 mmol/kg	Perkadox™ BC-FF 92.0 mmol/kg
Chemical name	Tert-butyl peroxybenzoate	Tert-butyl peroxy-2-ethyl hexanoate	Tert-amyl peroxy (2-ethyl) hexanoate	Tert-butyl peroxy-2-ethylhexyl carbonate	Dimyristyl peroxy dicarbonate	Dilauroyl peroxide	Dibenzoyl peroxide	Dicumyl peroxide
Inhibitor	Tert-butyl hydroquinone 500 ppm	Tert-butyl hydroquinone 500 ppm	Tert-butyl hydroquinone 500 ppm	Tert-butyl hydroquinone 500 ppm	Tert-butyl hydroquinone 500 ppm	Tert-butyl hydroquinone 500 ppm	Tert-butyl hydroquinone 500 ppm	Tert-butyl hydroquinone 500 ppm
Accelerator	-	-	-	-	-	-	-	-
Extrusion	Ok	Ok	Ok	Ok	Gel	Ok	Ok	Ok
$T_{>50\ ADR}$ (°C)	>130	>130	>130	>130		120	>130	>130
$T_{>70\ ADR}$ (°C)	>130	>130	>130	>130		>130	>130	>130

As can be seen from the results present in table 6 and table 5, by comparing examples 1.1, 1.2, 1.3 and 1.4 with respectively 2.1, 2.2, 2.3 and 2.4, a transition metal catalyst, for example cobalt is required to ensure sufficient cure at a temperature of below 130°C for 15 minutes in case a perester or monopercarbonate is used in the powder coating composition of the invention.

Example 3 Amount of peroxide needed to ensure sufficient cure.

Table 7 Different amounts of Trigonox™ C.

Exp-#	3.1	3.2	3.3	3.4	3.5	3.6	3.7	3.8
Resin	B	B	B	B	B	B	B	B
Co-crosslinker	I	I	I	I	I	I	I	I
Initiation system								
Initiator	Trigonox™ C 3.8 mmol/kg	Trigonox™ C 9.2 mmol/kg	Trigonox™ C 18.4 mmol/kg	Trigonox™ C 36.8 mmol/kg	Trigonox™ C 55.2 mmol/kg	Trigonox™ C 73.6 mmol/kg	Trigonox™ C 92.0 mmol/kg	Trigonox™ C 184.0 mmol/kg
Chemical name	Tert-butyl peroxybenzoate	Tert-butyl peroxybenzoate	Tert-butyl peroxybenzoate	Tert-butyl peroxybenzoate	Tert-butyl peroxybenzoate	Tert-butyl peroxybenzoate	Tert-butyl peroxybenzoate	Tert-butyl peroxybenzoate
Inhibitor	Tert-butyl hydroquinone 500 ppm	Tert-butyl hydroquinone 500 ppm	Tert-butyl hydroquinone 500 ppm	Tert-butyl hydroquinone 500 ppm	Tert-butyl hydroquinone 500 ppm	Tert-butyl hydroquinone 500 ppm	Tert-butyl hydroquinone 500 ppm	Tert-butyl hydroquinone 500 ppm
Accelerator	Co 3.0 mmol/kg	Co 3.0 mmol/kg	Co 3.0 mmol/kg	Co 3.0 mmol/kg	Co 3.0 mmol/kg	Co 3.0 mmol/kg	Co 3.0 mmol/kg	Co 3.0 mmol/kg
$T_{>50\ ADR}$ (°C)	>130	>130	110	110	100	90	90	80
$T_{>70\ ADR}$ (°C)	>130	>130	110	110	100	90	90	90

As can be seen from the above table 7, the optimal amount of perester or monopercarbonate can easily be determined by the person skilled in the art.

Example 4 Amount of cobalt needed to ensure sufficient cure

Table 8 Different amounts of cobalt

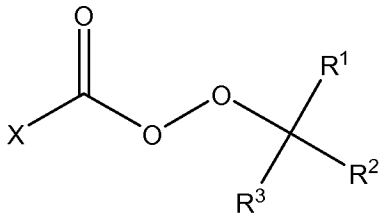
Exp-#	4.1	4.2	4.3	4.4	4.5	4.6	4.7	4.8	4.9
Resin	B	B	B	B	B	B	B	B	B
Co-crosslinker	I	I	I	I	I	I	I	I	I
Initiation system									
Initiator	Trigonox™ C 73.6 mmol/kg	Trigonox™ C 73.6 mmol/kg	Trigonox™ C 73.6 mmol/kg	Trigonox™ C 73.6 mmol/kg	Trigonox™ C 73.6 mmol/kg	Trigonox™ C 73.6 mmol/kg	Trigonox™ C 73.6 mmol/kg	Trigonox™ C 73.6 mmol/kg	Trigonox™ C 73.6 mmol/kg
Chemical name	Tert-butyl peroxybenzoate	Tert-butyl peroxybenzoate	Tert-butyl peroxybenzoate	Tert-butyl peroxybenzoate	Tert-butyl peroxybenzoate	Tert-butyl peroxybenzoate	Tert-butyl peroxybenzoate	Tert-butyl peroxybenzoate	Tert-butyl peroxybenzoate
Inhibitor	Tert-butyl hydroquinone 500 ppm	Tert-butyl hydroquinone 500 ppm	Tert-butyl hydroquinone 500 ppm	Tert-butyl hydroquinone 500 ppm	Tert-butyl hydroquinone 500 ppm	Tert-butyl hydroquinone 500 ppm	Tert-butyl hydroquinone 500 ppm	Tert-butyl hydroquinone 500 ppm	Tert-butyl hydroquinone 500 ppm
Accelerator	-	Co 0.5 mmol/kg	Co 1.0 mmol/kg	Co 1.5 mmol/kg	Co 2.0 mmol/kg	Co 3.0 mmol/kg	Co 4.5 mmol/kg	Co 6.0 mmol/kg	Co 12.0 mmol/kg
$T_{> 50 ADR}$ (°C)	>130	120	100	100	100	90	90	90	90
$T_{> 70 ADR}$ (°C)	>130	120	100	100	100	90	90	90	90

As can be seen from the above table 8, the person skilled in the art can easily determine using routine experimentation the optimal amount of transition metal catalyst.

CLAIMS

1. One component heat-curable powder coating composition comprising
   - a resin containing reactive unsaturations and wherein all said reactive unsaturations are carbon carbon double bonds connected directly to an electron withdrawing group
   - a thermal initiation system comprising a transition metal catalyst and a peroxide,
     wherein the peroxide is chosen from the group of peroxyesters, mono-peroxycarbonates and mixtures thereof and
   - a co-crosslinker chosen from the group of vinylethers, vinylesters, vinylamides, itaconates, enamines and mixtures thereof.

2. Composition according to claim 1, wherein the peroxide is a peroxyester or monoperoxycarbonate of formula (1)



(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.

3. Composition according to claim 1 or claim 2, wherein 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.

4. Composition according to any one of claims 1-3, wherein the transition metal catalyst is a Mn, Fe, Co or Cu salt or complex.

5. Composition according to any one of claims 1-4, wherein the co-crosslinker is chosen from the group of vinylethers, vinylesters and mixtures thereof.

6. Composition according to any one of claims 1-5, wherein the resin is a polyester.

7. Composition according to any one of claims 1-6, wherein the composition further comprises an inhibitor.

8. Composition according to claim 7, wherein the inhibitor is a hydroquinone or a catechol, more preferably a hydroquinone.

9. Composition according to any one of claims 1-8, wherein the amount of thermal initiation system is preferably chosen such that when the powder coating composition is applied to a substrate and cured at a temperature of 130°C for 20 minutes, the resulting coating resists at least 50 acetone double rubs.

10. Process for the preparation of a powder coating composition according to any one of claims 1-9 comprising the steps of:
    a. mixing the components of the powder coating composition to obtain a premix
    b. heating the premix, preferably in an extruder, to obtain an extrudate
    c. cooling down the extrudate to obtain a solidified extrudate and
    d. breaking the solidified extrudate into smaller particles to obtain the powder coating composition.

11. Process for coating a substrate comprising the following steps:
    1) applying a powder coating composition according to any one of claims 1-9 to a substrate
    2) heating the substrate.

12. Substrate that is fully or partially coated with a powder coating composition according to any one of claims 1-9.

13. Use of a powder coating composition of any one of claims 1-9 to coat a heat-sensitive substrate.

14. Use according to claim 13, wherein the heat-sensitive substrate is wood.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/064728

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D5/03 C08K5/00 C09D167/00

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 0 844 286 A1 (MORTON INT INC [US]) 27 May 1998 (1998-05-27) claims 1-3,15-17,18,19-20	1,5-6, 11-14
A	DATABASE WPI Week 198015 Thomson Scientific, London, GB; AN 1980-26082C XP002569869 & JP 55 027324 A (ASAHI CHEM IND CO LTD) 27 February 1980 (1980-02-27) abstract	1,6
A	EP 0 957 141 A1 (FERRO CORPORATION) 17 November 1999 (1999-11-17) claims 1,6,11,12,13-14	1,6, 11-14

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
15 March 2010	31/03/2010

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Miao, Kathryn

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2009/064728

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