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(54) Title: POWDER COATING COMPOSITION

(57) Abstract: A masterbatch composition, a method for the preparation of a masterbatch composition, a powder coating composition, the use of a masterbatch composition for a powder coating composition or for increasing the opacity of a cured powder coating and a reaction product of a polyester (A) with an unsaturated component (B) is disclosed.



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Powder coating composition

The present invention relates to a masterbatch composition, a method for the preparation of a masterbatch composition, a powder coating composition, the use of a masterbatch composition for a powder coating composition or for increasing the opacity of a cured powder coating and a reaction product of a polyester (A) with an unsaturated component (B).

On basis of the techniques disclosed in the prior art it is difficult to incorporate high amounts of titanium dioxide in a powder coating composition. Generally, the TiO_2 particles are melt mixed in an extruder together with the other components of the powder coating composition. The amount of TiO_2 particles which can be incorporated in powder coating compositions of the prior art can reach levels up to a range of 35 to 40 wt.-%, based on the total amount of the powder coating composition. However, powder coating compositions on basis of conventional polyesters and epoxy resins lead to the degradation of the surface smoothness once the amount of TiO_2 particles is at the highest level, i.e., 40 wt.-%. Consequently, the amount of TiO_2 in powder coating composition is limited to a range of 35 to 40 wt.-%. The resulting opacity of the coatings is poor, i.e. full coverage can only be obtained at a relatively high film thickness of approximately 80 to 90 μm . The opacity of white pigmented powder coatings is much lower than that of liquid paints, e.g. alkyd paints which are made of alkyd resin. The limitation of opacity is most of all a problem for white pigmented and light shade powder coatings. This is most likely attributed to the poor dispersibility of the titanium dioxide in the polymer matrix.

Additionally, the incorporation of high amounts of titanium dioxide requires more mixing time and energy in an extruder which however leads to less output. Moreover, according to the prior art an increase of the amount of titanium dioxide above 40 wt.-% does not lead to a further increase in opacity.

US 2007/0248825 A1 discloses powder coating compositions comprising at least a resin, at least one anti-bridging agent and at least 40 wt.-% of a pigment. However, even though the amount of pigment has been increased to a level up to more than 40 wt.-% the opacity of the coatings obtained is not significantly increased.

SUMMARY OF THE INVENTION

It was an object of the present invention to provide a powder coating composition which can be converted to cured powder coatings having an increased opacity and to provide a special resin system for this purpose. Further, it was an object of the present invention to provide powder coatings with reduced film thicknesses, thus saving coating material and cure energy.

It has surprisingly been found that a composition comprising a high amount of TiO_2 particles together with a polyester having non-terminal unsaturated groups or a mixture of polyester and an unsaturated organic compound having non-terminal unsaturated groups can be used to increase the opacity of powder coatings.

DETAILED DESCRIPTION OF THE INVENTION

A first embodiment of the invention is a composition comprising

- a) at least 40 wt.-% of TiO_2 particles and
- b) at least one component which comprises
 - b1) a reaction product of
 - i) a saturated or unsaturated polyester (A) having at least one terminal carboxyl group with
 - ii) an unsaturated organic compound (B) having at least two carbon-carbon double bonds and/or at least one carbon-carbon triple bond which are not terminal and wherein said compound (B) has at least one functional group which is capable of reacting with the carboxyl group of polyester (A) or
 - b2) a mixture of (A) and (B) or
 - b3) any mixture of b1) and b2),

wherein the wt.-% is based on the total weight of the composition.

An essential component of the composition according to the present invention is titanium dioxide (TiO_2) which is present in the form of particles. Titanium dioxide is the most widely used pigment due to its brightness and very high refractive index in which it is surpassed only by a few other materials. TiO_2 is also an effective opacifier in powder form, where it is employed as a pigment to provide opacity to products such as paints, coatings, plastics, papers, inks, foods, medicines as well as tooth pastes.

The composition according to the present invention comprises at least 40 wt.-%, preferably at least 45 wt.-%, more preferably at least 55 wt.-% of TiO_2 particles wherein the amount is based on the total weight of the composition. According to a preferred embodiment of the present invention, the titanium dioxide particles are present in the composition in an amount ranging from 40 to 80 wt.-%, preferably 42 to 70 wt.-% and most preferably 45 to 60 wt.-%, based on the total weight of the composition.

The opacity is improved by optimal particle size of the titanium dioxide particles. Therefore, according to a preferred embodiment of the present invention the composition comprises particles of titanium dioxide having an average particle size of 0.05 to 0.5 μm , preferably 0.08 to 0.4 μm and more preferably 0.1 to 0.3 μm determined according to BS ISO 13318-3:2004: Centrifugal X-ray method.

According to a preferred embodiment the composition of the present invention comprises TiO_2 particles having an oil absorption capacity of 12 to 22 $\text{cm}^3/100\text{g}$, preferably 14 to 20 $\text{cm}^3/100\text{g}$, most preferably of 16 to 19 $\text{cm}^3/100\text{g}$ determined according to palette-knife-method-ISO 787, part 5.

Titanium dioxide particles within the meaning of the present invention are particles comprising at least 90 weight percent of titanium dioxide based on the total weight of the individual particle. According to a preferred embodiment the titanium dioxide particles are surface treated with oxides selected from the group of metals consisting of aluminium, silicon, zirconium and any mixture thereof.

In order to improve the processability of the TiO_2 particles the surface of said particles are preferably treated with organic components.

Examples of commercially available TiO_2 particles suitable for use herein include Kronos[®] 2160, 2340, 2315, 3645, 2222, 2305 available from Kronos; Ti-Pure[®] 706, 960 available from Du Pont; Tiona[®] 595 available from Millennium; and Tioxide TR92[®] or TR 81[®] ex Huntsman.

Component b):

The composition according to the present invention further comprises b) which is b1) or b2) or b3).

Component b1) is a reaction product of

- i) a saturated or unsaturated polyester (A) having at least one terminal carboxyl group with
- ii) an unsaturated organic compound (B) having at least two carbon-carbon double bonds and/or at least one carbon-carbon triple bond which are not terminal and wherein said compound (B) has at least one functional group which is capable of reacting with the carboxyl group of polyester (A).

Mixture b2) is a mixture of

- i) a saturated or unsaturated polyester (A) having at least one terminal carboxyl group and
- ii) an unsaturated organic compound (B) having at least two carbon-carbon double bonds and/or at least one carbon-carbon triple bond which are not terminal and wherein said compound (B) has at least one functional group which is capable of reacting with the carboxyl group of polyester (A).

b3) is any mixture of b1) and b2).

Preferably, component b) is present in an amount of at least 15 wt.-%, preferably in an amount ranging from 20 to 60 wt.-%, more preferably ranging from 45 to 55 wt.-%, wherein the wt.-% is based on the total weight of the composition.

Significantly improved results in terms of opacity of cured powder coating compositions can be obtained with a composition wherein the weight ratio of component a) to component b) is within a certain range. Therefore, according to a preferred embodiment, the weight ratio of component a) to component b) is 2:3 to 4:1, preferably 9:11 to 3.5:1 and more preferably 7:3 to 1:1.

Component b1):

Component b1), the reaction product of a polyester (A) with an unsaturated compound (B), is described in more detail below.

Polyester (A):

Polyester (A) is a saturated or unsaturated polyester which has at least one terminal carboxyl group.

Suitable polyesters are those which are based on a condensation reaction of linear aliphatic, branched aliphatic and cyclo-aliphatic polyols with aliphatic, cyclo-aliphatic and/or aromatic poly carboxylic acids and anhydrides. The ratio of polyol and acids or anhydrides is such that there is an excess of acid or anhydride over alcohol so as to form a polyester which has free carboxylic groups.

Preferred polyester (A) for use herein comprise units of, for example, isophthalic acid, terephthalic acid, 2,6-naphthalene dicarboxylic acid, 4,4'-oxybisbenzoic acid, 3,6-dichlorophthalic acid, tetrachlorophthalic acid, tetrahydrophthalic acid, trimellitic acid, pyromellitic acid, hexahydroterephthalic acid (cyclohexane dicarboxylic acid), hexachloroendomethylene tetrahydrophthalic acid, phthalic acid, azelaic acid, sebacic acid, decane dicarboxylic acid, adipic acid, succinic acid, maleic acid, fumaric acid, and mixtures thereof. These acids may be used as such, or, in so far as available as their anhydrides, acid chlorides, and/or lower alkyl esters. Preferably, the polyester is based on at least one of isophthalic acid and/or terephthalic acid. Trifunctional or higher functional acids may be used also. Examples of suitable acids include trimellitic acid or pyromellitic acid. These tri-or higher functional acids may be used as end groups or to obtain branched polyesters.

Useful polyalcohols comprise, in particular diols which can be reacted with the carboxylic acids to obtain the polyester; preferred are aliphatic diols. Examples are ethylene glycol, propane-1,2-diol, propane-1,3-diol, butane-1,2-diol, butane-1,4-diol, butane-1,3-diol, 2,2-dimethylpropane-1,3-diol (neopentyl glycol), hexane-2,5-diol, hexane-1,6-diol, 2,2-bis-(4-hydroxy-cyclohexyl)-propane (hydrogenated bisphenol-A), 1,4-dimethylolcyclohexane, diethylene glycol, dipropylene glycol, 2,2-bis[4-(2-hydroxy ethoxy)-phenyl]propane, the hydroxy pivalic ester of neopentyl glycol, 2-ethyl-2-butyl propane-1,3-diol, 2-ethyl-2-methyl propane-1,3-diol and 2-methylpropane-1,3-diol.

Tri-or higher functional alcohols may be used in order to obtain branched polyesters. Examples of suitable polyols include glycerol, hexanetriol, trimethylol ethane, trimethylol propane, tris-(2-hydroxyethyl)-isocyanurate, penta erythritol and sorbitol.

The polyester may be prepared according to conventional procedures by esterification or transesterification, optionally in the presence of customary esterification catalysts for example dibutyltin oxide or tetrabutyl titanate. Preparation conditions and the COOH/OH ratio can be selected so as to obtain end products that have a particular desired acid number.

Polyester (A) is preferably prepared in a series of steps known to those skilled in the art. In the last step of which an aromatic or, preferably, aliphatic acid is esterified so as to obtain an acid-functional polyester. As known to those skilled in the art, in an initial step terephthalic acid is allowed to react in the presence of an excess of diol. Such reactions produce a mainly hydroxyl functional polyester. In a second or subsequent step, an acid functional polyester is obtained by allowing further acid to react with the product of the first step. A further acid

includes, among others, isophthalic acid, adipic acid, succinic anhydride, 1,4-cyclohexane dicarboxylic acid and trimellitic anhydride. If trimellitic anhydride is used at a temperature of 170-200°C, a polyester with a relatively high number of trimellitic acid end groups is obtained.

Polyester (A) preferably comprises two terminal carboxyl groups.

Preferably, polyester (A) has an acid value between 15 and 200 mg KOH/gram polyester and more preferably between 20 and 120 mg KOH/gram polyester.

According to a preferred embodiment polyester (A) has a number average molecular weight (Mn) ranging from 1000 to 20000 Dalton, preferably from 3000 to 6000 Dalton determined by gel permeation chromatography in tetrahydrofurane (THF) according to ISO 16014-1.

Compound (B):

Compound (B) is an unsaturated organic compound having at least two carbon-carbon double bonds and/or at least one carbon-carbon triple bond which are not terminal and wherein said organic compound has at least one functional group which is capable of reacting with the carboxyl group of polyester (A).

Compound (B) used to obtain component b1) has at least two carbon-carbon double and/or at least one triple bond which is not terminal. Terminal means that the carbon-carbon double or triple bond is located at the end of a main chain or a side chain of a molecule. Further, according to a preferred embodiment compound (B) is selected from the group consisting of cycloalkadiene, cycloalkyne, alkadiene, alkyne, polyene or any mixtures thereof which have at least one functional group which is capable of reacting with the carboxyl group of polyester (A).

In order to form the reaction product b1) it is necessary that compound (B) has at least one, preferably two or more, functional group(s) which is/are capable of reacting with the carboxyl group of polyester (A). Preferably, compound (B) comprises at least one functional group selected from the group consisting of hydroxy, amino, epoxy, carboxyl, anhydride, ester, amide and imino. According to an especially preferred embodiment compound (B) comprises at least one functional group selected from the group consisting of hydroxyl, amino, epoxy and imino. Compound (B) can also comprise two or more different functional groups, e.g. hydroxyl and amino.

Good results have been achieved if compound (B) has a number average molecular weight of at least 300 g/mol. Preferably the compound (B) has a number average molecular weight ranging from 400 to 10000 Dalton, more preferably ranging from 500 to 5000 Dalton.

The number average molecular weight can be determined by gel permeation chromatography in tetrahydrofuran (THF) according to ISO 16014-1.

It has been found that the density of unsaturation of compound (B) has an impact on the opacity of the powder coating compositions for which component b) can be used.

Therefore, according to a preferred embodiment compound (B) has an iodine value of at least 50 $\text{gl}_2/100\text{g}$, preferably at least 90 $\text{gl}_2/100\text{g}$ according to DIN 53241.

Preferably, compound (B) is a functionalized homopolymer of butadiene or a copolymer of butadiene with a vinyl or allyl compound selected from the group consisting of acrylonitrile, styrene, acrylic acid, methacrylic acid, acrylic or methacrylic acid esters, maleic acid and maleic acid anhydride.

The homopolymers or copolymers of butadiene are functionalized with groups which are capable of reacting with the carboxyl group of polyester (A), preferably the functional groups are selected from the group consisting of amino, hydroxy, epoxy, carboxy and anhydride. Functionalized homopolymers or copolymers of butadiene can be prepared by methods known to the person skilled in the art.

According to a further preferred embodiment compound (B) is selected from the group consisting of dimerized or trimerized unsaturated fatty acid, amine terminated butadiene acrylonitrile copolymer, carboxyl terminated butadiene acrylonitrile copolymer, functionalized and partly epoxidized polybutadiene, polyamidoamine derivatives of unsaturated fatty acid dimers or trimers, butyne diol, or any mixture or reaction product thereof.

Especially preferred as component b1) is a reaction product of a saturated polyester (A) having a number average molecular weight (M_n) ranging from 3000 to 6000 Dalton with compound (B) having a number average molecular weight of at least 300 Dalton, preferably selected from the group consisting of dimerized unsaturated fatty acid, amine terminated butadiene-acrylonitrile copolymer, carboxyl terminated butadiene acrylonitrile copolymer and partly epoxidised polybutadiene.

Usually, the reaction of polyester (A) with unsaturated compound (B) is carried out under conditions wherein the temperature does not exceed 250 °C, preferably at temperatures not higher than 220 °C.

Mixture b2):

b2) is a mixture of polyester (A) and compound (B).

The composition of the present invention can comprise a mixture of polyester (A) and compound (B). Preferred embodiments of polyester (A) and compound (B) are as defined above.

According to a preferred embodiment mixture b2) comprises (A) and (B) in a weight ratio of (A) to (B) which ranges from 5000:1 to 2:1, preferably 1000:1 to 10:1.

Preferably, the composition according to the present invention is solid at 25 °C. Preferably, the glass transition temperature of the composition is higher than 25°C.

Another further embodiment of the present invention is a method for the preparation of a masterbatch composition comprising the steps:

- a) providing a composition according to the present invention, and
- b) melt mixing the composition provided in step a) at a temperature of at least 60°C.

Preferably melt mixing step b) is conducted at a temperature in the range of 70 to 200°C, more preferably in a range of 80 to 140°C.

According to a preferred embodiment melt mixing step b) is conducted for at least 30 sec, more preferably in a range from 40 to 120 sec.

Preferably the composition according to the present invention is premixed at 25°C. The premixing step can be conducted in a blender drum for a time sufficient to thoroughly mix the component of the composition according to the present invention, e.g. 10 to 20 min.

The melt mixing step is preferably conducted in an extruder, more preferably in a single screw extruder such as Buss TCS 30 or in a twin screw extruder. In the extruder the composition provided in step a) is melt mixed, preferably at a temperature of 60 to 200°C, more preferably 70 to 140 °C and a residence time of at least 30 sec, more preferably for a residence time in a range from 40 to 120 sec.

A further embodiment of the present invention is a masterbatch composition which is obtainable or obtained by the method for the preparation of a masterbatch composition according to the present invention.

The masterbatch composition of the invention is used as an essential component of a powder coating composition in order to increase the opacity of the cured powder coatings made thereof.

A further embodiment of the present invention is a powder coating composition comprising

- a) a masterbatch composition of the invention and
- b) at least 10 wt.-% of an epoxy resin,

wherein the wt.-% is based on the total weight of the powder coating composition.

The powder coating composition of the invention comprises an epoxy resin which is present in an amount of at least 10 wt.-%, preferably at least 15 wt.-% based on the total weight of the powder coating composition. An epoxy resin within the meaning of the present invention is an organic component comprising at least one epoxy group.

The powder coating composition according to the present invention preferably comprises an epoxy resin having a softening temperature of at least 60°C, preferably at least 70 °C, more preferably at least 80°C and most preferably in a range of 85 to 120°C determined according to DIN 51920 on a Mettler apparatus.

Further, a powder coating composition is preferred wherein the epoxy resin has an epoxy content of at least 0.5 eq/kg, preferably in a range of 1.2 to 3.0 eq./kg and more preferably in a range of 1.25 to 1.6 eq/kg determined according to ISO 3001.

Suitable epoxy resin include, for example, epoxidized oils wherein the oil is linseed oil, soybean oil, safflower oil, oiticica oil, caraway seed oil, rapeseed oil, castor oil, dehydrated castor oil, cotton seed oil, wood oil, vernonia oil (a natural oil), sunflower oil, peanut oil, olive oil, soybean leaf oil, maize oil, fish oil such as, for example, herring or sardine oil, and non-cyclic terpene oils. The epoxidized oil is preferably epoxidized soybean oil and/or epoxidized linseed oil.

Especially preferred epoxy resin are glycidyl ethers of aromatic components having at least one phenolic hydroxyl group. Preferred are bisphenol A or bisphenol F diglycidyl ethers which are preferably further reacted with bisphenol A or bisphenol F, or any mixture thereof.

The powder coating composition preferably additionally comprises one or more additive(s) selected from the group consisting of pigment, filler, flow agent, matting agent, degassing aids, curing catalysts, or any mixtures thereof.

Very suitable additives include for example additives which improve the tribo-charging properties of a polyester/epoxy system and additives which inhibit discoloration that may be caused by overbake or hardening in a gas oven.

The additives may comprise a flow-promoting agent, a degassing agent and if desired a stabilizer and/or a catalyst.

The powder coating composition of the invention is preferably obtainable or obtained by a method comprising the steps:

- a) preparing a masterbatch composition according to the method for the preparation of a masterbatch composition of the present invention, and
- b) mixing the masterbatch composition obtained in step a) with a composition comprising at least 10 wt.-% of an epoxy resin.

Preferably, the masterbatch composition according to the present invention is premixed with the epoxy resin and optionally other components of the powder coating composition at 25°C for preferably 10 to 20 min.

According to a preferred embodiment step b) of the method for the preparation of the powder coating composition is a melt mixing step, which is conducted at a temperature of at least 60°C, preferably in the range of 70 to 200°C, more preferably in a range of 80 to 140°C. Preferably, step b) is a melt mixing step which is conducted for at least 30 sec, preferably in a range from 40 to 120 sec.

The melt mixing step is preferably conducted in an extruder, more preferably in a single screw extruder or a twin screw extruder at a temperature of 60 to 200°C and preferably at a residence time of at least 30 sec, preferably 40 to 120 sec.

Optionally, the extrudate obtained is cooled and grinded, e.g. in a Retsch bench mill. Subsequently, the grinded extrudate can be sieved in order to obtain a powder coating composition having a suitable particle size.

A further embodiment of the present invention is a cured powder coating obtainable or obtained by curing a powder coating composition according to the present invention.

Preferably, the powder coating composition according to the present invention can be thermally cured. Generally, the powder coating composition is applied on a surface, e.g. a metal sheet, and subsequently the applied powder coating composition is heat cured preferably at a temperature of 150 to 250°C, more preferably 170 to 230°C, most preferably 180 to 200°C. Heat curing is preferably conducted for 5 to 40 min, more preferably 10 to 20 min. The powder coating composition according to the present invention can be applied on a substrate by techniques known to the person skilled in the art, e.g. electrostatic spraying. The film thickness of the cured powder coating composition on a substrate is preferably 20 to 100 µm, more preferably 30 to 90 µm and most preferably 40 to 70 µm.

A further embodiment of the present invention is the use of a composition according to the present invention or a masterbatch composition according to the present invention for a powder coating composition or for increasing the opacity of a cured powder coating.

The cured powder coatings according to the present invention can be prepared with reduced film thickness while maintaining a high level of opacity compared to TiO₂-based powder coatings in the prior art. Additionally, since reduced film thicknesses can be used to obtain the same degree of opacity curing material and cure energy can be saved.

It has surprisingly been found that the reaction product (component b1) of polyester (A) as defined above with compound (B) as defined above can be used as a powerful additive in powder coating composition.

Thus, a further embodiment of the present invention is the reaction product of

- i) a saturated or unsaturated polyester (A) having at least one terminal carboxyl group with
- ii) an unsaturated organic compound (B) having at least two carbon-carbon double bond and/or at least one carbon-carbon triple bond which are not terminal and wherein said compound (B) has at least one functional group capable of reacting with the carboxyl group of polyester (A).

The preferred embodiments for polyester (A) and compound (B) are identical to those mentioned above in conjunction with the composition of the invention.

A further embodiment of the invention is the use of the reaction product for a powder coating composition.

EXAMPLES

The following components mentioned in Table A are used in the examples:

Component	supplier and quality
TiO ₂ particles	TiO₂ Tioxide TR 92 ex Huntsman TiO ₂ content: min. 92,5% Inorganic coating: Alumina, Zirconia Organic coating: Present Particle size: 0,24 µm Oil absorption (Palette-knife method- ISO 787/5:1980) : 18 cm ³ /100g pigment
BaSO ₄	Blanc Fix N ex Sachtleben Chemie GmbH Synthetic Barium Sulfate BaSO ₄ content (DIN EN ISO 3262-3): approx 99% pH (DIN EN ISO SC 209): approx. 9 Median Value d ₅₀ (Sed) (DIN EN ISO SC 216): approx. 3 µm
Benzoine	Benzoine ex Fluka Degasing agent
Uralac [®] P 5170	Uralac P 5170 ex DSM Solid saturated polyester resin with carboxylic end groups for so-called polyester/epoxy hybrid powder coatings -Acid value 32-38 (TM 2400: mg KOH necessary to neutralise the acid constituents in 1g polyester resin). -Tg: approx. 54°C (TM 2076: DSC-5°C/min) -Carboxylated polyester resins for powder coatings are polymers of ethylene glycol, neopentyl glycol, terephthalic acid and adipic acid. Carboxylated polyester resins for powder coatings may contain catalysts to promote the cure reaction with epoxy resins, as well as other additives (antioxidants, tribo additives, etc.)
Araldite [®] GT 6750	Araldite GT 6750 ex Huntsman Solid epoxy resin obtained via reaction of bisphenol A with liquid bisphenol A diglycidyl ester. This resin contains 2,5% flow agent

	(liquid polybutyl acrylate). Epoxy content: 1,31-1,42 Eq/kg (ISO 3001) Softening temperature (Mettler, DIN 51920): Approx. 87°C
Matrimid® 5292 A	Matrimid 5292 A ex Huntsman - bismaleimide of diamino diphenyl methane as insaturated solid modifying substance - Melting point: 150-160°C - Maleimide double bond content > 85% of theoretical
Hycar® ATBN 1300/35	Hycar ATBN 1300/35 ex NOVEON Amine terminated butadiene-acrylonitrile copolymer with following features: Mol weight: approx 3400 Amine value: 80
Hycar® CTBN 1300X13	Hycar CTBN 1300X13 ex NOVEON Carboxyl terminated butadiene-acrylonitrile copolymer with following features: Mol weight: approx 3150 Carboxyl value: 32
Pripol® 1017	Pripol 1017 ex Uniquema Dimerized fatty acid (unsaturated) Acid value (mg KOH/g): 190-197
Almatex® PD 6100	Solid Polyglycidylmethacrylate copolymer for powder coatings ex Mitsui-Toatsu Chemicals Epoxy equivalent: 980-1090
Almatex® PD 6200	Solid Polyglycidylmethacrylate copolymer for powder coatings ex Mitsui-Toatsu Chemicals Epoxy equivalent: 700-750
Almatex® PD 6300	Solid Polyglycidylmethacrylate copolymer for powder coatings ex Mitsui-Toatsu Chemicals Epoxy equivalent: 510-560
Poly BD® 600	PolyBD 600 (Sartomer): Polybutadiene epoxydized Epoxy content 2,22 Eq/kg <i>Mn 1350</i>

Examples

I) General procedure for the preparation of the masterbatch composition

The TiO₂ particles and the component b) (reaction product b1 or mixture b2) or b3) are premixed in a blender drum at 25°C for 20 min. Subsequently, the premixed composition is melt mixed in a single screw extruder (TCS 30 ex Buss; Switzerland) at a temperature of 125°C and a residence time of 30 sec (screw speed: 400 rpm).

1. Masterbatch composition A

a) Preparation of mixture A

Mixture A is obtained by mixing the following composition in a single screw extruder (TCS 30 ex Buss; (Switzerland) at a temperature of 90°C and a residence time of 30 sec (screw speed: 400 rpm).

Mixture A	Amount in wt.-%
Uralac [®] P 5170	9870
Matrimide [®] 5292A	1.30

b) Composition B

Composition A of the invention is obtained by mixing 52 wt.-% of mixture A with 48 wt.-% of Tioxide[®] TR 92.

c) Masterbatch composition A of the invention is obtained by melt mixing composition A as described above in the general procedure.

2. Masterbatch Composition B

a) Preparation of mixture B

Mixture B is obtained by mixing the following composition in a single screw extruder (TCS 30 ex Buss; (Switzerland) at a temperature of 90°C and a residence time of 30 sec (screw speed: 400 rpm).

Mixture B	Amount in wt.-%
Uralac [®] P 5170	98.75
Butyne diol	1.25

b) Composition B

Composition B is obtained by mixing 52 wt.-% of mixture B with 48 wt.-% of Tioxide TR 92.

c) Masterbatch composition B of the invention is obtained by melt mixing composition B described above in the general procedure.

3. Masterbatch Composition C

a) Preparation of mixture C

Mixture C is obtained by mixing the following composition in a lab glass reactor with anchor stirrer for 1 hour at 150°C.

Mixture C	Amount in wt.-%
Uralac [®] P 5170	98.72
CTBN 1300X13	1.28

b) Composition C

Composition C is obtained by mixing 52 wt.-% of mixture C with 48 wt.-% of Tioxide[®] TR 92.

c) Masterbatch Composition C of the invention is obtained by melt mixing composition C as described above in the general procedure.

4. Masterbatch Composition D

a) Preparation of mixture D

Mixture D is obtained by mixing the following composition in a lab glass reactor with anchor stirrer for 1 hour at 150°C.

Mixture D	Amount in wt.-%
Uralac [®] P 5170	98.72
ATBN 1300X35	1.28

b) Composition D

Composition D is obtained by mixing 52 wt.-% of mixture D with 48 wt.-% of Tioxide[®] TR 92.

c) Masterbatch composition D is obtained by melt mixing composition D as described above in the general procedure.

5. Masterbatch Composition E

a) Preparation of mixture E

Mixture E is obtained by mixing the following composition in a lab glass reactor with anchor stirrer for 1 hour at 150°C.

Mixture E	Amount in wt.-%
Uralac [®] P 5170	95.7
Pripol [®] 1017	4.3

b) Composition E

Composition E is obtained by mixing 52 wt.-% of mixture E with 48 wt.-% of Tioxide[®] TR 92.

c) Masterbatch composition E is obtained by melt mixing composition E as described above in the general procedure.

6. Masterbatch Composition F

a) Preparation of mixture F

Mixture F is obtained by mixing the following composition in a lab glass reactor with an anchor stirrer for 1 hour at 150°C.

Mixture F	Amount in wt.-%
Uralac [®] P 5170	98.72
ATBN Hycar [®] 1300X35	1.28

b) Composition F

Composition F is obtained by mixing 54 wt.-% of mixture F with 46 wt.-% of Tioxide[®] TR 92.

c) Masterbatch composition F is obtained by melt mixing composition F as described above in the general procedure.

7. Masterbatch Composition G

a) Preparation of mixture G

Mixture G is obtained by mixing the following composition in a lab glass reactor with anchor stirrer for 1 hour at 150°C.

Mixture G	Amount in wt.-%
Uralac [®] P 5170	98.72
ATBN Hycar [®] 1300X35	1.28

b) Composition G

Composition G is obtained by mixing 52.4 wt.-% of mixture G with 47.6 wt.-% of Tioxide[®] TR 92.

c) Masterbatch composition G is obtained by melt mixing composition G as described above in the general procedure.

8. Masterbatch Composition H

a) Preparation of mixture H

Mixture H is obtained by mixing the following composition in a lab glass reactor with an anchor stirrer for 1 hour at 150°C.

Mixture H	Amount in wt.-%
Uralac [®] P 5170	98.72
ATBN Hycar [®] 1300X35	1.28

b) Composition H

Composition H is obtained by mixing 48.5 wt.-% of mixture H with 51.5 wt.-% Tioxide TR 92.

c) Masterbatch composition H is obtained by melt mixing composition H as described above in the general procedure.

9. Masterbatch Composition I

a) Preparation of reaction product I

The polyester resin (Uralac P 5170, 691g) is introduced into 1 l glass 3 neck reactor equipped with a PT 100 temperature gauge, a nitrogen inlet pipe, a water condenser and a stainless steel anchor. The polyester is heated with an oil bath.

The oil bath is heated up to 175°C giving a reactor inner temperature of 160°C. The polyester resin is completely molten after 40 minutes. The epoxy resin (PolyBD 600E, 9.1g) is then introduced to the polyester and mixed for 2 hours at 160°C.

An aliquot is taken and the epoxy content is measured giving a value of 0.021 +/- 0.002 Eq/kg.

The catalyst (Benzalconium chloride 0.105g) is then added to the homogeneous mixture. The oil bath temperature is then increased to 180°C. The reactor temperature raises to 168°C. Stirring at this temperature is maintained for 2 hours.

The reaction mixture is then cooled down to 150°C, then passed through the cooling rolls and finally broken down into chips (Ø 2-3mm, thickness 1.0-1.5 mm). The measurement of epoxy content of the resulting product gives 0.009 +/- 0.002 Eq/kg. The measurement of the apparent epoxy content of the polyester resin Uralac P5170 gives 0.007 ± 0.002 Eq/kg.

b) Composition I

Composition I is obtained by mixing 52 wt.-% of reaction product I with 48 wt.-% of Tioxide TR 92.

c) Masterbatch composition I is obtained by melt mixing composition I as described above in the general procedure.

II) General procedure for the preparation of the powder coating composition as well as the cured powder coatings.

The powder coating composition which are described in the following tables have been prepared by the following general procedure.

The components of the powder coating composition are premixed in a blender drum at 25°C for 20 min. Subsequently, the premixed composition is melt mixed in a single screw extruder (TCS 30 ex Buss; Switzerland) at a temperature of 80°C and a screw speed of 400 rpm and a residence time of 30 sec.

Subsequently, the obtained extrudate is cooled to room temperature and grinded in a Retsch bench mill. The grinded extrudate is sieved on a 60 microns screen.

The powder coating composition obtained is applied on standard white/black contrast panels (T124 Metopac[®] ex Leneta) by electrostatic spraying with a Gema electrostatic gun. Subsequently, the coated pannels are heated in an electrical oven at 200°C for 20 min.

III) Determination of the parameters

The test panels with the thermally cured powder coating composition have been analysed as follows:

a) Minimum film thickness for opacity

The minimum film thickness for opacity defines the minimum film thickness which is sufficient that the black and white underlying coatings (of contrast panels) cannot be distinguished beneath the cured powder coating. The minimum film thickness which does not allow to distinguish between the coated black area and the coated white area of the panel is visually determined by three persons.

b) Parameter "Σ"

Optical colour parameter difference (ΔL and ΔE) between the white and the black parts of contrast white/black panels in the range of film thickness 50-90 μ m has been determined according to the following formula:

$$\Sigma = \Delta L(\text{White-Black}) (50\mu\text{m}) + \Delta L(\text{White-Black}) (60\mu\text{m}) + \Delta L(\text{White-Black}) (90\mu\text{m}) + \Delta E(\text{White-Black}) (60\mu\text{m}) + \Delta L(\text{White-Black}) (75\mu\text{m}) + \Delta L(\text{White-Black}) (90\mu\text{m})$$

The values in parenthesis indicate the thickness of the cured powder coating on the test panel.

ΔL and ΔE are determined according to the CIELAB (CIE 1976) on a Tricolor II apparatus of Dr. Lange, Germany.

The lower Σ the higher the opacity and, as a consequence the lower the minimum film thickness which does not allow to distinguish between the coated black area and the coated white area of the panel.

All components below are given in weight %.

Table 1: Powder coating composition

Components°	Comparative Example 1	Comparative Example 2	Example 1
Uralac® P 5170	38.50	-	-
Araldite® GT 6750	16.50	16.5	16.5
Mixture A	-	38.50	-
Masterbatch Composition A	-	-	73.5
TiO ₂ Tioxide® TR92	35.0	35.0	-
Blanc Fix N® (BaSO ₄)	9.70	9.70	9.7
Benzoine	0.30	0.30	0.3
Processing conditions	Extruder Buss TCS 30, 400 rpm, 80°C		
Coating substrate / Cure conditions	White/Black contrast panels / 200°C-20min		
Minimum film thickness for opacity	85 µm	70 µm	60 µm
Σ	2.1	1.1	1.1

Table 2: Powder coating composition

Components	Comparative Example 3	Comparative Example 4	Example 1
Uralac® P 5170	38.50	-	-
Araldite® GT 6750	16.50	16.5	16.5
Mixture B	-	38.5	-
Masterbatch Composition B	-	-	73.5
TiO ₂ Tioxide® TR92	35.0	35.0	-
Blanc Fix N® (BaSO ₄)	9.70	9.7	9.7
Benzoine	0.30	0.3	0.3
Processing conditions	Extruder Buss TCS 30, 400 rpm, 80°C		
Coating substrate / Cure conditions	White/Black contrast panels / 200°C-20min		
Minimum film thickness for opacity	85 µm	80 µm	70 µm
Σ	2.1	2.3	2.0

Table 3: Powder coating composition

Component	Comparative Example 5	Comparative Example 6	Example 3
Uralac® P 5170	38.50	-	-
Araldite® GT 6750	16.50	16.5	16.5
Mixture C	-	38.5	-
Masterbatch Composition C	-	-	73.5
TiO ₂ Tioxide® TR92	35.0	35.0	-
Blanc Fix N® (BaSO ₄)	9.70	9.7	9.7
Benzoine	0.30	0.3	0.3
Processing conditions	Extruder Buss TCS 30, 400 rpm, 80°C		
Coating substrate / Cure conditions	White/Black contrast panels / 200°C-20min		
Minimum film thickness for opacity	85 µm	60 µm	50 µm
Σ	2.1	0.8	0.4

Table 4: Powder coating composition

Component	Comparative Example 7	Comparative Example 8	Example 4
Uralac® P 5170	38.50	-	-
Araldite® GT 6750	16.50	16.5	16.5
Mixture D	-	38.5	-
Masterbatch Composition D	-	-	73.5
TiO ₂ Tioxide® TR92	35.0	35.0	-
Blanc Fix N® (BaSO ₄)	9.70	9.7	9.7
Benzoine	0.30	0.3	0.3
Processing conditions	Extruder Buss TCS 30, 400 rpm, 80°C		
Coating substrate / Cure conditions	White/Black contrast panels / 200°C-20min		
Minimum film thickness for opacity	85 µm	80 µm	60 µm
Σ	2.1	1.2	0.6

Table 5: Powder coating composition

Component	Comparative Example 9	Comparative Example 10	Example 5
Uralac® P 5170	38.50	-	-
Araldite® GT 6750	16.50	16.5	16.5
Mixture E	-	38.5	-
Masterbatch Composition E	-	-	73.5
TiO ₂ Tioxide® TR92	35.0	35.0	-
Blanc Fix N® (BaSO ₄)	9.70	9.7	9.7
Benzoine	0.30	0.3	0.3
Processing conditions	Extruder Buss TCS 30, 400 rpm, 80°C		
Coating substrate / Cure conditions	White/Black contrast panels / 200°C-20min		
Minimum film thickness for opacity	85 µm	70 µm	65 µm
Σ	2.1	1.7	1.5

Table 6: Powder coating composition

Components	Comparative Example 11	Example 6
Uralac® P 5170	41.2	-
Almatex® PD 6300	13.8	13.8
Masterbatch Composition F	-	76.2
TiO ₂ Tioxide® TR92	35.0	-
Blanc Fix N® (BaSO ₄)	9.70	9.7
Benzoine	0.30	0.3
Processing conditions	Extruder Buss TCS 30, 400 rpm, 80°C	
Coating substrate / Cure conditions	White/Black contrast panels / 200°C-20min	
Minimum film thickness for opacity	90 µm	65 µm
Σ	4.0	1.8

Table 7: Powder coating composition

Components	Comparative Example 12	Example 7
Uralac [®] P 5170	38.5	-
Almatex [®] PD 6200	16.5	16.5
Masterbatch Composition G	-	73.5
TiO ₂ Tioxide [®] TR92	35.0	-
Blanc Fix N [®] (BaSO ₄)	9.70	9.7
Benzoine	0.30	0.3
Processing conditions	Extruder Buss TCS 30, 400 rpm, 80°C	
Coating substrate / Cure conditions	White/Black contrast panels / 200°C-20min	
Minimum film thickness for opacity	90 µm	55 µm
Σ	5.7	0.7

Table 8: Powder coating composition

Components	Comparative Example 13	Example 8
Uralac [®] P 5170	33.0	-
Almatex [®] PD 6100	22.0	22.0
Masterbatch Composition H	-	68.0
TiO ₂ Tioxide [®] TR92	35.0	-
Blanc Fix N [®] (BaSO ₄)	9.70	9.7
Benzoine	0.30	0.3
Processing conditions	Extruder Buss TCS 30, 400 rpm, 80°C	
Coating substrate / Cure conditions	White/Black contrast panels / 200°C-20min	
Minimum film thickness for opacity	> 100 µm	80 µm
Σ	14.5	2.1

Table 9: Powder coating composition

Components	Comparative Example 14	Example 9
Uralac [®] P 5170	38.50	-
Araldite [®] GT 6750	16.50	16.5
Masterbatch Composition I	-	73.5
TiO ₂ Tioxide [®] TR92	35.0	-
Blanc Fix N [®] (BaSO ₄)	9.70	9.70
Benzoine	0.30	0.30
Processing conditions	Extruder Buss TCS 30, 400 rpm, 80°C	
Coating substrate / Cure conditions	White/Black contrast panels / 200°C-20min	
Minimum film thickness for opacity	85 µm	65 µm
Σ	2.1	1.7

Claims:

1. Composition comprising
 - a) at least 40 wt.-% of TiO_2 particles and
 - b) at least one component which comprises
 - b1) a reaction product of
 - i) a saturated or unsaturated polyester (A) having at least one terminal carboxyl group with
 - ii) an unsaturated organic compound (B) having at least two carbon-carbon double bonds and/or at least one carbon-carbon triple bond which are not terminal and wherein said compound (B) has at least one functional group which is capable of reacting with the carboxyl group of polyester (A) or
 - b2) a mixture of (A) and (B) or
 - b3) any mixture of b1) and b2),wherein the wt.-% is based on the total weight of the composition.
2. Composition according to claim 1 wherein the unsaturated organic compound (B) comprises at least one functional group selected from the group consisting of hydroxy, amino, epoxy, carboxyl, anhydride, ester, amide and imino.
3. Composition according to claim 1 or 2, wherein polyester (A) has a number average molecular weight (M_n) ranging from 1000 to 20000 Dalton, preferably from 3000 to 6000 Dalton determined by gel permeation chromatography in tetrahydrofuran (THF) according to ISO 16014-1.
4. Composition according to at least one of the preceding claims wherein compound (B) has an average molecular weight of at least 300 g/mol.
5. Composition according to at least one of the preceding claims wherein compound (B) has an iodine value of at least 50 $\text{gl}_2/100\text{g}$, preferably at least 90 $\text{gl}_2/100\text{g}$ according to DIN 53241.
6. Composition according to at least one of the preceding claims wherein component b) is present in an amount of at least 15 wt.-%, preferably in an amount ranging from 20 to 60 wt.-%, more preferably ranging from 45 to 55 wt.-%, wherein the wt.-% is based on the total weight of the composition.

7. Composition according to at least one of the preceding claims wherein compound (B) is a functionalized homopolymer of butadiene or a copolymer of butadiene with a vinyl or allyl compound selected from the group consisting of acrylonitrile, styrene, acrylic acid, methacrylic acid, acrylic or methacrylic acid esters, maleic acid and maleic acid anhydride.
8. Composition according to at least one of claims 1 to 6 wherein compound (B) is selected from the group consisting of dimerized or trimerized unsaturated fatty acid, amine terminated butadiene acrylonitrile copolymer, carboxyl terminated butadiene acrylonitrile copolymer, functionalized and partly epoxidized polybutadiene, polyamidoamine derivatives of unsaturated fatty acid dimer or trimer, butyne diol, or any mixture or reaction product thereof.
9. Method for the preparation of a masterbatch composition comprising the steps:
 - a) providing a composition according to at least one of the preceding claims and
 - b) melt mixing the composition provided in step a) at a temperature of at least 60°C.
10. Masterbatch composition obtainable by a method according to claim 9.
11. Powder coating composition comprising
 - a) a masterbatch composition according to claim 10 and
 - b) at least 10 wt.-% of an epoxy resin wherein the wt.-% is based on the total weight of the powder coating composition.
12. Cured coating composition obtainable by curing the powder coating composition according to claim 11.
13. Use of a masterbatch according to claim 10 or a composition according to claims 1 to 9 for a powder coating composition for increasing the opacity of a cured powder coating.
14. Reaction product of
 - i) a saturated or unsaturated polyester (A) having at least one terminal carboxyl group with
 - ii) an unsaturated organic compound (B) having at least two carbon-carbon double bond and/or at least one carbon-carbon triple bond which are not terminal and

wherein said compound (B) has at least one functional group capable of reacting with the carboxyl group of polyester (A).

15. Use of a reaction product as defined in claim 14 for the powder coating composition.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/060803

A. CLASSIFICATION OF SUBJECT MATTER

INV. C09D5/03 C08J3/24 C08J3/22 C09D163/00 C09D167/06
ADD. C08K3/22

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 C08J

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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	WO 2010/089242 A1 (HUNTSMAN ADV MAT SWITZERLAND [CH]; GOTTIS PHILIPPE [FR]) 12 August 2010 (2010-08-12) page 9, paragraph 6 page 10, paragraph 4 claims 1, 7; examples 1,3,9; table A	1-8,11, 12,14,15
A	EP 0 600 546 A1 (DSM NV [NL]) 8 June 1994 (1994-06-08) page 7, line 11 - line 12 page 8, line 37 - line 44 claims 1,5,7,9,12; examples 4,5,9	1-15
A	US 4 226 760 A (FELDMAN MARTIN L ET AL) 7 October 1980 (1980-10-07) examples 1-1	1



Further documents are listed in the continuation of Box C.



See patent family annex.

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- "O" document referring to an oral disclosure, use, exhibition or other means
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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