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(54) Title: EPOXY-FREE, HEAT CURABLE COATING SYSTEM

(57) Abrégé/Abstract:

The invention relates to an epoxy-free, heat-curable coating system of binder resin comprising a hydroxyl-terminated polyester resin with a hydroxyl number of from 20 to 200 mg KOH/g and a glass transition temperature of at least 40°C; a carboxyl-group-containing, reversibly blocked polyisocyanate; a β-hydroxyalkylamide having at least two β-hydroxyalkylamide groups per molecule; and optionally further additives. The invention also relates to a process for preparing the coating system and to the use thereof. The so-obtained epoxy-free, heat-curable coating system can be made by melt-extrusion of all its components. This coating system is toxicologically unobjectionable and can be used to produce weather-resistant protective coatings with mat surfaces.

ABSTRACT

The invention relates to an epoxy-free, heat-curable coating system of binder resin comprising a hydroxyl-terminated polyester resin with a hydroxyl number of from 20 to 200 mg KOH/g and a glass transition temperature of at least 40^0C; a carboxyl-group-containing, reversibly blocked polyisocyanate; a β-hydroxyalkylamide having at least two β-hydroxyalkylamide groups per molecule; and optionally further additives. The invention also relates to a process for preparing the coating system and to the use thereof. The so-obtained epoxy-free, heat-curable coating system can be made by melt-extrusion of all its components. This coating system is toxicologically unobjectionable and can be used to produce weather-resistant protective coatings with mat surfaces.

EPOXY-FREE HEAT-CURABLE COATING SYSTEM

The invention relates to an epoxy-free, heat-curable coating system of binder resin comprising a hydroxyl-terminated polyester resin, a blocked polyisocyanate containing carboxyl group, and a β-hydroxyalkylamide.

When heat-curable powder coatings are applied, they do not give off any organic solvents and therefore have clear ecological advantages over liquid paints. The crosslinking under heat takes place by way of polyaddition or polycondensation reactions between the functional groups contained in the binders. Typical binder systems are epoxy resins/curing agents; carboxyl-polyester/epoxies, hydroxyl-polyester/isocyanates, hydroxylacrylates/isocyanates, carboxyl-acrylates/epoxies, epoxy-acrylates/dicarboxylic acids, carboxyl-polyester/ or carboxyl-acrylates/β-hydroxyalkylamides, and so forth. The binder systems listed differ from one another not only in their technical properties as paints but especially in their resistance to outdoor weathering, but all have high-gloss surfaces, or in other words a gloss index of more than 80 (DIN 67530, angle of incidence 60^0).

There is presently an increasing need for powder coating with mat or semigloss surfaces with a gloss index of less than 60 at an angle of incidence of 60^0 (DIN 67530) and good outdoor weathering resistance for applications such as architecture, automobiles, and furniture.

The usual matting additives in the liquid paint industry, such as chalks, finely dispersed silicic acids, talcum, etc., exhibit only a very slight matting effect in powder coating, and when added in relatively large quantities, they make the technical properties for painting purposes unacceptably worse. Although additives that are incompatible with the binder, such as waxes, etc., do produce so-called silken-sheen surfaces (gloss index more than 60 at an angle incidence of 60^0), nevertheless in actual use, the enrichment of incompatible additives has undesirable effects on the surface.

US Patent 3,842,035 therefore proposes a method for preparing mat powdered paint coatings by what is known as dry-blending of finished powder coating of adequately differing reactivity, in other words powder coating with very short and very long gel times. Although this process leads to coatings of the desired mat quality, nevertheless dry blending of finished powder coating is very complicated and expensive, and demixing, especially with overspray return, means that a uniform, reproducible surface is no longer assured. There has accordingly been no lack of attempts to produce powder coating with a mat surface by coextrusion of all the components without demixing problems and with good replicability.

German laid-open Patent Application DE-A 2,324,696 proposes a process for preparing mat coatings by using a special curing agent that reacts with epoxy groups, the agent being the salt of cyclic amidines, with certain polycarboxylic acids. Cross-linking of the powdered paint occurs in this process with differing reactivity at different temperatures, and as a result microstructures that have a mat surface formed on the surface. However, the use of this process is limited to epoxy- and carboxyl-polyester/epoxy powder coating, with the exception of carboxyl-polyester/triglycidylisocyanurate (TGIC) powder coating, and therefore powder coating with adequate outdoor weathering resistance cannot be produced by this process.

European Patent EP 0,366,608 B1 also proposes a process for producing powder coating with mat surfaces. It relates to powder coating based on epoxy resins or epoxy compounds, such as triglycidylisocyanurate (TGIC) and mixtures of di, tri- or tetrakis-(β-carboxyethyl) cyclohexanones, or di-, tri- or tetrakis-(β-carboxyethyl) cyclopentanones, and carboxyl-terminated polyester resins. The mat effect is ascribed here to the differing reactivity between the aliphatic carboxyl groups of the cross-linking agent and the aromatic carboxyl groups of the carboxyl-terminated polyester resin.

Finally, German laid-open Patent Application DE-A 3,232,463 describes the production of powder coating with mat surfaces with a binder system based on hydroxyl-terminated polyester resins, epoxy compounds such as TGIC, and special reversibly blocked polyisocyanates with free carboxyl groups as cross-linking agents. The blocked polyisocyanates contain more than one blocked isocyanate group per molecule, have an acid value of from 20 to 150 mg KOH/g, preferably 25 to 80 mg KOH/g, and an NCO content/acid value quotient of 0.075 to 0.340, preferably 0.100 to 0.300. This disclosure states it to be especially surprising that the acid value or the NCO content is not solely responsible for the attainment of mat surfaces, but rather the ratio between isocyanate and carboxyl groups, even though under the usual curing conditions for powder coating, isocyanate groups and carboxyl groups react hardly at all with one another. With a binder system described in another laid-open Patent Application (EP-A 0,056,167), which also has a blocked polyisocyanate crosslinking agent containing carboxyl groups but has a different ratio of isocyanate to carboxyl, only high-gloss coatings are therefore attained.

Although the processes proposed in the European patent EP 0,366,608 B1 and the German laid-open Patent Application DE-A 3,323,463, after coextrusion of all the components, lead to mat surfaces with good outdoor weathering resistance, nevertheless both binder systems have the substantial disadvantage that they contain epoxy compounds, especially triglycidylisocyanurate (TGIC), and are therefore extraordinarily objectionable on toxicological grounds.

The object of the invention is to provide an epoxy-free, heat-curable coating system of binder resin that can be made by melt-extrusion of all the components and that in contrast to the prior art is absolutely toxicologically unobjectionable and can be used to produce especially weather-resistant protective coatings with mat surfaces.

This object is achieved with an epoxy-free, heat-curable coating system of binder resin comprising at least one hydroxyl-terminated polyester resin; at least one carboxyl-group-containing, reversibly blocked polyisocyanate; and at least one β-hydroxyalkylamide as cross-linking agent.

More particularly, this coating system comprises:

[a] at least one hydroxyl-terminated polyester resin with a hydroxyl number in the range from 20 to 200 mg KOH/g and a glass transition temperature of at least 40^0C;

[b] at least one carboxyl-group-containing, reversibly blocked polyisocyanate having at least two blocked isocyanate groups per molecule and an acid value of from 20 to 150 mg KOH/g;

[c] at least one β-hydroxyalkylamide having at least two β-hydroxyalkylamide groups per molecule; and

optionally, further additives dictated by the usage and processing.

This coating system is suitable for a two-stage cross-linking. Indeed, the hydroxyl-terminated polyester resin is suitable

a) primarily for cross-linking with β-hydroxylalkylamide, and

b) subsequently, at temperatures of approximately 160^0C, after deblocking of the polyisocyanate, for further cross-linking.

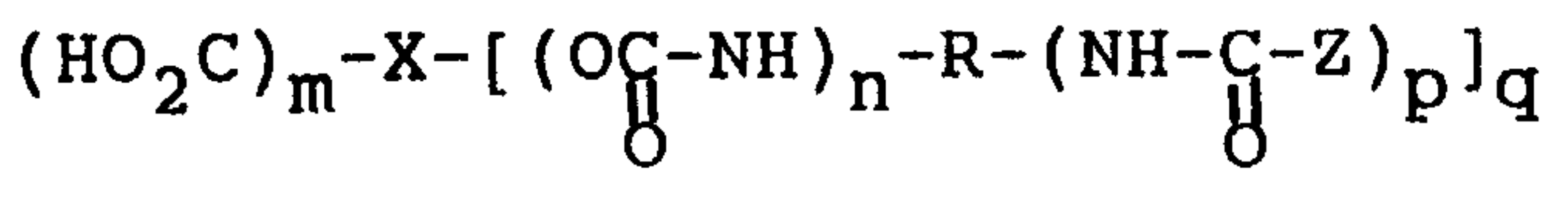
Preferably, the epoxy-free, heat-curable, weather-resistant and toxicologically unobjectionable coating system according to the invention comprises:

- a hydroxyl-terminated polyester resin with a hydroxyl number in the range from 20 to 200 mg KOH/g;
- a reversibly blocked polyisocyanate containing carboxyl groups, with an acid value of from 20 to 150 mg KOH/g; along with
- a β-hydroxylalkylamide having at least two and preferably from 2 to 4 β-hydroxylalkylamide groups per molecule; and
- optionally, typical additives for powder coating, such as wetting, flow-control or degassing agents, heat- or UV-stabilizers, pigments, colorants, fillers and accelerators such as DBTL, etc.

For the coating system according to the invention, polyesters that have hydroxyl numbers in the range from 20 to 200 mg KOH/g, preferably 30 to 120 mg KOH/g and glass transition temperatures (DSC) of more than 40^0C are suitable as carboxyl-terminated polyester resins.

The preparation of the hydroxyl-terminated polyester resins can be done in a known manner, viz. by jointly heating divalent and/or multivalent, linear or branched, aliphatic or cycloaliphatic polyalcohols with multivalent, preferably divalent or multivalent aliphatic, cycloaliphatic or aromatic carboxylic acids in the presence of an esterification catalyst to a temperature up to approximately 250^0C, and toward the end of the reaction under reduced pressure

The reversibly blocked polyisocyanates containing carboxyl groups are of the following general formula (1):



$$(HO_2C)_m\text{-}X\text{-}[(O\underset{O}{\underset{\|}{C}}\text{-}NH)_n\text{-}R\text{-}(NH\text{-}\underset{O}{\underset{\|}{C}}\text{-}Z)_p]_q \qquad (I)$$

in which:

X stands for a linear or branched aliphatic or cycloaliphatic group with a valence of (q*n + m);

R stands for a linear or branched aliphatic or cycloaliphatic group with a valence of (n + P);

Z stands for the radical of an isocyanate-blocking agent Z-H;

m stands for a number from 1 to 3, preferably 1;

n a number from 1 to 4, preferably 1 to 2;

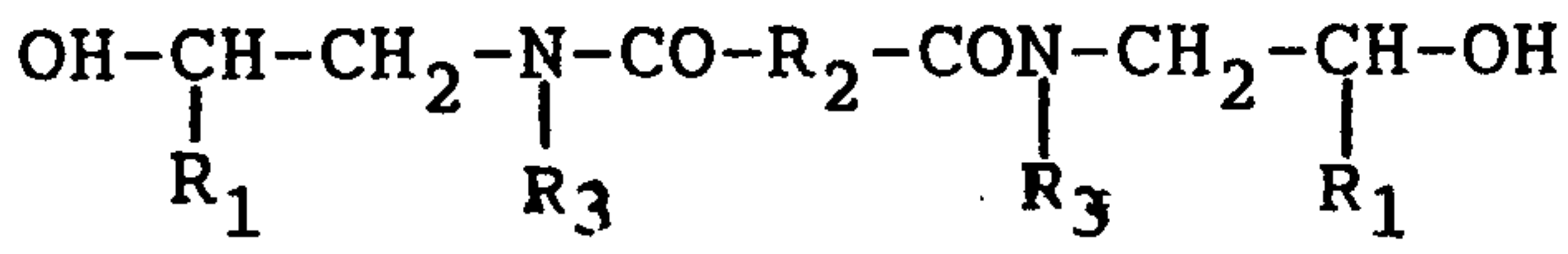
p a number from 1 to 4, preferably 1 to 2;

q a number from 1 to 4, preferably 1 to 2;

and the sum of p + q is greater than 2.

The preparation of the reversibly blocked isocyanate containing carboxyl groups can be done by known processes, viz. by reacting a hydroxycarboxylic acid with polyisocyanate in the presence of a blocking agent in heat and in solution with N_2 and subsequent isolation of the additive formed, analogously to the processes described in laid-open Patent Application DE-A 3,232,463. Preferred starting materials are in particular 2,2-bis(hydroxymethyl) propionic acid, as the hydroxycarboxylic acid; isophorone diisocyanate or hexamethylene diisocyanate or prepolymers or oligomers obtainable from them by self-addition, as the polyisocyanates; and lactams, preferably ε-caprolactam, as the blocking agents.

The β-hydroxyalkylamides used in the coating system according to the invention must contain at least two β-hydroxyalkylamide groups per molecule. These compounds are of the following formula (II):



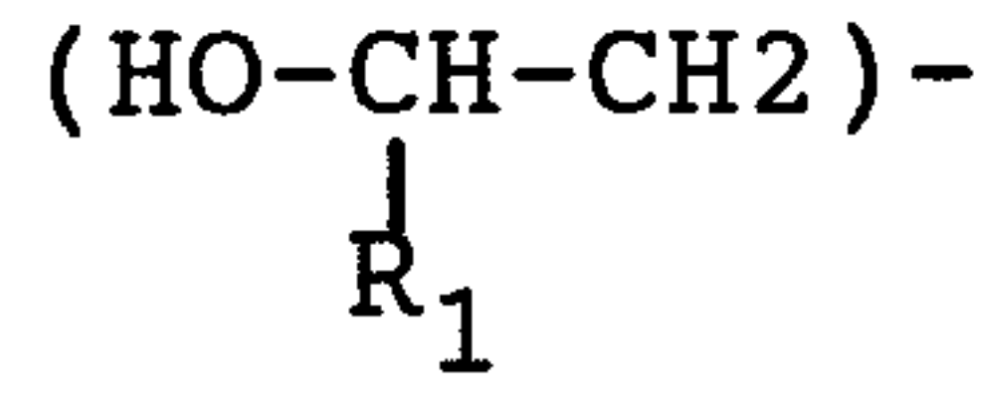
$$OH\text{-}\underset{R_1}{CH}\text{-}CH_2\text{-}\underset{R_3}{N}\text{-}CO\text{-}R_2\text{-}CO\underset{R_3}{N}\text{-}CH_2\text{-}\underset{R_1}{CH}\text{-}OH \qquad (II)$$

in which:

R1 stands for identical or different alkyl radicals having from 1 to 4 carbon atoms, or hydrogen;

R2 stands for an aliphatic, cycloaliphatic, araliphatic or aromatic radical;

R3 stands for



$$(HO-\underset{R_1}{\underset{|}{C}}H-CH2)-$$

or identical or different alkyl groups having from 1 to 4 carbon atoms, or hydrogen.

For the coating system according to the invention, β-hydroxyalkylamides that are especially preferred are as follows:

- N,N'-di(β-hydroxyethyl)acetamide
- bis(β-hydroxyethyl)adipamide
- bis(β-hydroxypropyl)adipamide
- bis[N,N'-di(β-hydroxyethyl)adipamide
- bis[N,N'-di(β-hydroxypropyl)adipamide

The ratio of the hydroxyl groups to isocyanate groups in the binder resin is advantageously between 0.5 and 1.5.

The preparation of the β-hydroxyalkylamides can be done in a known manner, viz. by reacting the esters of the corresponding dicarboxylic acid with alkanolamines in the presence of heat.

In the coating system of the invention, if good technical properties of the films are to be attained, a ratio of 0.5 to 1.5, preferably 0.8 to 1.2 between the β-hydroxyalkylamide groups and the carboxyl groups of the reversibly blocked, carboxyl-group-containing polyisocyanates according to the invention is required. Moreover, if good technical properties of the films are to be attained, β-hydroxyalkylamides or mixtures thereof must have a mean β-hydroxyalkylamide functionality of 2 to 4.

The coating system according to the invention is prepared by melt-extrusion of the components [a], [b] and [c] with preferably typical additives for powder coating as defined herein above, at temperatures between 80 and 130°C. The extrudate is then cooled, ground and screened to a particle size of less than 90 µm. In principle, other processes for preparing the coating system are also suitable, such as mixing the components in solution with ensuing settling out or distillative removal of the solvent, but these processes have no practical significance.

The coating system according to the invention can be used for coating, especially protective coatings with good weathering resistance and mat surfaces, with the usual processes for powder coating, such as electrostatic powdered paint spraying, triboelectric or corona process, fluidized bed process and so forth. The inventive coatings may be preferably used in the form of powder paint.

The coating system according to the invention can also be applied as a solution, by which means once again mat coatings with good technical properties of the films are obtained .

The coating systems according to the invention have good storage stability at normal ambient temperatures, and after cross-linking between 150 and 220°C exhibit good mechanical properties and have smooth and at the same time mat surfaces. They excel in weather resistance and moreover are toxicologically unobjectionable.

The examples and Table 1 characterize the preparation and the properties of the coating system according to the invention.

Example A: Hydroxyl-terminated polyesters

309.2 g (2.97 mols) of neopentyl glycol, 136.7 g (2.20 mols) of ethylene glycol, and 14.8 g (0.11 mols) of trimethylol propane are placed in a two-liter esterification reactor, equipped with a temperature sensor, agitator, reflux column and distillation bridge, and melted at 140°C, in an N_2 atmosphere that is maintained for the entire reaction time. While agitation is continued, 731.1 g (4.40 mols) of terephthalic acid and 0.6 g of esterification catalyst are added. After the internal temperature is raised in increments, the reaction is continued until such time as no further distillate appears. In a vacuum of 20 mbar, condensation is done until a melt viscosity of approximately 20 Pas at 160°C is reached. The polyester obtained has an acid value of less than 2 mg KOH/g, a hydroxyl number of 48 mg KOH/mg, an ICI melt viscosity at 160° of 18 Pas, and a glass transition temperature (DSC) of 64°C.

Example B: Reversibly blocked polyisocyanate that contains carboxyl groups

135 g (1.0 mols) of 2,2-bis(hydroxymethyl)propionic acid are dissolved, together with 226 g (2.0 mols) of ε-caprolactam in 2 ml of toluene and mixed in an N_2 atmosphere at 100°C within 30 minutes with 444 g (2.0 mols) of isophorone diisocyanate. Agitation is continued for approximately 1 h at approximately 115°C, and then the bulk of the toluene is removed by distillation in a vacuum. The product obtained as a residue is then freed, in a vacuum, of any toluene still adhering to it. The colourless crystals have an acid value of approximately 70 (mg KOH/g) and a pour point of 120 to 128°C.

Example C: Bis(β-hydroxyethyl)adipamate

348 g (2 mols) of dimethyladipamate and 244 g (4 mols) of ethanolamine are heated in an N_2 atmosphere in a reaction vessel, equipped with an agitator, thermometer and distillation attachment, to 110°C and reacted in reflux for 15 minutes. Next, at the same temperature, the reaction is continued for approximately 3 h with removal of the split-off methanol, and

after that the temperature is raised to approximately 148^{0}C. The contents of the reaction vessel are then, after a further 90 minutes in an N_2 atmosphere, poured into a porcelain dish and after solidifying are ground. The product obtained has a melting point of from 117 to 120^{0}C and still contains approximately 1% free ethanolamine.

For all the powder coating described in Table 1, the following production process was employed:

Preparation of the powder coating.

The ingredients in the formulation are mixed dry in a Henschel mixer for 30 seconds at 700 rpm and then extruded in a Buss-Co kneader (PLK 46*), with a barrel temperature of 100^{0}C, a cooled screw, and a screw speed of 150 rpm. The extrudate is cooled, ground, and screened to less than 90 µm.

Painting tests and evaluation of the surfaces are done on steel sheets (0.8 mm thick), degreased with trichloroethane, at a firing temperature of 200^{0}C for 30 minutes and a film thickness of 60 to 80 µm.

* trademark

Table 1

	1	2	3	4
OH-polymer Pts-per-wgt according to Example A	60	60	60	60
Blocked Polyisocyanate Pts-per-wgt according to Example B	18,5	18,5	18,5	18,5
Pridmid XL 552*1) Pts-per-wgt	1,6	0,8	-	1,1
Bis(β-hydroxyethyl) adipamate according to Example C	-	1,1	2,15	0,75
Titanium oxide (Kronos 2160*) pts-per-wgt	33	33	33	33
Resiflow PV 88*2) pts-per-wgt	0,6	0,6	0,6	0,6
Benzoin pts-per-wgt	0,5	0,5	0,5	0,5
Impact reverse (inch pounds) (ASTMD 2794)	≈40	≈110	≈20	≈60
Erichsen penetration Index (mm) DIN 53150	≈8	≈9	≈6	≈7
Gloss Index 60^0 DIN 67530	7	7	13	8

1) Bis[N,N'-di(β-hydroxyethyl)]adipamate
Commercial product of Rohm and Haas

2) Flow agent on polyacrylate Basis
Commercial product of Worlée-Chemie-GmbH

* trademarks

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. An epoxy-free, heat-curable coating system of binder resin comprising:

[a] at least one hydroxyl-terminated polyester resin with a hydroxyl number in the range from 20 to 200 mg KOH/g and a glass transition temperature of at least 40°C;

[b] at least one carboxyl-group-containing, reversibly blocked polyisocyanate having at least two blocked isocyanate groups per molecule and an acid value of from 20 to 150 mg KOH/g; and

[c] at least one β-hydroxyalkylamide having at least two β-hydroxyalkylamide groups per molecule.

2. A coating system according to claim 1, wherein it further comprises additives for powder coating.

3. A coating system according to claim 2, wherein the additives are selected from the group consisting of wetting, flow-control and degassing agent, heat- and UV-stabilizers, accelerators, pigments, colorants and fillers.

4. A coating system according to claim 1, wherein said at least one hydroxyl-terminated polyester resin [a] comprises at least one, at least divalent, linear or branched, aliphatic or cycloaliphatic polyol, and at least one, at least divalent, aliphatic, cycloaliphatic or aromatic carboxylic acid.

5. A coating system according to claim 3, wherein said at least one hydroxyl-terminated polyester resin [a] comprises at least one, at least divalent, linear or branched, aliphatic or cycloaliphatic polyol, and at least one, at least divalent, aliphatic, cycloaliphatic or aromatic carboxylic acid.

6. A coating system according to claim 1, wherein said at least one β-hydroxyalkylamide [c] comprises between two and four

β-hydroxyalkylamide groups.

7. A coating system according to claim 5, wherein said at least one β-hydroxyalkylamide [c] comprises between two and four β-hydroxyalkylamide groups.

8. A coating system according to claim 1, wherein between 0.5 and 1.5 blocked isocyanate groups are present per hydroxyl group in the binder resin.

9. A coating system according to claim 7, wherein between 0.5 and 1.5 blocked isocyanate groups are present per hydroxyl group in the binder resin.

10. A coating system according to claim 1, wherein between 0.5 and 1.5 blocked β-hydroxyalkylamide groups are present per carboxyl group in the binder resin.

11. A coating system according to claim 9, wherein between 0.5 and 1.5 blocked β-hydroxyalkylamide groups are present per carboxyl group in the binder resin.

12. A process for preparing an epoxy-free, heat-curable coating system as defined in claim 1, 4, 6, 8 or 10, wherein the components [a], [b], [c] are melt-extruded at 80 to 130^{0}C, cooled, granulated, ground, and screened to a particle size of less than 90 μm.

13. A process according to claim 12, further comprising typical additives for powder coating.

14. A process according to claim 13, wherein the additives are selected from the group consisting of wetting, flow-control and degassing agent, heat- and UV-stabilizers, accelerators, pigments, colorants and fillers.

15. The use of the coating system as defined in claim 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 or 11, for producing powder coating.

16. The use according to claim 15, wherein the powder coating is a protective coating with mat surfaces and good weather resistance.

17. The use according to claim 16, wherein the protective coating is produced by a triboelectric or corona powder spraying process or by a fluidized bed process.