PATENT SPECIFICATION (11) 1 562 408

1 562 408

(21) Application No. 38198/76 (22) Filed 15 Sept. 1976
(31) Convention Application No. 2 541 635
(32) Filed 18 Sept. 1975 in
(33) Fed. Rep. of Germany (DE)
(44) Complete Specification published 12 March 1980
(51) INT CL³ C09D 3/58, 5/40, 5/42//C08G 59/32
(52) Index at acceptance C3B 1D7 1F 1N1A 1N4J G

(72) Inventor THEMISTOKLIS KATSIMBAS

(19)

(54) HEAT-CURABLE PULVERULENT COATING COMPOSITIONS OF A MIXTURE OF COPOLYMERS CONTAINING GLYCIDYL GROUPS AND CURING AGENTS

(71) We, HOECHST AKTIENGESELLSCHAFT, a Body Corporate organised and existing under the laws of the Federal Republic of Germany, of D—6230 Frankfurt/Main 80, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to heat-curable, pulverulent coating compositions, frequently also referred to as powder lacquers, which can be used to apply a coherent coating having excellent properties after heat-curing. The coating compositions contain a specifically selected acrylic resin and a specific curing agent.

It is already known to manufacture, and use, heat-curable pulverulent coating compositions based on copolymers which contain glycidyl groups. However, such known products have the disadvantage that they have to be stoved at temperatures above 200°C to give resistant films.

If attempts are made to lower the stoving temperatures of such known pulverulent coating composition by addition of accelerators, the effect is inadequate or the films obtained yellow during the stoving process; at times, the adhesion is also impaired.

Such known powder coating compositions are described in German Published Specification (DT—OS) 2,240,314, 2,240,315, 2,057,577, 2,064,916, and 2,122,313 as well as claimed in German Displayed Specification (DT—AS) 2,424,809. Attention is also directed to the compositions claimed in British Specification No. 1,338,204, 1,334,354 and 1,449,640.

Desirable characteristics for a heat-curable, pulverulent coating composition to show improvements in various directions compared to the known pulverulent coating agents are:

1. It should be possible to manufacture the pulverulent composition by simple mixing, homogenising fusion and conjoint grinding of the requisite components.
2. The pulverulent coating composition manufactured by intensive mixing, homogenizing fusion and grinding should be stable on storage at the customary storage temperatures of between about −40 to +40°C.
3. The coating composition should, after application, give very glossy non-yellowing coatings, with good levelling properties and freedom from blisters and craters, merely by stoving at about 150 to 200°C for about 15 to 30 minutes.
4. The stoved films should not yellow and should show excellent weathering resistance and substantially improved resistance to organic solvents and chemicals, the comparison being relative to powder lacquers based on acrylate copolymers.
5. The stoved films should, after application on degreased motor-car bodywork or stainless steel, show an excellent adhesion and good impact strength.
6. The coating composition should, by using economical aliphatic dicarboxylic acids, be cheaper.

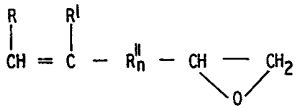
The present invention provides a pulverulent coating composition comprising a mixture of

(A) a low molecular weight copolymer of ethylenically unsaturated

compounds, the polymer containing glycidyl groups, and

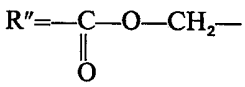
(B) at least one aliphatic dicarboxylic acid, in an amount corresponding to 0.8—1.1 acid groups per glycidyl group of the copolymer, wherein, (A) consists of 80 to 96% by weight of a copolymer having a Durran softening point of 90—120°C, soluble in organic solvents, and consisting of

a) 4 to 28% by weight of an ethylenically unsaturated epoxide monomer with 6—12 carbon atoms, of the general formula

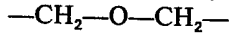


wherein

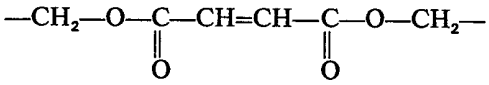
R and R′ = H or —CH_3 and n has the value 1 or zero,



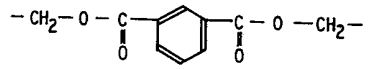
or



or



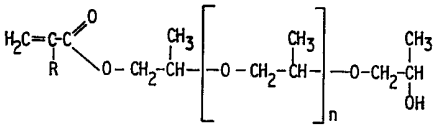
or



b) 50—70% by weight of acrylic acid tert.-butyl ester,

c) 5—30% by weight of styrene, vinyltoluene or methyl methacrylate, and

d) 4—20% by weight of a hydroxy-alkyl ester of acrylic acid or methacrylic acid, the hydroxy-alkyl group containing 2—4 carbon atoms, and/or a hydroxy-alkyl ester of the formula



(I)

wherein

n is from 2 to 6, R means hydrogen or a methyl group and the compound of the formula (I) or the mixture therewith has a hydroxyl number of 100 to 200, the amounts of the components a), b), c) and d) adding to 100% by weight, and

(B) consists of 4—20% by weight of a straight-chain aliphatic dicarboxylic acid with 4—14 carbon atoms,

The composition may optionally also contain

(C) 0.1 to 2% by weight of a curing accelerator,

(D) 0.5 to 3% by weight of a flow control agent, which agent is a polymer of molecular weight ($\overline{M_n}$) of at least 1,000 and has a glass transition temperature which is at least 50°C lower than the glass transition temperature of the copolymer (A), and/or

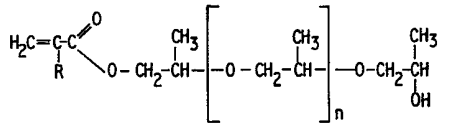
(E) other customary additives.

In a preferred embodiment of the invention the component (A) consists of a copolymer formed of:

a) 10—16% by weight of glycidyl methacrylate,
b) 65—70% by weight of tert.-butylacrylate,
c) 15—25% by weight of styrene,
d) 8—14% by weight of hydroxy-ethyl acrylate.

As component (a) it is possible to use, for example, glycidyl acrylate, glycidyl methacrylate, allyl glycidyl ether, methallyl glycidyl ether, glycidyl crotonate, vinyl glycidyl ether, allyl glycidyl maleate, allyl glycidyl phthalate and butadiene monoxide.

For component (d), as of hydroxy-alkyl esters of acrylic acid or methacrylic acid, it is possible to use hydroxy-ethyl acrylate, hydroxy-ethyl methacrylate, hydroxy-propyl acrylate, hydroxy-propyl methacrylate, hydroxy-butyl acrylate, hydroxy-butyl methacrylate, individually or as a mixture with a hydroxy (meth)acrylic acid ester of the formula



(I),

wherein

n is from 2 to 6, R means hydrogen or a methyl group and the compound of the formula (I) or the mixture has a hydroxyl numbers of 100 to 200.

The copolymers may be manufactured according to known processes of bulk polymerisation, solution polymerisation and dispersion polymerisation, preferably by solution polymerisation. Such processes are described, for example, in "Methoden der Organischen Chemie" (Methods of Organic Chemistry), Houben-Weyl, 4th Edition, Volume 14/1, pages 24 to 556 (1961).

If the polymerisation is carried out in solution, it is possible to employ solvents, such as methylene chloride, ethanol, iso-propanol, n-propanol, n-butanol, iso-butanol, tert.-butanol; the methyl, ethyl, propyl or butyl esters of acetic acid, acetone, methyl ethyl ketone, benzene and toluene.

The polymerisation is usually carried out at temperatures of 40 to about 120°C.

Examples of initiators which can be employed are percarbonates, peresters, such as tert.-butyl perpivalate or peroctoate, benzoyl peroxide, o-methoxybenzoyl peroxide, dichlorobenzoyl peroxide and azodiisobutyro dinitrile, in amounts of 0.5 to 8% by weight, based on monomers.

Furthermore, customary molecular weight regulators, such as n-dodecylmercaptan or tert.-dodecylmercaptan, can be co-used.

The copolymer solution may be freed from the solvent by distilling off the latter in vacuo or in suitable apparatuses, preferably vapouriser screws, at temperatures of 90—220°C, and is cooled, granulated and ground. However, the product can also be isolated in accordance with other processes, e.g. by spray drying, removal of the solvent with steam and simultaneous dispersion in water, or precipitation with water from a water-miscible solvent.

Examples of dicarboxylic acids which have 4 to 14 carbon atoms are succinic acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, decane-1,10-dicarboxylic acid. In general, aliphatic dicarboxylic acids with a melting point in the range from 80 to 160°C are preferred.

As the component (C), that is as curing accelerator, the following are suitable:

2,4,6-tris(N',N",N'''-dimethylaminomethyl)-phenol, 2-methyl-imidazole, 2-ethyl-imidazole, 2-methyl-4-ethyl-imidazole, 2-ethyl-4-methyl-imidazole, triphenyl-phosphine, N,N'-bis-(dimethylamino-iso-butylidene)-melamine, 2-methyl-imidazoline, 2,4-dimethyl-imidazoline, 2-ethyl-imidazoline, 2-ethyl-4-methyl-imidazoline, 2-benzyl-imidazoline, 2-phenyl-imidazoline, 2-(o-toluyl)-imidazoline, 2-(p-toluyl)-imidazoline, tetramethylene-bis-imidazoline, 1,1,3-trimethyl-1,4-tetramethylene-bis-imidazoline, 1,3,3-trimethyl-1,4-tetramethylene-bis-imidazoline, 1,1,3-trimethyl-1,4-tetramethylene-bis-4-methyl-imidazoline, 1,3,3-trimethyl-1,4-tetra-methylene-bis-4-methyl-imidazoline, 1,2-phenylene-bis-imidazoline, 1,3-phenylene-bis-imidazoline, 1,4-phenylene-bis-imidazoline, 1,4-phenylene-bis-4-methylimidazoline, tetrabutylammonium bromide, tetrabutylammonium iodide, tetraethylammonium chloride(-bromide or iodide), tetramethylammonium chloride(-bromide or -iodide), trimethylbenzylammonium chloride, dodecyl-dimethyl-(2-phenoxy ethyl)-ammonium bromide and diethyl-(2-

hydroxyethyl)-methyl-ammonium bromide, triethylenediamine, N,N-diethyl-cyclohexylamine and N-methyl-morpholine, alkyl-acrylic poly(ethyleneoxy)-phosphates, alkyl poly(ethyleneoxy)-phosphates, stannous octoate, zinc naphthenate, cobalt-naphthenate, zinc octoate, stannous-2-ethyl hexoate, phenyl-mercuric propionate, lead neodecanoate, dibutyl tin-dilaurate and lithium benzoate.

As the flow control agent (D) it is possible to use, in the pulverulent coating agent, an acrylic polymer having a glass transition temperature which is at least 50°C lower than the glass transition temperature of the copolymer used in the mixture. The component (D) is, if it is used, applied in the amounts of 0.5 to 3% by weight.

Preferred acrylic polymers which can be used as flow control agent are polylauryl acrylate, polybutyl acrylate, poly(2-ethylhexyl acrylate), polylauryl methacrylate and polyisodecyl methacrylate.

The flow control agent can also be a fluorinated polymer which has a lower surface tension, at the stoving temperature of the powder mixture than, the copolymer used in the mixture. If a fluorinated polymer is used as the flow control agent, esters of the polyethylene glycol or polypropylene glycol and fluorinated fatty acids are preferred. An example of a suitable flow control agent is an ester of polyethylene glycol, of molecular weight above 2,500, and perfluorooctanoic acid. Furthermore, levelling agents, such as silicones, polyesters, ketone resins, epoxide resins and cellulose derivatives, can be added to the melts. It is also possible to add pigments, flow control agents and other additives customary in such coating agents.

The solvent-free, optionally pigmented components, which are brittle in the non-crosslinked state, are preferably ground to particles of 100 to 300 μm size, fused at 95—110°C whilst mixing or kneading thoroughly, cooled and, after solidification, again ground to particles of 30 to 120 μm size and optionally sifted by particle size.

The pulverulent coating compositions according to the invention are typically still free-flowing at temperatures of at least 30°, preferably 40°C, have levelling temperatures of approx. 80 to 120°C and may be stoved at temperatures from 130°C, preferably 160—180°C, at which cross-linking takes place.

The pulverulent coating compositions may be applied to suitable substrates, especially metals, in accordance with the known methods, for example of the electrostatic powder spraying process.

The stoved films of the pulverulent coating compositions according to the invention have excellent adhesion and hardness coupled with elasticity. Furthermore, they are distinguished by high gloss, very good weathering resistance and very good resistance to wash liquors.

The powders can be used for coating household equipment, metal components in automobile manufacture, metal components exposed to weathering factors, such as facade panels, pipes, wire netting, equipment for forestry and agriculture and other metal components for interior design.

The examples which follow describe the manufacture of the powders and their use as electrostatically sprayable powders. The parts and percentages mentioned in the examples are by weight, unless stated otherwise.

Example 1.

220 g of toluene are initially introduced into a two-litre stirred pot equipped with a reflux condenser, thermometer and two dropping funnels. The toluene is brought to the temperature of about 100°C and two mixtures are added dropwise thereto simultaneously over the course of 3 hours, the mixtures being:

a) 173 g of styrene,

648 g of tert.-butyl acrylate,

173 g of glycidyl methacrylate,

86 g of hydroxy-ethyl methacrylate and

b) 36 g of tert.-butyl peroctoate and

50 g of toluene.

The mixture is then kept under reflux for a further hour and at the same time an additional 2 g of tert.-butyl peroctoate are added dropwise. Polymerisation is then continued for a further 2 hours under reflux at about 102 to 104°C. The resulting copolymer has a Gardner-Holdt viscosity of H measured on a 50% strength solution in toluene at 20°C. On distilling off the toluene at temperatures up to 120°C under reduced pressure at 40 mm Hg, a brittle, clear solid resin which can easily be powdered, is obtained, having a Durran softening point of 88—103°C.

300 g of the resulting solid resin are ground with

36 g of adipic acid,

6 g of pigment-wetting agent and

140 g of titanium dioxide (of the rutile type) of particle size about 80—200 μm. The powder mixture is then mixed for 3 minutes in an extruder at 104°C and the melt is chilled to room temperature and ground to give particles of approx. 80 μm.

The pulverulent coating composition is applied by means of an electro-spray gun onto degreased phosphatised galvanised steel sheets and then stoved for 30 minutes at 190°C.

Coatings having the following properties are obtained:

coating thickness:	55—60 μm
levelling, assessed visually:+	0—1
folding test:+	0
yellowing:+	0
xylene resistance, 2 hours+	0—1
pencil hardness:	H4
Erichsen deep-drawing value:	7.2 mm
gloss, by the Lange method:	94
grid cut:+	0
storage life of the ready-made powder, 7 days at 40°C:+	0—1

+) 0 = best value

5 = worst value

Example 2.

The resin according to Example 1 was used, whereby as hardening component azelaic acid and dodecanedioic acid have been put in. The following Table shows the results of the practical tests demonstrating the technical advance achieved, that is in comparison with an acrylate resin, manufactured according to DT—AS 2,424,809.

TABLE

	Acrylate resin manufactured according to DT–AS 2 424 809 with curing agent based on		Acrylate resin according to Example 1 of the invention with curing agent based on	
	azelaic acid	dodecanedioic acid	azelaic acid	dodecanedioic acid
stoving conditions	170°C/190°C 10 mins.	170°C/190°C 30 mins.	170°C/190°C 30 mins.	170°C/190°C 30 mins.
levelling of coating thickness	about 45 – 55 μ		about 45 – 55μ	
levelling	3/3–4	2/2–3	1–2/1–2	1–2/1–2
gloss, by the Lange method	84/82	103/105	98/96	96/96
Erichsen deep-drawing value	5.6/7.8	9.5/10.3	4.8/7.4	5.5/8.1
grid cut	0–1/0	0–1/0–1	0–1/0–1	0–1/0–1
xylene resistance, 15 mins.	1/0–1	1–2/0–1	2/1–2	2/1–2
impact test inch pound				
front	<4/ <4	<4/ <4	16/34	22/50
reverse	<4/ <4	<4/ <4	4/8	6.16
block resistance after 30 days at 40°C	2	0	0	0

It can be seen by the comparison investigation (Table) that, using the mixed polymerisates of the invention, coatings are obtained showing better stability on storage, better levelling and better impact strength.

Example 3.

220 g of toluene are initially introduced into a two-litre stirred pot equipped with a reflux condenser, thermometer and two dropping funnels. The toluene is brought to the temperature of about 100°C and two mixtures are added dropwise thereto simultaneously over the course of 3 hours, the mixtures being:

a) 195 g of styrene,

691 g of tert.-butyl acrylate,

108 g of glycidyl methacrylate,

86 g of hydroxyethyl methacrylate and

b) 36 g of tert.-butyl peroctoate and

50 g of toluene.

The mixture is then kept for a further hour under reflux temperature and at the same time an additional 2 g of tert.-butyl peroctoate are added dropwise. Polymerisation is then continued for a further 2 hours under reflux at about 102 to 104°C. The resulting copolymer has a Gardner-Holdt viscosity of G—H measured on a 50% strength solution in toluene at 20°C. On distilling off the toluene at temperatures up to 120°C under reduced pressure at 40 mm Hg, a brittle, clear

solid resin which can easily be powdered, is obtained, which resin has a Durran softening point of 92—106°C.

300 g of the resulting solid resin are ground with

36 g of adipic acid,

6 g of a pigment-wetting agent and

140 g of titanium dioxide (of the rutile type) of particle size about 80—200 μm.

The powder mixture is then mixed for 3 minutes in an extruder at 104°C and the melt is chilled to room temperature and ground to give particles of approx. 80 μm.

The pulverulent coating composition is applied by means of an electro-spray gun onto degreased phosphatised galvanised steel sheets and then stoved for 30 minutes at 190°C.

Coatings having the following properties are obtained:

coating thickness:	55—60 μm
levelling, assessed visually:+	0—1
folding test:+	0
yellowing:+	0
xylene resistance, 2 hours:+	1—2
pencil hardness:	H3
Erichsen deep-drawing value:	6.8 mm
gloss, by the Lange method:	96
grid cut+	0
storage life of the ready-made powder, 7 days at 40°C:+	0—1

+) 0 = best value

5 = worst value

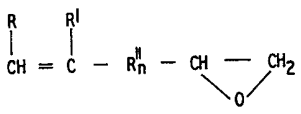
WHAT WE CLAIM IS:—

1. A pulverulent coating composition comprising a mixture of

(A) a low molecular weight copolymer of ethylenically unsaturated compounds, the copolymer containing glycidyl groups, and

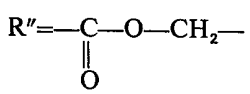
(B) at least one aliphatic dicarboxylic acid, in an amount corresponding to 0.8—1.1 acid groups per epoxy group of the copolymer, wherein (A) consists of 80 to 96% by weight of a copolymer, having a Durran softening point of 90—120°C, soluble in organic solvents, and consisting of

a) 4 to 28% by weight of an ethylenically unsaturated epoxide monomer with 6—12 carbon atoms, of the general formula

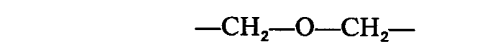


wherein

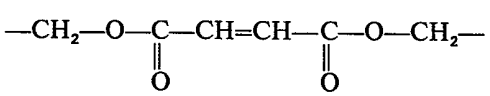
R and R′ = H or —CH_3 and n has the value 1 or zero,



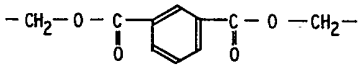
or



or



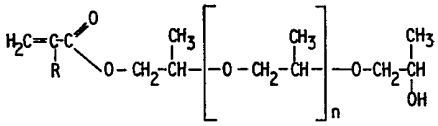
or



b) 50—70% by weight of acrylic acid tert.-butyl ester,

c) 5—30% by weight of styrene, vinyltoluene or methyl methacrylate, and

d) 4—20% by weight of a hydroxy-alkyl ester of acrylic acid or methacrylic acid, the hydroxy-alkyl group containing 2—4 carbon atoms, and/or a hydroxy-alkyl ester of the formula



(I)

wherein

n is from 2 to 6, R means hydrogen or a methyl group and the compound of the formula (I) or the mixture therewith has a hydroxyl number of 100 to 200, the amounts of the components a), b), c) and d) adding to 100% by weight, and

(B) consists of 4—20% by weight of straight-chain aliphatic dicarboxylic acid with 4—14 carbon atoms,

2. A composition according to Claim 1, wherein component (A) consists of a copolymer formed of:

a) 10—16% by weight of glycidyl methacrylate,

b) 65—70% by weight of tert.-butylacrylate,

c) 15—25% by weight of styrene,

d) 8—14% by weight of hydroxy-ethyl acrylate.

3. A composition according to Claim 1 or 2 comprising 0.1 to 2% by weight of a curing accelerator.

4. A composition according to Claim 1, 2 or 3 comprising 0.5 to 3% by weight of a flow control agent, which is polymer of molecular weight ($\overline{M}_n$) of at least 1,000 and has a glass transition temperature which is at least 50°C lower than the glass transition temperature of the copolymer (A).

5. A composition according to any one of Claims 1 to 4 comprising other customary additives.

6. A composition according to Claim 1 substantially as described in any one of the Examples.

7. A process for the manufacture of a pulverulent coating composition according to any one of Claims 1 to 6 wherein the pulverulent coating composition is manufactured by mixing, homogenising fusion and conjoint grinding of the requisite components.

8. A method for forming a coating on a substrate comprising providing on the substrate a layer of a pulverulent coating composition according to any one of Claims 1 to 7, and stoving the layer.

BROOKES & MARTIN,
High Holborn House,
52/54 High Holborn,
London WC1V 6SE.
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1980.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.