

[54] HEAT-CURABLE PULVERULENT COATING AGENT CONSISTING OF A MIXTURE OF COPOLYMERS CONTAINING GLYCIDYL GROUPS, DICARBOXYLIC ACID ANHYDRIDES AND CURING ANHYDRIDES

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[58] Field of Search..... 260/836

Table with 3 columns: Patent No., Date, and Name. Includes references like Malamet, Labana, Theodore, and Labana with various dates and patent numbers.

References Cited
UNITED STATES PATENTS

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[57] ABSTRACT
The invention relates to heat-curable pulverulent coating agents, frequently also called powder lacquers, which are suitable for applying a coherent coating which possesses excellent properties after heat-curing.

6 Claims, No Drawings

HEAT-CURABLE PULVERULENT COATING AGENT CONSISTING OF A MIXTURE OF COPOLYMERS CONTAINING GLYCIDYL GROUPS, DICARBOXYLIC ACID ANHYDRIDES AND CURING ANHYDRIDES

Matter enclosed in heavy brackets [] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue.

BACKGROUND OF THE INVENTION

It is already known to manufacture heat-curable pulverulent coating agents based on copolymers which contain glycidyl groups, and to use such coating agents. However, such known products suffer from the disadvantage that they must be stoved at temperatures above 200° in order to obtain resistant films. If attempts are made to lower the stoving temperatures of such known pulverulent coating agents by addition of accelerators, the effect is inadequate or the resulting films yellow already during the stoving process, and at times the adhesion is also interfered with.

Such known pulverulent coating agents are described in German Offenlegungsschriften No. 2,240,312, 2,240,314, 2,240,315, 2,057,577, 2,064,916, 2,214,650 and 2,122,313.

1. It is the task of the present invention to provide a heat-curable pulverulent coating agent which shows simultaneous improvements in various directions compared to the known pulverulent coating agents. One objective is that it should be possible to manufacture the pulverulent coating agent by simple mixing, homogenising fusion and conjoint grinding of the requisite components.

2. The pulverulent coating agent manufactured by thorough mixing, homogenising fusion and grinding should be storage-stable at the customary storage temperatures between about -40 and +40° C.

3. The coating agent should, after application, give very glossy, non-yellowing coatings of good levelling characteristics and freedom from blisters and craters, merely by stoving for about 15 to 30 minutes at about 150° to 180° C.

4. The stoved films should not yellow and should not only exhibit excellent weathering resistance but also substantially improved resistance to organic solvents and chemicals, the comparison of these properties being with powder lacquers which are formulated on the basis of acrylate copolymers.

SUMMARY

The subject of the invention is a pulverulent coating agent of a mixture of

A. a copolymer of relatively low molecular weight, which contains glycidyl groups and is a copolymer of several ethylenically unsaturated compounds,

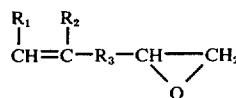
B. at least one dicarboxylic acid anhydride in an amount corresponding to 0.4-1.0 anhydride groups per epoxy group (glycidyl groups) of the copolymer and

C. a curing accelerator in the form of an organic base,

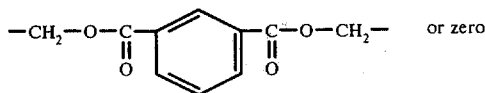
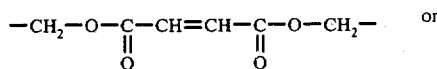
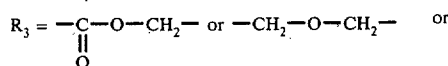
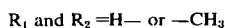
D. a flow control agent in an amount of at least 0.05 per cent by weight of the mixture, which agent is a polymer of molecular weight (M_n) of at least 1,000 and

has a glass transition temperature which is at least 50° C lower than the glass transition temperature of the copolymer (A), characterised in that the component (A) consists of 84 to 94 per cent by weight of copolymers containing epoxide groups and hydroxyl groups, which copolymers have Durran softening points of about 90°-120° C and are soluble in organic solvents and comprise:

- a. 6-24 per cent by weight of ethylenically unsaturated epoxide monomers with 6-12 carbon atoms, of the general formula



wherein



- b. 4-20 per cent by weight of hydroxyalkyl esters of acrylic acid or methacrylic acid, with the hydroxyalkyl ester group being saturated and containing 2-4 C atoms,

- c. 25-50 per cent by weight of methyl methacrylate and

- d. 25-45 per cent by weight of other acrylic acid esters or methacrylic acid esters of aliphatic saturated monoalcohols with 1 to 8 carbon atoms, the component (B) consisting of 6-16 per cent by weight of at least one dicarboxylic acid anhydride with melting points of about 60°-140° C, the component (C) consisting of 0.5-1.8 per cent by weight of N',N'-bis-(dimethylaminoisobutylidene)-melamine and the optional component (D) consisting of a flow control agent and other customary additives.

A preferred embodiment of the invention comprises:

- a. 12 to 16 per cent by weight of glycidyl methacrylate,

- b. 14 to 18 per cent by weight of hydroxyethyl methacrylate,

- c. 34 to 44 per cent by weight of methyl methacrylate and

- d. 25 to 35 per cent by weight of ethyl acrylate.

A special embodiment of the present invention relates to a pulverulent coating agent according to claim 1, characterised in that component (A) consists of a copolymer formed of:

- a. 12 to 16 per cent by weight of glycidyl methacrylate,

- b. 14 to 18 per cent by weight of hydroxyethyl methacrylate,

- c. 34 to 44 per cent by weight of methyl methacrylate and

- d. 30 to 40 per cent by weight of butyl methacrylate.

size of 30 to 120 μ , and optionally screened according to particle size.

The pulverulent coating agents to be used according to the invention are still free-flowing at temperatures of at least 30°–40° C, preferably 40° C, have flow temperatures of approx. 80° to 120° C and are stoved at temperatures above 130° C, preferably at 160° to 180° C, whereupon crosslinking occurs.

The pulverulent coating agents are applied to suitable substrates, especially metals, in accordance with known methods, for example the electrostatic powder spraying process.

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

The powders are used for coating household utensils, metal parts used in car manufacture, metal parts which are exposed to weathering factors, such as facade panels, pipes, wire braids, equipment used in forestry and agriculture and other metal articles for interior architecture.

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

EXAMPLE 1

226 g of toluene are introduced into a 1-liter stirring pot equipped with a reflux condenser, thermometer and two dropping funnels. The toluene is brought to the reflux temperature by heating to about 112° C and two monomeric mixtures, namely

(a)

120 g of ethyl acrylate,
64 g of hydroxyethyl methacrylate,
64 g of glycidyl methacrylate and
152 g of methyl methacrylate
and

(b)

32 g of tert.-butyl peroxoate and
40 g of toluene
are simultaneously added dropwise thereto over the course of about 4 hours. The mixture is then kept under reflux for a further hour and during this time an additional 4 g of tert.-butyl peroxoate are added dropwise. The mixture is then after-polymerised for a further 2 hours under reflux at about 118°–120° C. The resulting copolymer has a Gardner-Holdt viscosity of S-T measured as a 50% strength solution in toluene at 20° C. After addition of 3.2 g of a flow control agent (Modaflo of Messrs. Monsanto Chemicals), the toluene is distilled off by heating up to 160° C and under reduced pressure at 40 mm Hg, giving a brittle clear solid resin which can readily be powdered.

300 g of the resulting solid resin are ground together with 32 g of a mixture of dicarboxylic acid anhydride and curing accelerator, consisting of 92% by weight of phthalic anhydride and 8% by weight of N',N'-bis-(dimethylaminoisobutylidene)-melamine, and an added pigment, namely 132 g of titanium dioxide (of the rutile type) of particle size about 80–200 μ . The powder mixture is then mixed for 4 minutes in an extruder at 100° C, the melt is shockchilled to room tem-

perature and the product is ground to give particles of approx. 80 μ .

The pulverulent coating is applied by means of an electro-spray gun onto degreased phosphatised galvanised steel sheets and then stoved for 30 minutes at 180° C.

Coatings having the following properties are obtained;

Coating thickness, μ :	44–48	
Levelling, assessed visually:	0–1	(0 means "very good" and 5 means "bad")
Folding test:	0–1	
Yellowing:	0–1	
Xylene resistance, 2 hours:	0	
Pencil hardness:	H ₁	
Erichsen deep-drawing value:	7.2 mm	
Gloss by Lange's method:	108	
Grid-cut test:	0	

EXAMPLE 2

The procedure followed is as in Example 1, but a copolymer is produced by using the following monomer mixture: 128 g of methyl methacrylate, 152 g of butyl methacrylate, 64 g of hydroxyethyl methacrylate and 56 g of glycidyl methacrylate. This copolymer is converted to a pulverulent coating agent in accordance with the instructions of Example 1.

The stoved coatings have similar properties to the coatings which have been produced in accordance with Example 1.

EXAMPLE 3

The procedure followed is as in Example 1 with the modification of using the following monomer mixture: 150 g of methyl methacrylate, 130 g of butyl methacrylate, 60 g of hydroxyethyl methacrylate and 60 g of glycidyl methacrylate.

This copolymer is converted to a pulverulent coating agent in accordance with the instructions of Example 1. The obtained coating agent shows good lacquer properties. The pulverulent copolymer has excellent storage stability.

EXAMPLE 4

The procedure followed is as in Example 1 with the modification of employing the following monomer mixture: 300 g of methyl methacrylate, 40 g of hydroxyethyl methacrylate and 60 g of glycidyl methacrylate. The obtained copolymer is converted to a pulverulent coating agent in accordance with instructions of Example 1. This coating agent shows good lacquer properties. The pulverulent copolymer has excellent storage stability.

What is claimed is:

1. Pulverulent coating agent of a mixture of
 - A. a copolymer of relatively low molecular weight, which contains glycidyl groups and is a copolymer of several ethylenically unsaturated compounds,
 - B. at least one dicarboxylic acid anhydride in an amount corresponding to 0.4–1.0 anhydride groups per epoxy group (glycidyl group) of the copolymer and
 - C. a curing accelerator in the form of an organic base,
 - D. a flow control agent in an amount of at least 0.05 per cent by weight of the mixture, which agent is a

