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(54) PULVERULENT COATING MEDIUM

(71) We, VEBA-CHEMIE AKTIENGESELLSCHAFT, a German Body corporate of 4660 Gelsenkirchen-Buer, Pawikerstraße 30, 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 present invention relates to a pulverulent coating medium.

The electrostatic powder spraying technique for lacquering of mainly metallic objects is at the present time one of the most important lacquering methods. On a worldwide basis, powder lacquers based on epoxy resins are predominant. Apart from some special products, in general hardeners based on dicyandiamide are used. It is known that the reactivity of such powder resins can be varied over a comparatively wide range. As a result, different application temperatures, which are in the range from 140 to 200°C, are used. All these products nevertheless have the common feature that at room temperature or slightly elevated temperature they react to a limited degree at varying rates. This leads to higher-molecular weight fractions which subsequently become noticeable through deterioration of flow properties of the product when the powder lacquer is applied. Thus, depending on the different temperatures to which it has been subjected, an epoxy resin powder lacquer produces an appearance which may vary considerably. Reproducibility of surface quality is therefore not achieved.

Because of the cross-linkage reaction which starts even at a moderately elevated temperature, complications may arise in the production of powder lacquers of this kind. As is well known, powder lacquers are produced by extruding physical mixtures of the resins together with pigments and lacquer adjuvants. For this purpose it is common to use temperatures of from 90 to 105°C as the mass temperature of the molten resins. Even if it is possible to

operate the production extruder in a constant and reproducible manner, there are always faulty batches, resulting for example from mixing errors or deviations in the required colour shade. After mixing with the additives necessary for correction purposes, a batch of this kind must be re-extruded. This necessarily leads to a further partial reaction, which subsequently results in poor flow properties in the hardened film of lacquer.

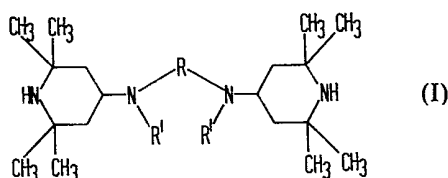
Further problems arise in the transport or storage of finished powder lacquers. Even if a number of precautions are taken, it is impossible to prevent powder lacquers from being exposed to temperatures of the order of 40°C for days or weeks, particularly in warmer countries. This also results in problems in connection with reproducibility and surface quality. For the reasons given above, the powder lacquers are often transported and stored in refrigerating units.

Hardeners which eliminate all these difficulties have now surprisingly been found. These are derivatives of 2,2,6,6-tetramethyl-4-amino-piperidine which hereinafter will be referred to by the abbreviation TAD. The hardeners used in the present invention are primarily characterised by the fact that the primary amino group of TAD is converted in a suitable manner by condensation or addition during the production of the hardener, so that it is no longer available in that form for hardening the epoxy resin. This resultant hardener permits the production of the pulverulent coating media which are stable in storage.

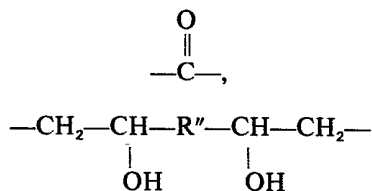
Accordingly, the present invention provides pulverulent coating compositions having a grain size smaller than 0.25 mm, preferably from 0.02 to 0.06 mm, which compositions include at least one 1,2-epoxy compound containing more than one 1,2-epoxy group per molecule and which begins to melt at a temperature greater than 40°C, and a heterocyclic hardener of the general formula (I)

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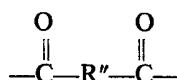
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wherein R represents a



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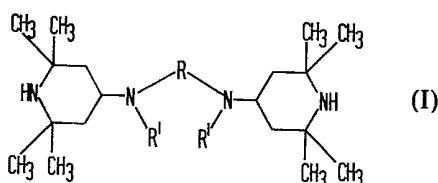


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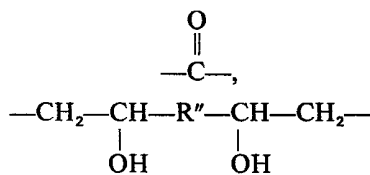
R' represents a hydrogen atom or an alkyl radical, preferably a C₁₋₅ alkyl radical, and R'' represents a bivalent, aliphatic, aromatic, or heterocyclic radical.

The molecular weights of the heterocyclic hardeners of formula (I) are from 300 to 2300, preferably from 350 to 1300.

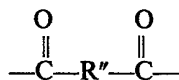
The present invention also provides a method for the production of coatings based on powder lacquers which method comprises reacting at elevated temperature a finely divided mixture including at least one 1,2-epoxy compound having at least one 1,2-epoxy group per molecule and which begins to melt at a temperature greater than 40°C, and a heterocyclic hardener of the general formula (I)



wherein R represents a



or



group,

R' represents a hydrogen atom or an alkyl radical, preferably a C₁₋₅ alkyl radical and R'' represents a bivalent, aliphatic, aromatic, or heterocyclic radical, the heterocyclic hardeners being used in amounts such that from 0.5 to 1.1, preferably from 0.75 to 1.0, hydrogen amide equivalents are present for each 1,2-epoxy equivalent.

The advantages of these compositions of the present invention whose hardener component is based on TAD, include:

1. Extremely good storage stability, even at higher temperatures.

2. Very good flow properties, such as otherwise can be obtained practically only with solvent-containing lacquers.

3. Problem-free processing in extruders and similar machines.

4. Improved UV and weather stability in comparison with customary amine-hardening epoxy resin systems.

1,2-epoxy compounds containing more than one 1,2-epoxy group per molecule and which begin to melt at a temperature greater than 40°C are used for producing the finely divided compositions of the invention which are to be used as powder lacquers. Examples of suitable such epoxy compounds are firstly polyepoxy compounds which are solid at or below 40°C, such as higher-molecular compounds (so-called solid resins), and those that are solid because of their symmetrical construction or the size of the carbon systems bound to the 1,2-epoxy group, and secondly those compounds which have been produced by reacting liquid 1,2-epoxy compounds containing more than one epoxy group per molecule with primary or secondary amines in such an amount that the resultant adduct still contains, at least on average, one 1,2-epoxy group per molecule (so-called adduct hardeners).

The 1,2-epoxy compounds may be saturated or unsaturated and may also be aliphatic, cycloaliphatic, aromatic, or heterocyclic. They may in addition contain substituents which under the mixing or reaction conditions do not give rise to any undesirable side-reactions. No undesirable side-reactions are caused by alkyl or aryl substituents, hydroxyl groups, or ether groups.

Of the solid resins, 1,2-epoxy compounds containing more than one epoxy group per molecule and whose epoxy equivalent weight is from 500 to 1000 are preferred. Examples are the solid polymeric polyglycidyl polyethers of 2,2-bis-(4-hydroxyphenyl)-propane, which are obtained by reacting 2,2-bis-(4-hydroxyphenyl) propane with epichlorohydrin in molar ratios of 1:1.9 to 1.2 (in the presence of an alkali metal

hydroxide in aqueous medium). Polymeric polyepoxides of this kind can also be obtained by reacting a polyglycidyl ether of 2,2-bis(4-hydroxyphenyl)-propane with less than the equimolecular amount of a dihydric phenol, preferably in the presence of a catalyst, such as a tertiary amine, a tertiary phosphine, or a quaternary phosphonium salt. The polyepoxide may also be a solid epoxidised polyester, obtained for example by reacting a polyhydric alcohol and/or a polybasic carboxylic acid or its anhydride with a low-molecular polyepoxide. Examples of such polyepoxides of low molecular weight are liquid diglycidyl ether of 2,2-bis(4-hydroxyphenyl)-propane, diglycidyl phthalate, diglycidyl adipate, diglycidyl tetrahydrophthalate, diglycidyl hexahydrophthalate, diglycidyl maleate, and the 3,4-epoxycyclohexylmethyl ester of 3,4-epoxycyclohexanecarboxylic acid.

Mixtures of solid polyepoxides can also be used, for example a mixture of a polyepoxide whose melting point is from 120 to 160°C, and a polyepoxide having a melting point from 60 to 80°C (melting point determined by the Durrans mercury method). Suitable mixtures contain between 30 and 50 weight % of a solid polyglycidyl ether of 2,2-bis(4-hydroxyphenyl)-propane with an epoxy equivalent weight from 1650 to 2050 and a melting point of from 120 to 160°C, and from 60 to 70 weight % of a solid polyglycidyl polyether of 2,2-bis(4-hydroxyphenyl)-propane having an epoxy equivalent weight from 450 to 525 and a melting point of from 60 to 80°C.

If high epoxy functionality appears desirable, a preferred polyepoxide is the polyglycidyl ether of 1,1,2,2-tetra(hydroxyphenyl)-ethane.

As previously mentioned, in addition to the so-called solid resins, "adduct hardeners" are also suitable. Such solid adduct hardeners may for example be produced from liquid polyepoxides of polyunsaturated hydrocarbons, such as vinyl cyclohexene, and dicyclopentadiene, epoxy ethers of polyhydric alcohols and phenols, and aliphatic, cycloaliphatic, and aromatic diamines. A prerequisite for the suitability of an adduct of this kind is that the lower melting point should be above 40°C.

Conventional additives may, of course, be added to the compositions of the present invention. For the purpose of improving the flow properties of the resultant lacquers, so-called flow agents are added during their preparation. These agents may be chemical compounds, or mixtures of compounds, of very different chemical natures, for example polymeric or monomeric compounds, acetals, such as polyvinyl formal, polyvinyl acetal, polyvinyl butyral, polyvinyl acetobutyral, or di - 2 -

ethylhexyl - i - butyraldehyde, di - 2 - ethylhexyl - n - butyraldehyde - acetal, diethyl - 2 - ethyl - hexanol acetal, di - n - butyl - 2 - ethylhexanol - acetal, di - i - butyl - 2 - ethylhexanol - acetal and di - 2 - ethyl - hexyl - acetaldehyde - acetal, ethers such as the polymeric polyethylene and polypropylene glycols, copolymers of n - butyl acrylate, and vinylisobutyl ether, ketone - aldehyde condensation resins, solid silicone resins, or mixture of zinc soaps, fatty acids, and aromatic carboxylic acids. Products, such as Modaflow, are also available commercially for this purpose, their chemical character being unknown to consumers; this product appears to be a complex polymeric active liquid based on polyacrylates. Flow agents of this kind can be contained in the compositions of the invention in amounts of from 0.2 to 5.0 weight % based on the total weight of powder lacquer.

The amounts of other conventional additives for the powder lacquer mixture, such as pigments, dyes and fillers, may vary over a wide range.

After the powdered coating composition (or powder lacquer) has been applied to the objects which are to be lacquered, the latter are heated for curing purposes to temperatures of from 130 to 210°C, preferably from 140 to 180°C. The resulting coating then provides the advantages described.

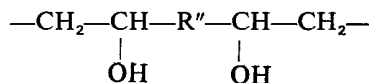
Before their application to an object to be lacquered the components of the powder lacquer are intimately mixed, extruded, and then ground. For practical application a particle size of >100μ should preferably be aimed at, while the maximum particle size should be from 30 to 50μ.

The powder lacquer is applied by known methods to the article which has to be coated, for example by electrostatic powder spraying, fluidised bed coating or electrostatic fluidised bed coating.

The derivatives of 2.2.6.6 - tetramethyl - 4 - amino - piperidine used according to the invention as hardeners can be produced by known methods. Thus, the compounds in which R is a



group can be produced by reacting 2 moles of TAD with one mole of urea, urea compounds, carbon dioxide, or diethyl carbonate, optionally followed by alkylation. Compounds in which R is a



group can be prepared, among other

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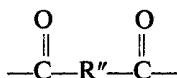
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methods, by reacting 2 moles of TAD with one mole of an aliphatic, aromatic, or heterocyclic diepoxide. When triepoxides are used instead of diepoxides, the molar ratios being amended, hardeners are obtained which also contain a third TAD radical, that is to say are substituted at R".

The



grouping can be prepared by reacting 2 moles of TAD once again with one mole of, for example a dicarboxylic acid or tricarboxylic acid similarly to the triepoxides, or their mono- or diesters. When esters are used as reaction partners, it is expedient to use those having low alkyl radicals (C₁—C₃). The methods given above are intended only to give a general survey of possible methods of preparation.

The present invention will now be illustrated by the following Examples:

Example 1

A. Preparation of the hardener

624 g (4 moles of TAD are heated to 60°C in a three-necked glass flask, and mixed over a period of 10 minutes with 760 g of a diepoxide base on Bis Phenol-A with an epoxide equivalent weight of about 190 g. After a homogeneous mixture had been formed, the temperature was raised to above 70°C. At this temperature the addition reaction started and because of the exothermic reaction the temperature of the reaction mixture rose to about 110°C. During the reaction cooling was effected with a mixture of ice and water. In order to complete the reaction the mixture was kept for a further 30 minutes at 80°C. After cooling to room temperature a solid, brittle resin having melting point of about 65°C was obtained.

B. Preparation of epoxy resin powder lacquer

A bifunctional solid epoxy resin having an epoxide equivalent weight of 850—940 g was used as a basis for formulating powder lacquer.

For this purpose 252 g of the resin described under A above, 1310 g of a solid epoxide having an epoxide equivalent weight of 850—940 g, 925 g of titanium dioxide white pigment (of the rutile type) and 12.5 g of a flow agent based on a polyacrylate were intensively mixed in a mixer for solid materials, and thereupon extruded in a single-screw extruder with a stock temperature of 95 to 100°C. The extruded melt, when cold, was ground to a powder in a peg mill, and the grain size fraction larger than 100 μ was separated by sifting. The finished powder was applied

electrostatically in the usual manner to a 1mm steel sheet and hardened for 30 minutes at 180°C.

C Properties of the powder lacquer 65

Coating thickness	60—70 μ	
Hardness (DIN 53157)	180—190 sec.	
Elasticity (DIN 53156)	8—10 mm	
Adhesion (DIN 53151)	0	
Gloss (ASTM-D-523)	95	70
Flow after storage for 30 days at 40°C	very good, no "orange peel effect"	
Flowability after storage for 30 days at 40°C	practically unchanged, very good	75
Accelerated weathering in a 450 LF Xenotest apparatus (according to DIN 53231)		80
Loss of gloss after 500 hours	12%	
Loss of gloss after 1000 hours	23%	85
Loss of gloss after 1500 hours	31%	
Loss of gloss after 2000 hours	35%	90

Example 2:

A. Preparation of the hardener

2 moles of TAD (312 g) were condensed with 1 mole of urea (60 g) by stirring the materials, at 150°C for about 2 hours. After 2 hours about 80% of the theoretical amount of NH₃ had been separated. For the completion of the reaction, condensation was continued for a further hour at a temperature of from 210 to 220°C, followed by heating in a vacuum of about 2 mm Hg for 30 minutes at 170°C.

The hardener prepared in this manner had a H-active equivalent weight of 167.

B. Preparation of an epoxy resin powder lacquer 105

A powder lacquer of the following formulation was prepared by the method described in Example 1:

57.1 weight % of bifunctional epoxy resin of epoxide equivalent weight: 850—940 g
5.4 weight % of TAD-adduct, see under 2A

37.0 weight % of white pigment, rutile type
0.5 weight % flow agent based on polyacrylate

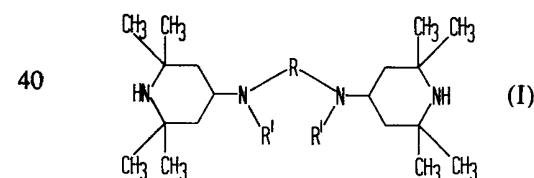
After electrostatic application to 1 mm steel sheets, the lacquer was hardened at 220°C for 15 minutes. 120

C. Properties of the powder lacquer	
Coating thickness	50—60 μ
Hardener (DIN 53157)	190—200 sec.
Elasticity (DIN 53156)	9 mm
5 Adhesion (DIN 53151)	0
Gloss (ASTM-D-523)	100
Flow	very good no "orange peel" effect
10 Flow after storage for 30 days at 40°C	Unchanged, very good
Flowability after storage for 30 days at 40°C	very good, free flowing
15 Accelerated weathering in the 450 LF Xenotest apparatus (according to DIN 53231)	
20 Loss of gloss after 500 hours	13%
Loss of gloss after 1000 hours	24%
25 Loss of gloss after 1500 hours	34%
Loss of gloss after 2000 hours	37%

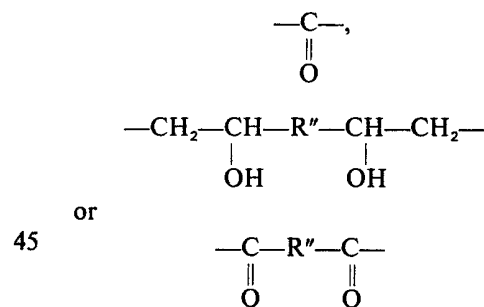
Similar thermosettable compositions are described and claimed in our Application No. 37364/77, (Serial No. 1,550,733).

WHAT WE CLAIM IS:—

1. Pulverulent coating compositions having a grain size smaller than 0.25 mm, which compositions include at least one 1,2-epoxy compound containing more than one 1,2-epoxide group per molecule and which begins to melt at a temperature greater than 40°C, and a heterocyclic hardener of the general formula (I)



wherein R represents a



group,

R' represents a hydrogen atom or an alkyl radical and

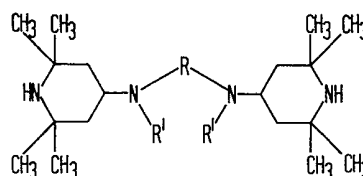
R'' represents a bivalent aliphatic, aromatic, or heterocyclic radical, the hardener being present in such an amount that there are from 0.5 to 1.1 hydrogen amide equivalents for each 1,2-epoxy equivalent.

2. A composition according to Claim 1, having a grain size of from 0.2 to 0.06 mm.

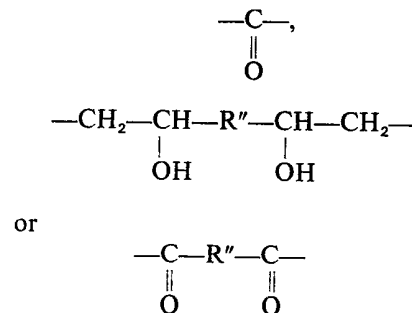
3. A composition according to Claim 1 or Claim 2, in which the hardener is present in such an amount that there are 0.75 to 1.0 hydrogen amide equivalents for each 1,2-epoxy equivalent.

4. A pulverulent coating composition according to Claim 1 substantially as described in Example 1 or Example 2.

5. A method of producing a coating from a pulverulent coating composition which method comprises reacting at elevated temperature a finely divided mixture of at least one 1,2-epoxy compound containing more than one 1,2-epoxy group per molecule and which begins to melt at a temperature greater than 40°C, and a heterocyclic hardener of the general formula (I)



wherein R represents a



group,

R' represents a hydrogen atom or an alkyl radical, and

R'' represents a bivalent, aliphatic, aromatic, or heterocyclic radical, the heterocyclic hardener being used in an amount such that there are 0.5 to 1.1 hydrogen amide equivalents for each 1,2-epoxy equivalent.

6. A method according to Claim 5, wherein the heterocyclic hardener is used in an amount such that there are 0.75 to 1.0 hydrogen amide equivalents for each 1,2-epoxy equivalent.

7. A method of producing coatings according to Claim 5 substantially as described in Example 1 or Example 2.

5 8. A coating prepared by a method as claimed in any one of Claims 5 to 7.

9. A coating prepared from a composition as claimed in any one of Claims 1 to 4.

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