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(54) Benævnelse: **Epoxyresiner med forbedret elasticitet**

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DESCRIPTION

[0001] The present invention relates to epoxy resins with improved elasticity. It also relates to aqueous dispersions of such elastic epoxy resins, to a process for the production of such elastic epoxy resins and aqueous dispersions therefrom, and a method of using such elastic epoxy resins or their aqueous dispersions as adhesives, as coatings, and as sealing materials.

[0002] Epoxy resins with improved elasticity have been known from EP-A 0 658 583 and EP-A 0 658 584, where epoxy resins are described that have been modified with polyoxyalkylene monoamines, and from EP 0 735 070 where curing agents for elastic epoxy resins are described. Though the modification with the cited polyoxyalkylene amines improves the elasticity, still higher elasticity is needed.

[0003] In JP 2003-192 873 A, a photo-curable mixture of an epoxy resin and a polyoxyalkylene compound is disclosed, with a photoinitiator which forms cations upon irradiation. The polyoxyalkylene compound and the photoinitiator are simply admixed to the epoxy resin. In EP 0 545 353 A1, there is described an intermediate in the production examples, particularly production example 1, where polytetramethylene glycol is reacted with a stoichiometric excess of isocyanate compounds, thereby providing a polytetramethylene ether having isocyanate end groups. This intermediate is then reacted with 3,4-epoxycyclohexyl methanol. In EP 0 747 371 A1, flexible epoxy resins are disclosed based on a tetrahydrofuran trimer compound having a molar mass of 250 g/mol and a hydroxyl number of 479.2 mg/g which is esterified at both end-hydroxyl groups with succinic acid to yield a bis-carboxylic acid, which bis-carboxylic acid in turn reacts with two molecules of an epoxy alcohol to form a bis-epoxide having a molar mass divided by the number of epoxide groups per molecule of 394 g/mol.

[0004] From US 4,423,170, a water reduced epoxy adhesive composition has been known which comprises the reaction product of a diepoxide which is the condensation product of epichlorohydrine with an aromatic diol such as bisphenol A diglycidyl ether, which diepoxide is partially reacted with a polyoxyalkylene amine, and a latent curative. The high amount of ethylene oxide units needed to provide hydrophilicity impairs the corrosion resistance of base metals coated therewith.

[0005] It was therefore the underlying problem of the present invention to provide an epoxy resin with further improved elasticity and good corrosion protection. Such resins are made available by the present invention.

[0006] The invention therefore relates to an epoxy resin **AB** according to claim 1.

[0007] The aliphatic polyether **B1** is linked to the epoxy resin part A by an ester linkage, - CO - O -. The ester linkage is introduced by reaction of the hydroxyl group-terminated polyether molecules **B1** or mixtures of these, with a dicarboxylic acid **B4** or an anhydride **B4'** thereof, under formation of a carboxyl group terminated intermediate which reacts with the epoxy terminal groups of an epoxy resin which forms the polyether structure **A** under ring opening and formation of an ester bond.

[0008] The invention also relates to an epoxy resin **ABC** according to claim 2.

[0009] The invention further relates to a process for the preparation of epoxy resins **AB** with improved elasticity comprising reacting a hydroxy functional aliphatic polyether **B1** with a dicarboxylic acid **B4** or an anhydride **B4'** thereof, under formation of a carboxyl group terminated intermediate. This intermediate reacts with an epoxy resin which forms the polyether structure **A** under ring opening and formation of an ester bond through the action of the carboxylic acid groups on the epoxy groups.

[0010] At least two of the hydroxy functional polyether **B1** segments are linked to each other by at least two urethane bonds, formed by reaction of at least two of the hydroxyl group-terminated polyether molecules **B1** with a polyfunctional isocyanate, **B3.**

[0011] This urethane-modified epoxy resin is made by reaction of the hydroxy functional aliphatic polyether **B1** with a multifunctional isocyanate **B3** which is introduced in a quantity to make sure that hydroxyl groups are present in stoichiometric excess, ranging from a ratio of the amount of substance of hydroxyl groups to the amount of substance of isocyanate groups from 2:1, thus forming compounds of the type

HO-B1-O-CO-N-B3-N-CO-O-B1-OH ,

to 10:9, thus forming compounds of the type

HO-B1-[O-CO-N-B3-N-CO-O-B1]$_9$ OH.

[0012] The water-dilutable epoxy resin **ABC** is made by incorporation of a reaction product **C** of an aliphatic polyol **C1** with an epoxy resin **C2** which has at least two epoxy groups per molecule, by a process comprising the steps of

1. (a) preparation of an emulsifier **C** by reaction of an aliphatic polyol **C1** of a number average molar mass M_n of from 200 g/mol to 20 000 g/mol, having a mass fraction of oxyethylene units in its structure of at least 20 %, preferably a polyoxyethylene glycol or a hydroxy functional copolyether comprising oxyethylene and oxypropylene groups, with an epoxide compound **C2** having at least two epoxy groups per molecule, the ratio of the number of hydroxyl groups in **C1** to the number of epoxy groups in **C2** being from 1 : 0.85 to 1 : 7, which reaction is preferably conducted in the presence of a catalyst such as Lewis acids or complexes thereof,
2. (b) reacting a hydroxy functional aliphatic polyether **B1** with a dicarboxylic acid **B4** or an anhydride **B4'** thereof, under formation of a carboxyl group terminated intermediate.
3. (c) reacting this intermediate in mixture with a polyhydric phenol with an epoxy resin which forms the polyether structure **A** under ring opening and formation of an ester bond through the action of the carboxylic acid groups on the epoxy groups, in the presence of a catalyst such as triphenyl phosphine
4. (d) adding the emulsifier **C** and water to achieve the desired mass fraction of solids of from about 40 % to about 65 %.

[0013] In a preferred embodiment, step (b) is complemented by first reacting the polyether **B1** with a substoichiometric amount of multifunctional isocyanate **B3** to supply a chain-extended hydroxy functional compound which is then converted to carboxyl functionality by reaction with the dicarboxylic acid **B4** or its anhydride, **B4'**.

[0014] The aliphatic polyether **B1** has oxyalkylene groups with at least 4 carbon atoms in the alkylene group. It is also possible, however, to use copolyethers having minor amounts, i. e. less than 50 % of the mass of the oxyalkylene groups, replaced by oxypropylene or oxyethylene groups. It is preferred that the mass fraction of oxyalkylene groups with at least 4 carbon atoms in the alkylene group is at least 50 %, more preferably at least 60 %, and especially preferred at least 70 %, in the mass of all oxyalkylene groups in the polyether **B1.**

[0015] The polyfunctional isocyanates **B3** which connect two or more of the hydroxyl group terminated polyether **B1** can be aromatic or aliphatic, and are preferably difunctional, although a mass fraction of trifunctional isocyanates or isocyanates with still higher functionality is tolerated. Preferably, the average number of isocyanate groups per molecule shall not exceed 2.4, particularly preferred, not exceed 2.3, and most preferred, be not more than 2.2. Both aliphatic and aromatic isocyanates can be used, alone or in combination, such as 1,6-diisocyanato hexane, isophorone diisocyanate, bis-(4-isocyanatophenyl)methane, tetramethylxylylene diisocyanate and both 2,4- and 2,6-toluylene diisocyanate and the commercial mixture thereof.

[0016] The dicarboxylic acids **B4** or the anhydrides thereof can also be aliphatic or aromatic, and may be selected from dicarboxylic acids which may be aliphatic acids, especially preferred are malonic acid, succinic acid, glutaric acid, adipic acid, pimelic and suberic acids, as well as the so-called dimer fatty acids made by dimerisation of unsaturated fatty acids. Cyclic aliphatic acids such as cyclohexane 1,4-dicarboxylic acid, tetrahydro phthalic and hexahydro phthalic acids can also be used, as well as aromatic acids such as terephthalic or isophthalic acids.

[0017] The aliphatic polyols **C1** have a number average molar mass M_n of from 200 g/mol to 20 000 g/mol, and a mass fraction of oxyethylene units in their structure of at least 20 %. Preferred are polyoxyethylene glycols or hydroxy functional copolyethers comprising oxyethylene and oxypropylene groups. They are reacted with an epoxide compound **C2** having at least two epoxy groups per molecule, the ratio of the number of hydroxyl groups in **C1** to the number of epoxy groups in **C2** being from 1 : 0.85 to 1 : 7, the reaction preferably being conducted in the presence of a catalyst such as Lewis acids or complexes thereof.

[0018] The epoxy resins with improved elasticity of the present invention can be used to formulate adhesives, coating compositions, sealing compositions, and fillers. They can be used in bulk, in solvent borne form, with reactive diluents or in aqueous dispersion. Depending on the supply form they are cured with latent curatives, such as dicyandiamide, with solvent borne curatives, or with aqueously dispersed curatives. In comparison with unmodified epoxy resins, the epoxy resins of the present invention show improved elasticity, less propensity to crack formation when applied in thick layers, improved adhesion to substrates such as metals and concrete, and they impart improved corrosion protection.

[0019] These advantageous properties are shown in the examples.

Examples

Example 1 Preparation of a Modifier Resin

[0020] 1300 g of poly(oxy-1,4-butylene) glycol with a number average molar mass of 650 g/mol were heated to 80 °C, then 174 g of a commercial mixture of toluylene diisocyanate isomers were added under stirring. The reaction mixture was kept under these conditions until no more free isocyanate was detectable (mass fraction of NCO groups was less than 0.1 %). The reaction mixture was heated to 150 °C, then 296 g of phthalic anhydride were added. The reaction mixture was stirred at 150 °C until the acid number had reached 70 mg/g. 1770 g of pale yellow resin were isolated.

[0021] The acid number is defined, according to DIN EN ISO 3682 (DIN 53 402), as the ratio of that mass m_{KOH} of potassium hydroxide which is needed to neutralise the sample under examination, and the mass m_B of this sample, or the mass of the solids in the sample in the case of a solution or dispersion; its customary unit is "mg/g".

Example 2 Preparation of an Emulsifier

[0022] 1500 g of a commercial polyethylene glycol with a number average molar mass M_n of 3000 g/mol and 185 g of a bisphenol A based epoxy resin having a specific content of epoxy groups of 5.4 mol/kg were heated to 100 °C. Under stirring, 8 g of boron trifluoride - diethyl ether complex were added, as a solution in 1,4-dioxane, of 5 g/ 100 g strength. The temperature was raised to 130 °C and kept until the specific epoxy group content had reached a constant level. The ratio of the number of epoxy and hydroxyl groups was 1:1 in this case, the final specific epoxy group content was 2.7 mmol/kg.

Example 3 Modified Aqueous Epoxy Resin Dispersion

[0023] 1200 g of the resin of Example 1 were heated in a flask to 125 °C. 11 g of bisphenol A and 4380 g of bisphenol A diglycidyl ether were added, together with 6 g of triphenyl phosphine catalyst. The temperature of the mixture rose to 150 °C due to the heat of reaction. The mixture was kept at this temperature under stirring until the specific content of epoxy groups, defined as the amount of substance n_{EP} of epoxy groups divided by the mass m_B of the (solid) resin, had reached 2 mol/kg. The contents of the flask were then cooled to 100°C whereupon 628 g of methoxypropanol were added. Under stirring, 950 g of the emulsifier of Example 2 were added. The temperature was lowered further to 80 °C, and 5639 g of deionised water was added under careful stirring.

Example 4 Aqueous Curative

[0024] An aqueous amine-type hardener was prepared as described in EP-A 0 000 605, Example 1B, but without addition of the acrylonitrile. This hardener had a mass fraction of solids of 80 %, and a specific content of amine hydrogen atoms of 8.6 mol/kg.

Example 5 Preparation of an Aqueous Two Pack Coating Composition

[0025] 100 g of the dispersion of Example 3 were mixed with 23.2 g of the curative of Example 4, diluted to a mass fraction of solids of 40 % by addition of water, and a further 5.8 g of water. The viscosity of the mixture was determined according to DIN EN ISO 3219 at 23 °C, and a shear rate of 25 s^{-1}, to be 1125 mPa s. The pot life of this mixture, i.e. the time during which, counted from the moment of mixing the ingredient intimately, until the point in time when the resin dispersion did not form any longer a coherent film on the substrate, was three and one half hours. The dust-free drying time was one hour, and the tack-free drying time (at 22°C and a relative humidity of 45 %) was 6 hours.

Examples 6 Comparative epoxy resin dispersion

[0026] A commercial dispersion of a flexibilised type 1 epoxy resin in a mixture of isopropanol and water (®Beckopox EP 385, Surface Specialties Germany GmbH & Co. KG; mass fraction of solids 56 %, mass fraction of water 42 %, mass fraction of isopropanol 2 %; specific epoxide group content 2,0 mol/kg) was mixed with 26 g of the curative dispersion of Example 4, again diluted to a mass fraction of solids of 40 % by addition of water. The viscosity of the mixture, determined as described supra, was 636 mPa.s, the pot life was two and one half hours, the dust-free and tack-free drying times were the same as in Example 5.

Example 7 Comparative Testing

[0027] The mechanical and chemical resistance properties measured on a coated steel sheet were as shown in table 1:

Table 1 Test Results

Property	Unit	Dispersion of Ex. 5	Comparative (Ex. 6)
Pendulum Hardness (König)			
after 24 hours	s	49	49
after 48 hours	s	76	71
after 7 days	s	104	112
Film Thickness	µm	31 to 44	46 to 56
Erichsen Indentation	mm	5.7	4.9
Gardner Impact [m]	in lb	< 5	< 5
Gardner Impact [c]	in lb	50	40
Cross Hatch		Gt 0	Gt 0
Chemical Resistance			
Salt Spray Test [s]	h	124	< 24
Humidity	h	2000	500
Explanations: m: the steel ball falls on the (uncoated) metal side c: the steel ball falls on the coated side s: time until the corrosion length underneath the coating is 2 mm Salt Spray Test and Humidity Test were performed by coating untreated steel sheets. Gt 0 is the best rating in the Cross Hatch Test.			

[0028] It can be seen from this test that both flexibility (Erichsen test, impact test) and corrosion resistance have been markedly improved. Improved results can already be achieved with thinner coatings.

REFERENCES CITED IN THE DESCRIPTION

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Patentkrav

1. Epoxyresin **AB** omfattende, i dets polymerkæde, enheder med strukturen

-O-CO-B4-CO-O-B1-[O-CO-N-B3-N-CO-O-B1]$_n$-O-CO-B4-CO-O-

hvor n er mindst en, og op til ni, hvor de alifatiske polyethere **B1** har mindst 4 carbonatomer i alkylengruppen, hvor enheden, der er afledt af den alifatiske polyether **B1**, er bundet til epoxyresinet ved hjælp af en esterbinding dannet ved reaktion af et carboxylgruppetermineret mellemstof fremstillet ud fra en funktionel hydroxypolyether **B1** og en dicarboxylsyre **B4** eller en anhydrid **B4'** deraf, hvilken reagerer med de terminale epoxygrupper af epoxyresinet, hvor **B4** er en lineær, forgrenet eller cyklisk alifatisk eller aromatisk dicarboxylsyre, og hvor polyetheren **B1** omfatter, i sin polymerkæde, mindst to urethan-bindinger dannet ved reaktion af mindst to af de hydroxylgruppe-terminerede polyethermolekyler **B1** med et polyfunktionelt isocyanat **B3**, og hvor epoxyresinet har enheder afledt af 1,2,3-trihydroxypropan og enheder afledt af aromatiske dihydroxyforbindelser.

2. Epoxyresin **ABC,** der er vandfortyndbart grundet inkorporering i et epoxyresin **AB** ifølge krav 1 af et reaktionsprodukt **C** af et aliphatisk polyol **C1** omfattende, i dets struktur, mindst en massefraktion på 20 % af oxyethylengrupper, og som har en talgennemsnitlig molarmasse M_n, fra 200 g/mol til 20.000 g/mol, med et epoxyresin **C2**, der har mindst to epoxygrupper pr. molekyle, og som har et epoxygruppeindhold fra 0,5 mol/kg til 10 mol/kg, hvor forholdet mellem antallet af hydroxylgrupper i **C1** og antallet af epoxygrupper i **C2** er fra 1 : 0,85 til 1 : 7.

3. Epoxyresin ifølge krav 1, hvori **B4** er en cycloaliphatisk dicarboxylsyre.

4. Fremgangsmåde til frembringelse af epoxyresiner **AB** ifølge krav 1 omfattende trinnene at

- reagere, i første trin, en hydroxyfunktionel polyether **B1** omfattende urethangrupper indført ved reaktion med et polyfunktionelt isocyanat **B3** med en lineær, forgrenet eller cyclisk, aliphatisk dicarboxyl-

syre **B4**, hvori stofmængderne af **B1** og **B4** udvælges, således at stofmængderne af carboxylgrupper i **B4** er mindst 1,9 gange summen af stofmængde af hydroxylgrupper i **B1**,

- reagere, i andet trin, det syrefunktionelle produkt fra det første trin med en aromatisk dihydroxy-forbindelse og en epoxid-bestanddel med mindst to epoxygrupper pr. molekyle, i en advancement-reaktion for at danne epoxyresinerne **AB**.

5. Fremgangsmåde til frembringelse af epoxyresiner **ABC** med et inkorporeret reaktionsprodukt **C** af et aliphatisk polyol **C1** med et epoxyresin **C2**, der har mindst to epoxygrupper pr. molekyle omfattende trinnene at

(a) frembringe et emulgeringsmiddel ved reaktion af et aliphatisk polyol **C1** med en talgennemsnitlig molarmasse M_n fra 200 g/mol til 20.000 g/mol med en massefraktion af oxyethylen-enheder i dets struktur på mindst 20 %, fortrinsvist et polyoxyethylenglycol eller en hydroxyfunktionel copolyether omfattende oxyethylen- og oxypropylengrupper med en epoxid-forbindelse **C2** med mindst to epoxygrupper pr. molekyle, hvor forholdet mellem antallet af hydroxylgrupper i **C1** og antallet af epoxygrupper i **C2** er fra 1 : 0,85 til 1 : 7, hvilken reaktion udføres fortrinsvist ved tilstedeværelsen af en katalysator såsom Lewissyrer eller komplekser deraf,

(b) reagere en hydroxyl-funktionel aliphatisk polyether **B1** med en dicarboxylsyre **B4** eller en anhydrid **B4'** deraf, under dannelse af et carboxylgruppetermineret mellemstof,

(c) reagere dette mellemstof i en blanding med et polyvalent phenol med et epoxyresin, der danner polyetherstrukturen **A** under ringåbning og dannelse af en ester-binding ved indvirkning af carboxylsyregrupperne på epoxygrupperne ved tilstedeværelsen af en katalysator såsom triphenylphosphin

(d) tilsætte emulgeringsmidlet **C** og vand for at opnå den ønskede fedtstofmassefraktion fra ca. 40 % til ca. 65 %.

6. Fremgangsmåde ifølge krav 5, hvori trin (b) komplementeres ved først at reagere polyetheren **B1** med en understøkiometrisk mængde af multifunktionel isocyanat **B3** for at opnå en kædeforlænget funktionel hydroxyforbindel-

se, der herefter omdannes til carboxyl-funktionalitet ved reaktion med dicarboxylsyren **B4** eller dets anhydrid, **B4'**.

7. Fremgangsmåde til anvendelse af epoxyresinerne **AB** med forbedret elasticitet som beskrevet i krav 1 omfattende at blande epoxyresinet **AB** fra det andet trin med en hærder udvalgt fra gruppen bestående af syrehærdende midler, aminhærdende midler med mindst en primær eller sekundær aminogruppe eller mindst to tertiære aminogrupper, og at påføre blandingen på et substrat udvalgt fra gruppen bestående af blik, plastik, beton og at hærde det påførte lag.

8. Fremgangsmåde til anvendelse af epoxyresinerne **AB** med forbedret elasticitet som beskrevet i krav 1 omfattende at sammensætte klæbestoffer, coating-sammensætninger, tætnings-sammensætninger eller fyldemasse, der hærdes af hærdere udvalgt fra gruppen bestående af latente hærdere, hærdere indeholdende opløsningsmiddel og vanddispergerende hærdere, og at påføre det samme på substrater udvalgt fra gruppen bestående af metaller og beton.

9. Fremgangsmåde til anvendelse af epoxyresinerne **ABC** ifølge krav 2 omfattende at sammensætte klæbestoffer, coating-sammensætninger, tætningssammensætninger eller fyldemasse, der hærdes af hærdere udvalgt fra gruppen bestående af latente hærdere, hærdere indeholdende opløsningsmiddel og vanddispergerende hærdere, og at påføre det samme på substrater udvalgt fra gruppen bestående af metaller og beton.