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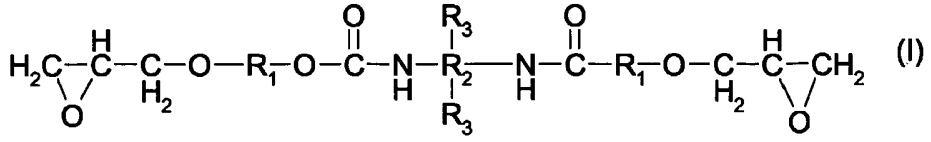
(54) Title: URETHANE AMINES



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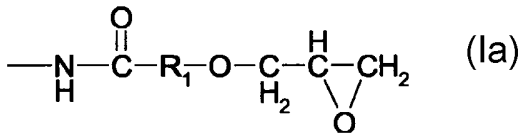

(Ia)

(57) Abstract: Urethane amine obtainable by reacting A) a urethane epoxide of the general formula (I)in which R_1 is a straight-chain or branched, saturated or unsaturated, aliphatic or cycloaliphatic hydrocarbon radical having 2 to 40 carbon atoms; R_2 is an aromatic, aliphatic, cycloaliphatic, araliphatic, unbranched or branched hydrocarbon radical having 1 to 30 carbon atoms; and R_3 = independently at each occurrence H or (Ia) with B) an amine compound containing at least 2 reactive amine hydrogens per molecule, and the use of these urethane amines as curing agents in curable epoxy resin compositions, which are suitable in particular for producing mouldings, adhesive bonds, coatings and foam materials.

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Urethane amines

The invention relates to specific urethane amines as curing agents for epoxy resins, to a curable composition comprising these products, and to the use of these curable compositions for producing mouldings and coatings.

Epoxy resins have long been in widespread use for the production of corrosion control coatings, abrasion-resistant coatings, casting compositions and adhesives which possess outstanding mechanical strength and have good chemical resistance. Owing to their high crosslinking density, amine-cured epoxy resins, especially those based on diphenyl propane and epichlorohydrin, are brittle and hard with glass transition ranges above 20°C.

In practice, the high hardness and high strength of amine-cured epoxy resins are not always necessary; at the same time, elasticization and reduction of brittleness, and in particular an improvement in the adhesion properties to a variety of substrates, are frequently desirable. For these purposes a variety of methods, though not always satisfactory, have been employed to date.

In principle the degree of elasticization can be increased internally by lowering the crosslinking density and externally by adding plasticizer.

External elasticizers are not reactive and not incorporated into the thermoset network. They produce a widening of the network only by means of space-filling. The external plasticizers include tar, phthalates, high-boiling alcohols, glycols, ketone resins, vinyl polymers, and similar products that are not reactive with epoxy resins and amine hardeners. This type of modification is suitable only for specific applications. With regard to elasticization it makes virtually no contribution, since the glass softening range is not substantially affected but the thermoset structure is highly disrupted. Internal elasticization of epoxy resins can be achieved by reducing the functionality of the hardener, as described for example in DE-A 22 00 717.

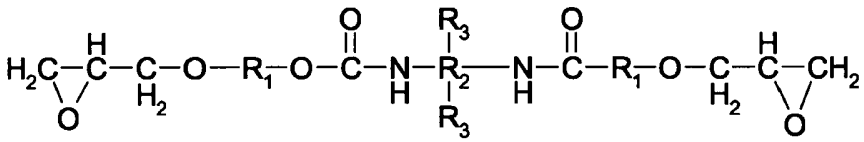
Compounds which have been customary for a long time already, and widely employed, are amino amides based on dimeric and trimeric fatty acids, which achieve a satisfactory pattern of properties as epoxy resin hardeners. The cured thermosets based on these amino amides

do have good adhesion properties to a variety of substrates, but also have an elasticity which is too low for many applications.

It was therefore an object to provide new curing agents for curable compositions, the intention being that the curing agent should make it possible to produce elasticized coatings, mouldings and adhesive bonds having good adhesion properties.

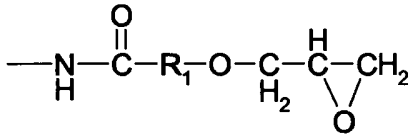
It has now surprisingly been found that this object can be achieved with new, specific urethane amines.

The present invention accordingly provides new urethane amines. These urethane amines are obtainable by reacting A) urethane epoxides of the general formula (I)



(I),

in which R_1 is a straight-chain or branched, saturated or unsaturated, aliphatic or cycloaliphatic hydrocarbon radical having 2 to 40, preferably 4 to 10, carbon atoms;
R_2 is an aromatic, aliphatic, cycloaliphatic, araliphatic, unbranched or branched hydrocarbon radical having 1 to 30, preferably 6 to 20, carbon atoms; and
R_3 = independently at each occurrence H or



(in the case where a polyisocyanate is used), with B) amine compounds containing at least 2 reactive amine hydrogens per molecule.

The urethane epoxides A) used for reaction of the amine compounds are obtainable by partially glycidylizing polyalcohols with epichlorohydrin and subsequently linking the products with di- or polyisocyanates via the remaining hydroxyl groups of the partially glycidylized polyols. By polyols here are meant polyhydric alcohols, containing at least two hydroxyl groups in the molecule.

The polyols are glycidylized by processes which are known per se, by reaction of the polyalcohols with epichlorohydrin in the presence of a catalyst and subsequent treatment with sodium hydroxide solution.

The molar ratio of polyol to epichlorohydrin is preferably chosen such that after the reaction there remains on average at least one free hydroxyl group per molecule for further reaction with the di- or polyisocyanate.

The reaction of the partially glycidylized polyols with the isocyanate compound takes place by addition of the polyisocyanate in the presence of a catalyst (e.g. dibutyltin laurate) to the initial charge of dewatered, partially glycidylized polyol at about 60°C with subsequent stirring for one hour.

The reaction ratio of the partially glycidylized polyols to the isocyanate compound is preferably chosen stoichiometrically, i.e. such that for each hydroxyl group still present in the partially glycidylized polyols use is made of one isocyanate group of the diisocyanate or isocyanate of higher functionality for the reaction. Through selection of the alcohol and of the isocyanate compound it is possible to adjust certain properties, such as the flexibility in particular. In this connection, the use of polyols and/or polyisocyanates of higher functionality tends to produce brittle properties while the use of polyols and polyisocyanates of lower functionality tends to produce elastic properties.

For the partial glycidylization it is possible to use any alcoholic compounds which have at least two hydroxyl groups per molecule. Possible examples would include diols, such as ethanediol, propandiol, hexanediol, dimer diol, etc.; triols, such as glycerol, trimethylolethane, trimethylolpropane, etc.; and tetrahydric alcohols, such as erythritol, pentaerythritol.

The isocyanates used in accordance with the invention for reaction of the partially glycidylized diols or polyols are the commercially customary aliphatic, araliphatic, cycloaliphatic or aromatic diisocyanates or polyfunctional isocyanates and also the trimerization products thereof. Preferred examples would include the following: tolylene diisocyanate, hexamethylene diisocyanate, isophorone diisocyanate, methylenedi(phenyl isocyanate) and tetramethylene diisocyanate. This compilation is not complete; however, there is no need to mention that in order to link the partially glycidylized dialcohols and polyalcohols it is possible in principle to use all isocyanates having a functionality of at least two. It is also possible to use prepolymeric

isocyanates which still contain reactive isocyanate groups for reaction with the partially glycidylized diols or polyols. In this case it is possible, depending on the identity and chain length of the prepolymeric isocyanates, to prepare compounds which in some cases are highly flexible. Very particular preference is given in this context to prepolymeric isocyanates which have been prepared with polyalkylene glycols.

As amine compounds B) which can be used additionally for the reaction of the urethane epoxides A) it is possible in principle to use all amines which have at least two reactive amine hydrogen atoms, examples being heterocyclic amines such as piperazine and N-aminoethylpiperazine; cycloaliphatic amines such as isophoronediamine, 1,2-(1,3; 1,4)diaminocyclohexane, aminopropylcyclohexylamine and tricyclododecanediamine (TCD); araliphatic amines such as xylylenediamine; aliphatic unsubstituted or substituted amines such as ethylenediamine, propylenediamine, hexamethylenediamine, 2,2,4-(2,4,4)trimethyl-hexamethylenediamine and 2-methylpentamethylenediamine; ether amines such as 1,7-diamino-4-oxaheptane, 1,10-diamino-4,7-dioxadecane, 1,14-diamino-4,7,10-trioxa-tetradecane, 1,20-diamino-4,17-dioxaeicosane and, in particular, 1,12-diamino-4,9-dioxadodecane. Use may also be made of relatively high molecular weight ether diamines based on propoxylated diols, triols and polyols ("Jeffamines" from the company Huntsman) with an average molar weight of above about 150. In addition it is possible to use polyalkylene polyamines such as diethylenetriamine, triethylenetetramine, dipropylenetriamine, tripropylenetetramine and also high molecular weight amines or adducts or condensates that contain free amine hydrogen. Preference is given to using polyethylene polyamines such as, for example, ethylenediamine, diethylenetriamine and N-aminoethylpiperazine and cycloaliphatic amines such as, for example, isophoronediamine or aminopropylcyclohexylamine.

The reaction of the urethane epoxides A) with the amine compounds B) takes place such that the amine compound is introduced as an initial charge and the urethane epoxide is added over the course of about an hour with stirring at 60°C to 90°C, and the mixture is subsequently stirred for 1 hour until reaction is complete. Any excess amine can be removed under reduced pressure. The molar ratios are chosen such that, following the reaction, there are on average at least two reactive amine hydrogens per molecule present in the reaction product. In order to set specific properties it is possible for the compounds of the invention to be subsequently adducted with epoxide compounds.

The urethane amines of the invention can be used in particular - alone or in a mixture with other amine hardeners customary in this field - as curing agents in curable epoxy resin compositions for producing elastic coatings, mouldings and adhesive bonds having improved adhesion.

The present invention therefore additionally provides a curable composition comprising
a) a urethane amine of the invention,
b) an epoxy resin having on average more than one epoxide group in the molecule,
c) if desired a further aminic curing agent other than a), and
d) optionally customary additives.

Examples of customary curing agents c) include the following: aliphatic amines, e.g. polyethylene polyamines and polypropylene polyamines, examples being diethylenetriamine and dipropylenetriamine, and 2,4,4-(2,2,4)trimethylhexamethylenediamine; cycloaliphatic diamines, such as 1-amino-3-aminomethyl-3,5,5-trimethylcyclohexane, also called isophoronediamine, and 3,3′-dimethyl-4,4′-diaminodicyclohexylmethane; heterocyclic amines, such as piperazine; long-chain polyether amines, such as 1,12-diamino-4,8-dioxadodecane; aromatic amines, such as phenylenediamine and diaminodiphenylmethane; polyamido amines formed from natural or synthetic fatty acids and polyamines; amine adducts; and phenol-aldehyde-amine condensates.

The epoxy resins b) that are used additionally can be cured hot and cold with the hardeners or hardener mixtures of the invention. They contain on average more than one epoxide group in the molecule and may be glycidyl ethers of monohydric or polyhydric alcohols, such as glycerol or hydrogenated diphenylolpropane, for example, or of polyhydric phenols, such as resorcinol, diphenylolpropane or phenol-aldehyde condensates, for example. It is also possible to use the glycidyl esters of polybasic carboxylic acids, such as hexahydrophthalic acid or dimerized fatty acids.

Particular preference is given to using liquid epoxy resins based on epichlorohydrin and diphenylolpropane having epoxide values of 0.4-0.6 epoxide groups/100 g of resin.

If desired it is also possible as reactive diluents to use monofunctional aliphatic and aromatic glycidyl ethers, such as butyl glycidyl ether and phenyl glycidyl ether, or glycidyl esters, such

as glycidyl acrylate, or epoxides, such as styrene oxide, or polyfunctional diglycidyl or triglycidyl ethers, particularly those of low molecular weight.

The combination of the long-chain polyether urethane amines, with a low degree of crosslinking, with high-crosslinking amine formulations allows the properties of the reactive resin composition to be adjusted within a wide range in respect of viscosity, reactivity and the like and allows the properties of the thermoset to be adjusted within a wide range in respect of the elasticity, crosslinking density, mechanical strength and chemical resistance.

Suitable components for formulating a reactive resin composition for coating, adhesive bonding or casting include the customary organic- and mineral-based additives d), pigments, plasticizers, accelerators, solvents and other adjuvants. For the production of foam materials it is possible to use the blowing agents that are customary in this field, particularly the silane compounds that give off hydrogen.

Not only the urethane amines of the invention themselves but also the curable compositions exhibit, surprisingly, a comparatively low viscosity, and the cured thermosets exhibit outstanding adhesion properties, particularly to metal sheets.

The compositions of the invention can be employed with particular advantage where there is a need for effective adhesion to the substrate and elasticity in order to bridge cracks in the substrate, and for reducing internal stress, including such applications at relatively low temperatures, and also as adhesives.

One important field of use, therefore, is the crack-bridging coating of concrete, for industrial flooring or impervious safety troughs, and for heating-oil tanks, for example. On account of their outstanding adhesion to iron and concrete and also on account of the adjustable elasticity, the compositions of the invention are additionally suitable as casting compositions for joints, adhesives, and crack-bridging membranes that are impervious to liquids. The low-shrink and low-stress curing also allows the production of shaped articles and mouldings in large format.

The present invention accordingly further provides a process for producing mouldings, coatings, adhesive bonds and foam materials, characterized in that they are produced using a curable composition of the invention.

Examples:

Example 1: Preparation of the urethane amines

A) Preparation of a partially glycidylized dialcohol or polyalcohol.

Reaction of 118 g of hexanediol (1 mol) and 92.5 g of epichlorohydrin (1 mol) by a known method - addition reaction in the presence of boron trifluoride etherate and ring closure in the presence of aqueous sodium hydroxide solution - gives 170 g of a hydroxyalkyl glycidyl ether.

B) Preparation of a urethane epoxide

170 g of the reaction product from A) (about 1 equivalent of A) are admixed by a known method over the course of 60 minutes with 111 g (1 equivalent) of isophorone diisocyanate in the presence of 0.1 g of dibutyltin laurate at approximately 60°C. This is followed by stirring for 60 minutes until reaction is complete. This gives 281 g of a urethane epoxide.

C) Preparation of a urethane amine

281 g (about 1 equivalent) of the urethane epoxide from B) are metered into 136 g (1 mol) of xylylenediamine over the course of about 60 minutes at 60°C to 90°C. This is followed by stirring for an hour until reaction is complete. The resulting urethane amine is homogenized with 278 g of benzyl alcohol (40% based on the total amount).

The dissolved urethane amine had the following characteristics:
Viscosity/25°C: 1500 mPa•s,
theoretical amine hydrogen equivalent: about 230.

In the same way as in Example 1 the urethane amines listed in Table 1 below were prepared from the hydroxyalkyl glycidyl ether of Example 1 A).

Table 1

Ex.	Equivalent of 1A)	Equivalent of isocyanate[2]	1 mol of amine[3]	Theoretical amine equivalent *	Visc./25°C**
2	1	IPDI	NAEP	about 340	3.0 Pa•s
3	1	TDI	IPD	about 240	4.9 Pa•s
4	1	HMDI	DTA	about 150	1.0 Pa•s

* 60% strength solution in benzyl alcohol,
** all viscosity figures measured using a VT 550 rotational viscometer from Haake.

Key:

2	IPDI	= isophorone diisocyanate
	TDI	= tolylene diisocyanate
	HMDI	= hexamethylene diisocyanate
3	NAEP	= aminoethylpiperazine
	IPD	= isophoronediamine
	DTA	= diethylenetriamine

Example 5: Comparative example with Aradur 45 (commercial, flexibilized polyamine from Huntsman)

Viscosity: 5.4 Pa•s/25°C;

Amine hydrogen equivalent: 185

Example 6: Comparative example with Aradur 145 (commercial polyamino amide from Huntsman)

Viscosity: 3.5 Pa•s/25°C;

Amine hydrogen equivalent: 95

Use examples:

The adhesion was measured manually after 7 days' curing at room temperature with the epoxy resin Araldite GY 783 (reactively diluted base resin, epoxide equivalent: about 190). The curing agents from Examples 1 to 6 were used in this case equivalently with the epoxy resin Araldite GY 783.

The curable composition is applied at a film thickness of approximately 0.5 mm to an unpretreated metal sheet and is cured at room temperature for 7 days. Subsequently the film is removed.

The adhesion to the metal sheet is evaluated as follows:

(-) = no adhesion at all

(o) = film can be removed easily

(⊕) = film is difficult to remove

(+) = film can be removed only in fragments

(++) = film cannot be removed

The results are shown in Table 2 below.

Table 2

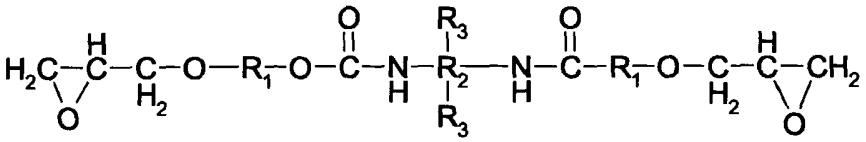
Ex.	Araldite GY 783	Curing agent	Adhesion after 7 d* at 20°C
1	100 g	121 g	(++)
2	100 g	179 g	(+)
3	100 g	126 g	(++)
4	100 g	79 g	(+)
5	100 g	97 g	(⊕)
6	100 g	50 g	(+)**

* d = days; ** very brittle

Claims

1) Urethane amine obtainable by reacting

A) a urethane epoxide of the general formula (I)

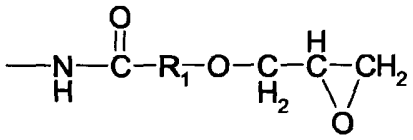


(I),

in which R_1 is a straight-chain or branched, saturated or unsaturated, aliphatic or cycloaliphatic hydrocarbon radical having 2 to 40 carbon atoms;

R_2 is an aromatic, aliphatic, cycloaliphatic, araliphatic, unbranched or branched hydrocarbon radical having 1 to 30 carbon atoms; and

R_3 = independently at each occurrence H or



with

B) an amine compound containing at least 2 reactive amine hydrogens per molecule.

2) Urethane amine according to Claim 1, wherein R_1 has 4 to 10 carbon atoms.

3) Urethane amine according to Claim 1, wherein R_2 has 6 to 20 carbon atoms.

4) Urethane amine according to Claim 1, characterized in that the amine compound for adducting the polyether urethane epoxide is an aliphatic, araliphatic or cycloaliphatic amine or an amino amide.

5) Urethane amine according to Claim 1, characterized in that the urethane amine contains at least 2 reactive amine hydrogens per molecule.

6) Urethane amine according to Claim 1, characterized in that the urethane amine is subsequently adducted with an epoxide compound, preferably a monofunctional epoxide compound.

7) Curable composition comprising
a) a urethane amine according to Claim 1,
b) an epoxy resin having on average more than one epoxide group in the molecule.

8) Curable composition according to Claim 7, further comprising an aminic curing agent other than a).

9) Curable composition according to either of Claims 7 and 8, further comprising organic- and mineral-based fillers, pigments, plasticizers, accelerators, solvents, blowing agents and/or other customary curing agents.

10) Use of a curable composition according to any one of Claims 7 to 9 for producing mouldings, adhesive bonds, coatings and foam materials.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2005/052852

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08G18/28 C08G59/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2004/003050 A (VANTICO AG; VOLLE, JOERG; SCHERZER, WOLFGANG) 8 January 2004 (2004-01-08) claim 1	1,3-10
X	US 3 533 983 A (FRANK N. HIROSAWA) 13 October 1970 (1970-10-13) Scheme of column 4 claim 1; example I	1-3,5
A	US 3 624 178 A (FRIEDRICH LOHSE ET AL) 30 November 1971 (1971-11-30) example 8	1-10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
4 August 2005	17/08/2005

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Lanz, S

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
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