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(54) Benævnelse: **Semicarbazoner som acceleratorer til at hærde epoxyharpikser**

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The present invention relates to the use of semicarbazones as latent accelerators for curing epoxy resin compositions by means of heat-activatable curing agents such as amines, amides, guanidines, biguanides, carboxylic acid anhydrides or polyphenols.

Curing epoxy resins

Thermosetting epoxy resins are widely used on account of their good chemical resistance, their very good thermal and dynamic-mechanical properties and their high electrical insulation capacity. Moreover, they exhibit good adhesion to several substrates. On account of these properties, they are preferably used as a low-shrinkage matrix for fibre composites, which are used as structural elements while at the same time having a low weight. In addition, epoxy resins are often found as a constituent of casting resins, electrolaminates, structural adhesives, powder coatings and casting compounds (see G.W. Ehrenstein, Faserverbund-Kunststoffe, **2006**, 2nd edition, Carl Hanser Verlag, Munich, pages 63-68; and M. Reyne, Composite Solutions, **2006**, JEC Publications, pages 31-37).

Epoxy resins are cured according to different mechanisms. In addition to curing using polyphenols or carboxylic acid anhydrides, curing is frequently carried out using amines or amides. For this purpose, the stoichiometric amount of hydrogen atoms, as supplied, for example, by bifunctional amines or amides, is added. Reference may be made in this connection to Chapter 2 "Curing Agents for Epoxy Resins" in "Chemistry and Technology of Epoxy Resins" by Bryan Ellis, published in 1993 by Blackie Academic & Professional. In that chapter it is described that crosslinking is often carried out by means of aromatic, aliphatic or cycloaliphatic amines, polyamides, polyamidoamines, polyetheramines, Mannich bases, anhydrides or polyphenols (phenol novolaks). Because of the mostly high reactivity and thus low pot life, such epoxy resin-curing agent compositions are frequently in two-component form. This means that the resin (A component) and the curing agent (B component) are stored separately and are only mixed in the correct ratio shortly before they are used. "Latent" in this connection means that a mixture of the individual components is stable under defined storage conditions and storage

times and cures rapidly only after mostly thermal activation (H. Sanftenberg, M. Fedke *Angew. Makrom. Chem.* **1995**, *225*, 99-107).

One-component, heat-curing mixtures, on the other hand, are prefabricated in ready-for-use form, whereby errors in mixing the individual components during use on site are excluded. This requires latent curing agent systems which are stable (storable) at room temperature but readily react to completion when heated. Dicyandiamide (Dicy), for example, is a particularly suitable and also inexpensive curing agent for such one-component epoxy resin formulations. Corresponding resin-curing agent mixtures can be stored ready-for-use for up to six (6) months under ambient conditions. The reason for this property is in particular the insolubility of Dicy in epoxy resins at ambient temperature (Bryan Ellis, *Chemistry and Technology of Epoxy Resins*, **1993**, published by Blackie Academic & Professional, page 49). However, owing to the pronounced slowness of Dicy to react, such systems require long curing times at high temperatures (R. Lopez, **1966**, US 3,391,113; G. Ott, **1949**, US 2,637,715 B1; J. v. Seyerl, **1984**, EP 0 148 365). In order to lower the curing temperatures, accelerators can be used in combination with the dicyandiamide curing agent. Compounds which have these properties are, inter alia, urones (Th. Güthner, B. Hammer, *J. Appl. Polym. Sci.*, **1993**, *50*, 1453-1459; Brockmann et al. *J. Adhesion & Adhesives*, **2000**, *20*, 333-340; Poisson et al. *J. Appl. Polym. Sci.*, **1998**, *69*, 2487-2497) or imidazoles (GB 1 050 679; Ricciardi et al. *J. Appl. Polym. Sci.*, **1983**, *21*, 1475-1490). While extraordinarily long latency times are described for urone systems, imidazole-resin formulations with or without dicyandiamide generally have a short pot life of only a few hours (Bryan Ellis, *Chemistry and Technology of Epoxy Resins*, **1993**, published by Blackie Academic & Professional, pages 58-60). Examples of the use of urones in storage-stable, latent-curing 1K (one-component) epoxy resin compositions are described in patent documents US 3,562,215, US 3,956,237, GB 1,153,639 A1, GB 1,293,142 A1, US 3,386,956, US 6,231,959 and DE 103 24 486 A1. However, urones are mostly solids having low solubility in the common organic solvents or water. In addition, many of the products which are currently commercially available contain substituted aromatic compounds, which in turn often carry the halogens chlorine or fluorine. Examples thereof are, inter alia,

monurone, diurone, chlorotoluron or fluometuron. The products, most of which have been known for a long time, are today considered to be harmful both toxicologically and from the point of view of occupational health and safety.

Accordingly, the object underlying this work was to provide latent accelerators for the production of storage-stable, latent-curing 1K epoxy resin compositions, which no longer have the disadvantages according to the described prior art. Surprisingly, it has been possible to achieve the stated object by the use of the substance class of the semicarbazones described below.

It has now been found that semicarbazones of formula (I) are particularly well suited as curing accelerators for epoxy resin compositions, in particular for epoxy resin compositions which comprise one or more heat-activatable curing agents, wherein the semicarbazones have the following structure:

formula (I)

where

R^1= a branched or linear alkyl functional group, cycloalkyl functional group, aryl functional group or alkylaryl functional group,

R^2 = H, a branched or linear alkyl functional group, cycloalkyl functional group, aryl functional group or alkylaryl,

R^3, R^4= simultaneously or independently of one another, H, a branched or linear alkyl functional group, cycloalkyl functional group, alkylaryl functional group, aryl functional group, heteroaryl functional group or CN;

or

R^1 = a branched or linear alkyl functional group, cycloalkyl functional group, aryl functional group or alkylaryl functional group,

R^2 = H, a branched or linear alkyl functional group, cycloalkyl functional group, aryl functional group or alkylaryl functional group, and

R^3 and R^4 = alkylene having $-(CH_2)_n-$ and $2 \leq n \leq 11$.

Particular preference is given to semicarbazones which have the following substituents R^1 to R^4:

R^1 = methyl, ethyl, benzyl or phenyl,

R^2 = H, methyl, ethyl, benzyl or phenyl,

R^3, R^4 = simultaneously or independently of one another, H, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, benzyl or phenyl,

or

R^1 = methyl, ethyl, benzyl or phenyl,

R^2 = H, methyl, ethyl, benzyl or phenyl,

R^3 and R^4 = alkylene having $-(CH_2)_n-$ and $2 \leq n \leq 6$.

These semicarbazones have a high latency in 1K epoxy resin compositions.

According to the invention, the semicarbazones are used as curing accelerators and not as the curing agent itself. This means that, by adding the semicarbazones, curing effected by a heat-activatable curing agent is accelerated. This acceleration is in particular latent, that is to say the accelerating action of the semicarbazones becomes effective only upon activation, in particular thermal activation.

Semicarbazides and semicarbazones

Semicarbazones of the general formula (I) are a substance class which has hitherto not been widely described in the literature.

formula (I)

Adams and Bowie (*Rapid Communications in Mass Spectrometry*, **1990**, *4(8)*, 275-6) studied the impact-induced fragmentation of acetone (R^1=R^2=R^3=R^4=Me) and acetophenone 4,4-dimethylsemicarbazone (R^1=R^2=R^3=Me, R^4=Ph) using a

mass spectrometer. Hadzi and Jan (*J. Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy*, **1967**, *23(3)*, 571-7) addressed the question of molecule configuration using the example of the 4,4-diethyl derivatives (R^1=R^2=Et, R^3=R^4=Me and R^1=R^2=Et, R^3=Me, R^4=Ph). Some carbo-substituted as well as heterocyclically substituted semicarbazones were studied, for example, by CoCENSYS INC. (WO 98/47869) or the University of Vienna (*J. Inorg. Chem.* **2007**, *101(11-12)*, 1946-1957) in relation to possible pharmaceutical activities. Other publications describe a pesticidal (US 4,344,893 A) or growth-regulating activity (*Biologizace a Chemizace Vyzivy Zvirat* **1977**, *13(4)*, 357-74). In addition, in 1994 Glöckler published a work (Zur Chemie der 1,3,4-Oxadiazoliumsalze, scientific work in the chemistry department at the University of Constance, June **1994**), in which he studied in detail the preparation and characterisation of some 4,4-dimethylsemicarbazones (I) starting from 4,4-dimethylsemicarbazide (II). Mention was made therein, for example, of the derivatives dicyclopropyl ketone, cyclopropyl phenyl ketone, acetophenone, acetone, benzophenone or cyclopentanone 4,4-dimethylsemicarbazone.

4,4-Dimethylsemicarbazide (II) and 4,4-diethylsemicarbazide (III) are obtained synthetically by processes known in the literature, as published, for example, by C. Vogelesang (*Rec. Trav. Chim.* **1943**, *62*, 5) or in WO 98/47869.

Further semicarbazides can be obtained analogously by reacting hydrazine with corresponding carbamoyl chlorides. The semicarbazides obtained in this way can be converted into the desired semicarbazones according to formula (I) in a following stage by reaction with corresponding ketones (see also Glöckler (Zur Chemie der 1,3,4-Oxadiazoliumsalze, scientific work in the chemistry department at the University of Constance, June **1994**)).

There is no mention in the literature of semicarbazones of composition (I) as curing agents or accelerators for crosslinking epoxy resins.

Surprisingly, it has further been found that the compounds of formula (I) according to the invention, preferably in combination with heat-activatable curing agents

such as amines, amides, guanidines, biguanides, carboxylic acid anhydrides or polyphenols, are outstandingly suitable as curing accelerators for the curing of epoxy resin compositions. According to the present invention, there are used for that purpose as curing accelerators semicarbazones of the general formula (I)

formula (I)

where

R^1= a branched or linear alkyl functional group, cycloalkyl functional group, aryl functional group or alkylaryl functional group,

R^2 = H, a branched or linear alkyl functional group, cycloalkyl functional group, aryl functional group or alkylaryl,

R^3, R^4= simultaneously or independently of one another, H, a branched or linear alkyl functional group, cycloalkyl functional group, alkylaryl functional group, aryl functional group, heteroaryl functional group or CN;

or

R^1 = a branched or linear alkyl functional group, cycloalkyl functional group, aryl functional group or alkylaryl functional group,

R^2 = H, a branched or linear alkyl functional group, cycloalkyl functional group, aryl functional group or alkylaryl functional group,

R^3 and R^4 = alkylene having $-(CH_2)_n-$ and $2 \leq n \leq 11$.

Particular preference is given in this case to semicarbazones which have the following substituents R^1 to R^4:

R^1 = methyl, ethyl, benzyl or phenyl,

R^2 = H, methyl, ethyl, benzyl or phenyl,

R^3, R^4 = simultaneously or independently of one another, H, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, benzyl or phenyl,

or

R^1 = methyl, ethyl, benzyl or phenyl,

R^2 = H, methyl, ethyl, benzyl or phenyl,

R^3 and R^4 = alkylene having $-(CH_2)_n-$ and $2 \leq n \leq 6$.

The substituents R^1 to R^4 can vary widely. Further preferred functional groups R^1 and R^2 are methyl, ethyl and benzyl. The substitution pattern for R^3 and R^4 is determined by the aldehyde or ketone used in the synthesis (G.W. Adams, J.H. Bowie *Rapid Communications in Mass Spectrometry*, **1990**, *4(8)*, 275-6; D.J. Hadzi *J. Spectrochimica Acta (A)* **1967**, *23(3)*, 571-7; St. Glöckler, Zur Chemie der 1,3,4-Oxadiazoliumsalze, scientific work in the chemistry department at the University of Constance, June **1994**). There are used in particular acetaldehyde, benzaldehyde, salicylaldehyde, cinnamaldehyde, anisaldehyde, acetone, methyl ethyl ketone, methyl propyl ketone, methyl isobutyl ketone, cyclopentanone, cyclohexanone, diethyl ketone, dicyclopropyl ketone, cyclopropyl phenyl ketone, acetophenone, benzophenone, 3-indolyl methyl ketone, phenyl 2-pyridyl ketone, methyl 2-pyridyl ketone or 1-cyano-2,2-dimethylpropanone.

Preference is given according to the invention to semicarbazones in which R^1 represents methyl, ethyl, benzyl or phenyl. Preference is further given according to the invention to semicarbazones in which R^2 represents H, methyl, ethyl, benzyl or phenyl, in particular methyl, ethyl, benzyl or phenyl.

Preference is further given to semicarbazones in which R^3 and R^4 represent, independently of one another, H, C_1-C_4 alkyl, benzyl or phenyl or R^3 and R^4 together form an alkylene having $-(CH_2)_n-$, wherein $2 \leq n \leq 6$.

Structurally, the semicarbazones (I) can be both in the form of geometric isomers ((Z), (E) isomers) and in the respective tautomeric forms (keto-enol tautomers). Depending on the functional groups R^1 to R^4, the compounds (I) are obtained in solid, semi-solid or in liquid-oil form. The substitution pattern also determines the solubility of the semicarbazones (I) in solvents or in epoxy resins.

By way of example and without implying any limitation in respect of the semicarbazones of the general formula (I) according to the invention, preferred representatives which are used are acetone 4,4-dimethylsemicarbazone (Ac-DMS),

methyl ethyl ketone 4,4-dimethylsemicarbazone (MEK-DMS), dicyclopropyl ketone 4,4-dimethylsemicarbazone (DCyPr-DMS), methyl isobutyl ketone 4,4-dimethylsemicarbazone (MIBK-DMS), cyclopentanone 4,4-dimethylsemicarbazone (CyPn-DMS), cyclohexanone 4,4-dimethylsemicarbazone (CyHx-DMS), acetophenone 4,4-dimethylsemicarbazone (AcPh-DMS), cyclopropyl phenyl ketone 4,4-dimethylsemicarbazone (CyPrPh-DMS), benzophenone 4,4-dimethylsemicarbazone (BzPh-DMS), acetone 4,4-diethylsemicarbazone (Ac-DES), cyclopentanone 4,4-diethylsemicarbazone (CyPn-DES) or acetophenone 4,4-diethylsemicarbazone (AcPh-DES).

Dicyandiamide in particular can be used as heat-activatable curing agent.

According to a further aspect of the present invention, it is provided that the semicarbazone or mixtures of the semicarbazones is/are used in an amount of from 0.1 to 15 wt.%, based on the epoxy resin composition, preferably in an amount of from 1 to 10 wt.%. Alternatively or in addition, however, it can also be provided that the semicarbazone or mixtures of the semicarbazones is/are used in a ratio of from 0.1 to 15 parts, based on 100 parts epoxy resin.

With regard to the epoxy resins to be cured, the present invention is not subject to any limitation. In particular all commercially available products that usually have more than one 1,2-epoxy group (oxirane) and may thereby be saturated or unsaturated, aliphatic, cycloaliphatic, aromatic or heterocyclic are suitable. The epoxy resins may additionally have substituents such as halogens and phosphorus and hydroxyl groups. Epoxy resins based on glycidyl polyethers of 2,2-bis(4-hydroxyphenyl)propane (bisphenol A) and the bromine-substituted derivative (tetrabromobisphenol A), glycidyl polyethers of 2,2-bis(4-hydroxyphenyl)methane (bisphenol F) and glycidyl polyethers of novolak resins and based on aniline or substituted anilines such as P-aminophenol or 4,4'-diaminodiphenylmethanes can be cured particularly well by the use of the compounds of formula (I) according to the invention in the presence of heat-activatable curing agents.

According to a further aspect, the present invention accordingly likewise provides an epoxy resin composition. This epoxy resin composition comprises

a) an epoxy resin having at least one reactive epoxy group,

b) at least one heat-activatable curing agent,

c) at least one semicarbazone of the general formula (I) as a curing accelerator

formula (I)

where

R^1 = a branched or linear alkyl functional group, cycloalkyl functional group, aryl functional group or alkylaryl functional group,

R^2 = H, a branched or linear alkyl functional group, cycloalkyl functional group, aryl functional group or alkylaryl,

R^3, R^4 = simultaneously or independently of one another, H, a branched or linear alkyl functional group, cycloalkyl functional group, alkylaryl functional group, aryl functional group, heteroaryl functional group or CN;

or

R^1 = a branched or linear alkyl functional group, cycloalkyl functional group, aryl functional group or alkylaryl functional group,

R^2 = H, a branched or linear alkyl functional group, cycloalkyl functional group, aryl functional group or alkylaryl functional group, and

R^3 and R^4 = alkylene having $-(CH_2)_n-$ and $2 \leq n \leq 11$.

Particular preference is given here to epoxy resin compositions which comprise a semicarbazone of the general formula (I) having the following substituents R^1 to R^4:

R^1 = methyl, ethyl, benzyl or phenyl,

R^2 = H, methyl, ethyl, benzyl or phenyl,

R^3, R^4 = simultaneously or independently of one another, H, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, benzyl or phenyl,

or

R^1 = methyl, ethyl, benzyl or phenyl,

R^2 = H, methyl, ethyl, benzyl or phenyl,

R^3 and R^4 = alkylene having $-(CH_2)_n-$ and $2 \leq n \leq 6$.

According to a preferred embodiment of the present invention, it is provided that in particular amines, amides, guanidines, biguanidines, carboxylic acid anhydrides or polyphenols are used as heat-activatable curing agents.

As preferred representatives of the heat-activatable curing agents used according to the invention there may be mentioned by way of example – and thus without implying any limitation – biguanides such as ortho-tolyl biguanide (OTB), methylenedianiline (MDA, DDM) and also the saturated form para-aminocyclohexylmethane (PACM) or derivatives of those amines, 3,3'- or 4,4'-diaminodiphenylsulfone (DDS) or mixtures thereof, polyetheramines (Jeffamines), dicyandiamide (DCD), dihydrazides of adipic or sebacic acid, anhydrides of pyromellitic, trimellitic or phthalic acid, derivatives thereof which may also be hydrogenated or partially hydrogenated, phenol novolaks or cresol novolaks.

The epoxy resin compositions within the meaning of the invention are prepared in accordance with the principles known to the skilled person. To that end, in a first step the resin and the curing agent are mixed homogeneously. The curing agent thereby preferably represents the crosslinking component and is accordingly used in the required, stoichiometric amount. The amount used is in most cases directly dependent on the molecular weight of the curing agent compound and thus also on the specific HEW value (hydrogen equivalent weight). This can either be taken from the manufacturer's data sheet or can be represented as a quotient, the molecular weight of the curing agent being divided by the number of reactive H functions. For the stoichiometric curing of 100 parts of epoxy resin, the quotient of the HEW (curing agent) and the EEW (resin) is formed and multiplied

by 100. The EEW value (epoxy equivalent weight) of the resin is obtained from the manufacturer's data sheet.

In a second step, the accelerators (I) according to the invention are added, wherein the order in which the mixture of resin, curing agent, accelerator and any further additives is prepared is not binding for the effectiveness of the invention. The auxiliary agents used are likewise not limiting for the implementation of the invention. Preferred ways of homogeneously blending the components are, for example, dissolvers or kneaders.

There are no limitations as regards the amount of accelerators (I) used according to the invention. Preferably from 0.01 to 20 parts of accelerator, more preferably from 0.1 to 15 parts, preferably from 0.1 to 10 parts and particularly preferably from 1 to 5 parts, are used per 100 parts of resin. A combination of a plurality of accelerators is also covered by this invention.

Curing of the epoxy resins by means of the compounds (I) used according to the invention generally takes place at temperatures of from 60 to 200 °C, preferably at from 80 to 180 °C and in particular at from 100 to 160 °C. The choice of curing temperature is dependent on the particular processing and product requirements and can be varied via the formulation, especially by adjusting the amounts of curing agent and by adding additives. The manner in which energy is supplied to the resin formulations is not important here. For example, it can be effected in the form of heat by means of a furnace or heating elements, but equally by means of infrared radiators or excitation by microwaves or other types of radiation.

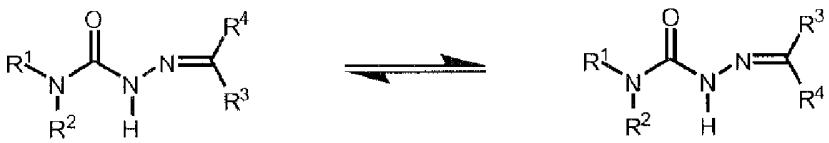
The curing profile of the formulations according to the invention can be varied by adding further commercially available additives, as are known to the skilled person for the curing of epoxy resins. For example, the activation temperatures can be lowered further depending on the amount added, or the gel times and thus the curing times can advantageously be adapted to technical specifications and thus to special customer requirements.

Additives for improving the processability of the uncured epoxy resin compositions or for adapting the thermo-mechanical properties of the thermosetting products to the profile of requirements include, for example, reactive diluents, fillers, rheological additives such as thixotropic agents or dispersing additives, anticaking agents, colourants, pigments, impact modifiers or fireproofing additives.

There are also no limitations as regards the physical form both of the resins and of the curing agents, accelerators or further additives. In particular, pulverulent components in micronised or in crystalline form can be used. The addition of solvents may also be advantageous in some applications. Examples of solvents are water, various esters of glycol ethers, and also ketones such as acetone, MEK, MIBK or solvents such as DMF, etc. These are used either to lower the viscosity or to prepare dissolved formulations. Both are highly advantageous in the impregnation of reinforcing fibres, as are used in the production of fibre composites. Accordingly, a particularly preferred variant is the use of semicarbazones (I) which are liquid or soluble in the resin formulation.

On account of the advantageous use properties of the accelerators according to the invention and their inexpensive production and, associated therewith, an advantageous cost-benefit ratio, said accelerators are particularly well suited to technical use.

The present invention describes the use of semicarbazones of the general formula (I) having the mentioned meanings for the functional groups R^1, R^2, R^3 and R^4 in epoxy resin compositions.



formula (I)

These semicarbazones have a high latency in epoxy resin compositions and are accordingly outstandingly suitable as latent curing accelerators for 1K epoxy resin compositions.

The following examples illustrate the advantages of the present invention.

Examples

The following resin, curing agent and accelerator components were used in the examples to illustrate the invention:

Epoxy resin:

Name	Short name	EEW	CAS No.
Bisphenol A liquid resin[1)]	Epikote 828	182-187	[25068-38-6]
	average molecular weight <= 700		

Curing agent:

Name	Short name	HEW	CAS No.
Dicyandiamide (cyanoguanidine)[2)]	DCD (Dicy)	12-14	[461-58-5]

Accelerator (comparison):

Name	Short name	CAS No.
Dyhard® UR500 (TDI-urone)[2)]	UR500	[26604-41-1]
Dyhard® PI-FF (2-phenylimidazole)[2)]	PI-FF	[670-96-2]

General preparation of semicarbazones of formula (I)

a) Synthesis of the semicarbazides

4,4-Dimethylsemicarbazide (II) and 4,4-diethylsemicarbazide (III) are obtained synthetically by processes known in the literature, as published, for example, by C. Vogelesang (*Rec. Trav. Chim.* **1943**, *62*, 5) or in WO 98/47869. As illustrated by way of example according to Example 26 of patent specification WO 98/47869,

for the preparation of 4,4-dimethylsemicarbazide (II), equimolar amounts of hydrazine hydrate and dimethylcarbamoyl chloride are made to react dropwise in the solvents ethanol and diethyl ether, with ice bath cooling, and post-reacted for one hour, with ice bath cooling. After filtration of the resulting solid, the reaction mixture is concentrated to yield the target compound (II) in the form of a white, crystalline solid.

b) Synthesis of the semicarbazones

In the following, the semicarbazides prepared according to a) are reacted with ketones to give the desired semicarbazones.

Again by way of example, the generally applicable reaction of the semicarbazides (II) to the semicarbazones (I) according to the invention is illustrated using cyclopentanone 4,4-dimethylsemicarbazone (R^1=R^2=Me; R^3 and R^4 = -$(CH_2)_4$-) as an example. To that end, according to Glöckler (Zur Chemie der 1,3,4-Oxadiazoliumsalze, scientific work in the chemistry department at the University of Constance, June **1994**), cyclopentanone in a 5-fold excess is reacted with the semicarbazide (II) in boiling ethanol. After 45 minutes, the reaction is complete and, after evaporation of the solvent and of the excess ketone, the residue is stirred under ice-cold pentane to yield a colourless — slightly yellowish powder. The structure and composition were confirmed by IR and NMR (^{1}H, ^{13}C) spectroscopic investigations as well as by CHN analysis.

The above semicarbazones mentioned herein are prepared analogously.

Accelerator (according to the invention):

Name	Short name	CAS No.

Acetone 4,4-dimethylsemicarbazone[4,6)]

Ac-DMS

[130652-43-6]

$C_6H_{13}N_3O$ (143.19) calc. C 50.33 % H 9.15 %
N 29.35 %

found C 48.97 % H 9.02 %
N 28.47 %

Methyl ethyl ketone 4,4-dimethylsemicarbazone

MEK-DMS

[no CAS No.]

$C_7H_{15}N_3O$ (157.21) calc. C 53.48 % H 9.62 %
N 26.73 %

found C 53.88 % H 9.70 %
N 25.48 %

Methyl isobutyl ketone 4,4-dimethylsemicarbazone

MIBK-DMS

[no CAS No.]

$C_9H_{19}N_3O$ (185.27) calc. C 58.35 % H 10.34 %
N 22.68 %

found C 57.71 % H 10.76 %
N 22.30 %

Cyclopentanone 4,4-dimethylsemicarbazone[6)]

CyPn-DMS

[no CAS No.]

$C_8H_{15}N_3O$ (169.22) calc. C 56.78 % H 8.93 %
N 24.83 %

found C 56.72 % H 8.96 %
N 24.83 %

Acetophenone 4,4-dimethylsemicarbazone[4,6)]

AcPh-DMS

[17106-64-8]

$C_{11}H_{15}N_3O$ (205.26) calc. C 64.37 % H 7.37 %
N 20.47 %

found C 64.18 % H 7.39 %
N 19.71 %

Cyclohexanone 4,4-dimethylsemicarbazone

CyHx-DMS

[no CAS No.]

$C_9H_{17}N_3O$ (183.25) calc. C 58.99 % H 9.35 %
N 22.93 %

found C 58.21 % H 9.05 %
N 23.22 %

Acetone 4,4-diethylsemicarbazone[5)]

Ac-DES

[14850-53-4]

$C_8H_{17}N_3O$ (171.24) calc. C 56.11 % H 10.01 %
N 24.54 %

found C 55.68 % H 10.49 %
N 24.33 %

Acetophenone 4,4-diethylsemicarbazone[5)]

AcPh-DES

[14850-67-0]

$C_{13}H_{19}N_3O$ (233.31) calc. C 66.92 % H 8.21 %
N 18.01 %

found C 66.25 % H 8.08 %
N 18.49 %

Preparation and origin of resin, curing agent and accelerator:

1) Hexion Speciality Chemicals

2) AlzChem GmbH, Trostberg

3) Sigma-Aldrich Group (further substances required for the synthesis)

4) G.W. Adams, J.H. Bowie, *Rapid Communications in Mass Spectrometry,* **1990**, *4(8)*, 275-6.

5) D.J. Hadzi, *J. Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy*, **1967**, *23(3)*, 571-7.

6) St. Glöckler, Zur Chemie der 1,3,4-Oxadiazoliumsalze, scientific work in the chemistry department of the University of Constance, **June 1994**.

Preparation of the sample

In order to prepare the resin-curing agent formulation, the components were weighed in the indicated ratios into a porcelain mortar and thoroughly mixed homogeneously by hand. Solids were triturated in the mortar beforehand.

Determination of the gel time

Approximately 700-800 mg of the freshly prepared sample was weighed into a small aluminium crucible which was introduced into a heating block preheated to the indicated temperature (start of timing). The test for gelation was carried out by means of a wooden stick, which was dipped into the liquid resin. If a stable strand formed when the stick was removed (no further dripping), this time was defined as the gel time.

Performance of the dynamic DSC measurements

In order to determine the DSC peak temperature (DSC peak T), the sample was heated from 30 to 250 °C at a heating rate of 10 K/min. The DSC onset temperature (DSC onset T) was determined from the same measurement by applying the tangent to the exothermic reaction peak. For determining the isothermal reaction time, a second sample was introduced by means of a sample loader into the DSC furnace heated to the indicated temperature, and that temperature was kept constant for at least 40 minutes. The position of the curing peak corresponded to the time of maximum release of heat of reaction and was defined as the isothermal reaction time.

Measurement of the glass transition temperature by means of DSC (end Tg)

For determining the maximum achievable glass transition temperature (end Tg), the pre-gelled sample from the gel time determination was used. The sample was cured completely by being heated to 200 °C (DSC temperature program: 30 to

200 °C, heating rate 20 K/min) and maintained at that temperature for 30 minutes. After cooling to 30 °C, the sample was again heated from 30 to 200 °C at a heating rate of 10 K/min, and the Tg was determined from the heating curve by applying the tangent at the point of inflection of the greatest change in heat capacity (ΔCp).

Performance of the latency experiments

In order to determine the latency (storage stability), approximately 10 g of the sample was freshly prepared and brought to the indicated temperature in a furnace. As a measure of the advancing crosslinking (curing) of the epoxy resin composition, the dynamic viscosity of a sample was determined at 25 °C in a cone(1°)-plate rheometer at the respective measuring times.

The experiments were evaluated by plotting the percentage increase in viscosity (%) over the time in hours (h) or days (d) and by extrapolating the individual data by means of an exponential or potential mathematical function.

Analytical devices used

Gel time	Heating block	VLM 2.0 HT
DSC measurements	DSC device	Mettler-Toledo DSC 822
Viscosity	Rheometer	Haake RheoStress 1

Example 1

Gel time, dyn. DSC and end Tg

The resin formulations of the general composition:

Epikote 828 (100 parts) : DCD (6.5 parts) : accelerator (x parts)

were prepared and tested as described above in accordance with Tables 1a and 1b.

Table 1a: Gel time, dyn. DSC and end Tg (not in accordance with the invention)

Composition	Accelerator (parts)	Gel time at 120 °C [min : sec]	Gel time at 140 °C [min : sec]	DSC peak temperature [°C]	End Tg (DSC) [°C]
1.01	UR500 (1.0 part)	12 : 40	04 : 00	150.2	150
1.02	UR500 (3.0 parts)	07 : 30	02 : 45	143.4	134
1.03	UR500 (5.0 parts)	05 : 50	02 : 25	140.3	126
1.04	PI-FF (1.0 part)	06 : 40	---	143.5	165
1.05	PI-FF (3.0 parts)	03 : 05	---	130.7	154
1.06	PI-FF (5.0 parts)	02 : 30	01 : 10	125.9	124
1.07	without accelerator	> 180	> 60	199.6	167

Table 1b: Gel time, dyn. DSC and end Tg (according to the invention)

Composition	Accelerator (parts)	Gel time at 120 °C [min : sec]	Gel time at 140 °C [min : sec]	DSC peak temperature [°C]	End Tg (DSC) [°C]

1.20	Ac-DMS (1.0 part)	12 : 10	03 : 20	148.9	149
1.21	Ac-DMS (3.0 parts)	05: 05	02 : 20	137.9	130
1.22	Ac-DMS (5.0 parts)	04 : 10	01 : 55	133.8	122
1.23	MEK-DMS (1.0 part)	14 : 15	03 : 10	156.2	147
1.24	MEK-DMS (3.0 parts)	05 : 55	02 : 45	140.2	132
1.25	MEK-DMS (5.0 parts)	04 : 40	02 : 15	135.3	123
1.26	MIBK-DMS (1.0 part)	17 : 50	05 : 10	152.0	151
1.27	MIBK-DMS (3.0 parts)	06 : 55	03 : 00	142.2	132
1.28	MIBK-DMS (5.0 parts)	05 : 35	02 : 40	139.0	123
1.29	CyPn-DMS (1.0 part)	15 : 15	05 : 00	154.6	151
1.30	CyPn-DMS (3.0 parts)	07 : 20	03 : 20	144.8	135

1.31	CyPn-DMS (5.0 parts)	05 : 30	02 : 15	142.1	125
1.32	CyHx-DMS (1.0 part)	16 : 00	04 : 25	157.3	145
1.33	CyHx-DMS (3.0 parts)	08 : 20	03 : 25	151.7	136
1.34	CyHx-DMS (5.0 parts)	06 : 40	02 : 50	145.0	125
1.35	AcPh-DMS (1.0 part)	17 : 35	04 : 20	154.4	145
1.36	AcPh-DMS (3.0 parts)	07 : 45	02 : 45	145.9	132
1.37	AcPh-DMS (5.0 parts)	06 : 15	02 : 30	141.7	124
1.38	Ac-DES (1.0 part)	-	18 : 40	184.2	153
1.39	Ac-DES (3.0 parts)	-	11 : 10	171.2	139
1.40	Ac-DES (5.0 parts)	-	08 : 00	167.6	124
1.41	AcPh-DES (1.0 part)	-	21 : 15	185.9	144
1.42	AcPh-DES (3.0 parts)	-	13 : 30	176.8	140

1.43	AcPh-DES (5.0 parts)	-	12 : 00	172.4	128

The accelerating action of the semicarbazones (I) according to the invention in conjunction with the curing agent DCD becomes clear in Examples 1.20 – 1.43 in comparison with Example 1.07. Without accelerator, the curing agent DCD, which is slow to react, is effective in the above-described epoxy resin matrix only at a temperature of 199.6 °C and above (see Example 1.07). At that temperature, polymerisation to the thermosetting network can be seen in the DSC experiment on the basis of the exothermal reaction peak. If the accelerators (I) according to the invention are added to the epoxy resin-curing agent mixture, the polymerisation reaction starts at low temperatures. For example, a peak temperature of 133.8 °C can be recorded for Example 1.22. This finding applies equally to the gel times, which become shorter as the amount of accelerator increases. The activity in respect of an epoxy resin-curing agent mixture can likewise be controlled via the nature of the substitution of the semicarbazones (I). By way of example, 1.20 – 1.22 can be compared with 1.35 – 1.37. A pronounced effect on the catalytic action is also illustrated by comparing 1.20 – 1.22 with 1.38 – 1.40, when the functional groups R^1 and R^2 are varied.

In comparison therewith are accelerators such as Dyhard UR500 or Dyhard PI-FF (Examples 1.01 – 1.06), which were introduced commercially a long time ago and have long been available. The accelerating action in an epoxy resin-curing agent mixture is equally affected by structural, chemical differences and by the amount used.

Example 2

Latency at 25 °C

The resin formulations of the general composition:

Epikote 828 (100 parts) : DCD (6.5 parts) : accelerator (x parts)

were prepared and tested as described above in accordance with Tables 2a and 2b.

Table 2a: Latency at 25 °C in hours (h) or days (d) (not in accordance with the invention)

		Percentage increase in viscosity as a measure of the latency			
Composition	Accelerator (parts)	20 %	50 %	100 %	300 %
1.01	UR500 (1.0 part)	44 d	57 d	65 d	80 d
1.02	UR500 (3.0 parts)	36 d	48 d	58 d	71 d
1.03	UR500 (5.0 parts)	22 d	43 d	54 d	62 d
1.04	PI-FF (1.0 part)	14 h = 0.58 d	28 h = 1.17 d	68 h = 2.83 d	90 h = 3.75 d
1.05	PI-FF (3.0 parts)	17 h = 0.71 d	19 h = 0.79 d	21 h = 0.88 d	27 h = 1.13 d

Table 2b: Latency at 25 °C in hours (h) or days (d) (according to the invention)

		Percentage increase in viscosity as a measure of the latency			
Composition	Accelerator (parts)	20 %	50 %	100 %	300 %
1.20	Ac-DMS (1.0 part)	16 d	26 d	34 d	46 d
1.21	Ac-DMS (3.0 parts)	6 d	12 d	17 d	26 d

		Percentage increase in viscosity as a measure of the latency			
Composition	Accelerator (parts)	20 %	50 %	100 %	300 %
1.22	Ac-DMS (5.0 parts)	4 d	7 d	11 d	20 d
1.23	MEK-DMS (1.0 part)	23 d	32 d	40 d	54 d
1.24	MEK-DMS (3.0 parts)	15 d	22 d	28 d	38 d
1.25	MEK-DMS (5.0 parts)	6 d	12 d	19 d	32 d
1.26	MIBK-DMS (1.0 part)	18 d	31 d	46 d	66 d
1.27	MIBK-DMS (3.0 parts)	14 d	21 d	29 d	46 d
1.28	MIBK-DMS (5.0 parts)	5 d	9 d	17 d	29 d
1.29	CyPn-DMS (1.0 part)	32 d	66 d	115 d	> 140 d
1.30	CyPn-DMS (3.0 parts)	38 d	71 d	111 d	> 140 d

		Percentage increase in viscosity as a measure of the latency			
Composi-tion	Accelera-tor (parts)	20 %	50 %	100 %	300 %
1.31	CyPn-DMS (5.0 parts)	10 d	26 d	60 d	> 140 d
1.32	CyHx-DMS (1.0 part)	40 d	100 d	> 150 d	--
1.33	CyHx-DMS (3.0 parts)	14 d	60 d	110 d	> 150 d
1.34	CyHx-DMS (5.0 parts)	10 d	20 d	42 d	103 d
1.35	AcPh-DMS (1.0 part)	30 d	70 d	120 d	> 150 d
1.36	AcPh-DMS (3.0 parts)	18 d	33 d	48 d	72 d
1.37	AcPh-DMS (5.0 parts)	3 d	9 d	17 d	35 d
1.38	Ac-DES (1.0 part)	8 d	20 d	30 d	37 d
1.39	Ac-DES (3.0 parts)	6 d	14 d	18 d	25 d

		Percentage increase in viscosity as a measure of the latency			
Composition	Accelerator (parts)	20 %	50 %	100 %	300 %
1.40	Ac-DES (5.0 parts)	4 d	9 d	13 d	16 d
1.41	AcPh-DES (1.0 part)	38 d	63 d	91 d	> 150 d
1.42	AcPh-DES (3.0 parts)	13 d	44 d	57 d	80 d
1.43	AcPh-DES (5.0 parts)	5 d	22 d	44 d	62 d

According to Examples 1.20 to 1.43, the accelerators (I) according to the invention are more latent in the tested resin formulation than the urone comparisons 1.01 to 1.03 but substantially more latent than the imidazole derivatives in Examples 1.04 to 1.05.

Example 3

Latency at 60 °C

The resin formulations of the general composition:

Epikote 828 (100 parts) : DCD (6.5 parts) : accelerator (x parts)

were prepared and tested as described above in accordance with Tables 3a and 3b.

Table 3a: Latency at 60 °C in hours (h) (not in accordance with the invention)

		Percentage increase in viscosity as a measure of the latency			
Composi-tion	Accelera-tor (parts)	20 %	50 %	100 %	300 %
1.01	UR500 (1.0 part)	6.75 h	9.0 h	10.75 h	13.5 h
1.02	UR500 (3.0 parts)	4.0 h	6.75 h	8.75 h	12.0 h
1.04	PI-FF (1.0 part)	2.25 h	3.0 h	3.0 h	4.5 h

Table 3b: Latency at 60 °C in hours (h) (according to the invention)

		Percentage increase in viscosity as a measure of the latency			
Composition	Accelerator (parts)	20 %	50 %	100 %	300 %
1.20	Ac-DMS (1.0 part)	3.0 h	5.0 h	6.5 h	9.0 h
1.21	Ac-DMS (3.0 parts)	1.5 h	2.5 h	3.5 h	5.0 h
1.23	MEK-DMS (1.0 part)	3.5 h	5.5 h	7.0 h	9.5 h
1.24	MEK-DMS (3.0 parts)	2.0 h	2.75 h	3.5 h	4.5 h
1.26	MIBK-DMS (1.0 part)	4.5 h	6.0 h	7.25 h	9.25 h
1.27	MIBK-DMS (3.0 parts)	3.5 h	4.5 h	5.0 h	6.0 h
1.29	CyPn-DMS (1.0 part)	6.5 h	9.0 h	11.0 h	15.0 h
1.30	CyPn-DMS (3.0 parts)	1.0 h	2.0 h	4.5 h	9.25 h

		Percentage increase in viscosity as a measure of the latency			
Composition	Accelerator (parts)	20 %	50 %	100 %	300 %
1.32	AcPh-DMS (1.0 part)	6.5 h	9.0 h	11.0 h	14.0 h
1.33	AcPh-DMS (3.0 parts)	2.0 h	4.5 h	6.5 h	9.5 h
1.34	AcPh-DMS (5.0 parts)	1.0 h	2.5 h	4.0 h	6.5 h

According to Examples 1.20 to 1.34, the accelerators (I) according to the invention are better in the tested resin formulation than the urone comparison Dyhard 500 (Examples 1.01 – 1.03). Compared with the imidazole derivative (Example 1.07), the novel semicarbazones (I) are substantially more latent (Examples 1.20 – 1.34).

Patentkrav

1. Anvendelse af mindst en semicarbazon med den almene formel (I),

formula (I)

hvor

R^1 = en forgrenet eller lineær alkyl-funktionel gruppe, cycloalkyl-funktionel gruppe, aryl-funktionel gruppe eller alkylaryl-funktionel gruppe,

R^2 = H, en forgrenet eller lineær alkyl-funktionel gruppe, cycloalkyl-funktionel gruppe, aryl-funktionel gruppe eller alkylaryl-funktionel gruppe,

R^3, R^4 = samtidigt eller af hinanden, H, en forgrenet eller lineær alkyl-funktionel gruppe, cycloalkyl-funktionel gruppe, alkylaryl-funktionel gruppe, aryl-funktionel gruppe, heteroaryl-funktionel gruppe eller CN;

eller

R^1 = en forgrenet eller lineær alkyl-funktionel gruppe, cycloalkyl-funktionel gruppe, aryl-funktionel gruppe eller alkylaryl-funktionel gruppe,

R^2 = H, en forgrenet eller lineær alkyl-funktionel gruppe, cycloalkyl-funktionel gruppe, aryl-funktionel gruppe eller alkylaryl-funktionel gruppe,

R^3 og R^4 = alkylen med $-(CH_2)_n-$ og $2 \leq n \leq 11$,

som en hærdningsaccelerator til at hærde epoxyharpikssammensætninger ved hjælp af varmeaktiverbar hærder.

2. Anvendelse ifølge krav 1, **kendetegnet ved, at** den varmeaktiverbare hærder er valgt fra gruppen bestående af aminer, amider, guanidiner, biguanider, carboxylsyreanhydrider eller polyphenoler.

3. Anvendelse ifølge enten krav 1 eller krav 2, **kendetegnet ved, at** dicyandiamid anvendes som den varmeaktiverbar hærder.

4. Anvendelse ifølge mindst et af de foregående krav 1 til 3, **kendetegnet ved, at** semicarbazon eller blandinger af semicarbazoner er/anvendes i en mængde på fra 0,1 til 15 vægt-%, baseret på epoxyharpikssammensætningen.

5. Anvendelse ifølge mindst et af kravene 1 til 4, **kendetegnet ved, at** semicarbazon eller blandinger af semicarbazoner er/anvendes i et forhold på fra 0,1 til 15 dele, baseret på 100 dele epoxyharpiks.

6. Epoxyharpikssammensætning, der omfatter

a) en epoxyharpiks med mindst en reaktiv epoxygruppe,

b) mindst en varmeaktiverbar hærder,

c) mindst en semicarbazon med den almene formel (I) som en hærdningsaccelerator

formula (I)

hvor

R^1 = en forgrenet eller lineær alkyl-funktionel gruppe, cycloalkyl-funktionel gruppe, aryl-funktionel gruppe eller alkylaryl-funktionel gruppe,

R^2 = H, en forgrenet eller lineær alkyl-funktionel gruppe, cycloalkyl-funktionel gruppe, aryl-funktionel gruppe eller alkylaryl-funktionel gruppe,

R^3, R^4 = samtidigt eller uafhængigt af hinanden, H, en forgrenet eller lineær alkyl-funktionel gruppe, cycloalkyl-funktionel gruppe, alkylaryl-funktionel gruppe, aryl-funktionel gruppe, heteroaryl-funktionel gruppe eller CN;

eller

R^1 = en forgrenet eller lineær alkyl-funktionel gruppe, cycloalkyl-funktionel gruppe, aryl-funktionel gruppe eller alkylaryl-funktionel gruppe,

R^2 = H, en forgrenet eller lineær alkyl-funktionel gruppe, cycloalkyl-funktionel gruppe, aryl-funktionel gruppe eller alkylaryl-funktionel gruppe,

R^3 og R^4 = alkylen med $-(CH_2)_n-$ og $2 \leq n \leq 11$.

7. Epoxyharpikssammensætning ifølge krav 6, **kendetegnet ved, at**

R^1 = methyl, ethyl, benzyl eller phenyl,

R^2 = H, methyl, ethyl, benzyl eller phenyl,

R^3, R^4 = samtidigt eller uafhængigt af hinanden, H, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, benzyl eller phenyl,

eller

R^1 = methyl, ethyl, benzyl eller phenyl,

R^2 = H, methyl, ethyl, benzyl eller phenyl,

R^3 og R^4 = alkylen med $-(CH_2)_n-$ og $2 \leq n \leq 6$.

8. Epoxyharpikssammensætning ifølge krav 7 eller krav 8, **kendetegnet ved, at** epoxyharpiksen er udvalgt fra gruppen bestående af glycidyl-polyether af 2,2-bis(4-hydroxyphenyl)-propan (bisphenol A), derivatet deraf, der er substitueret med brom (tetrabrombisphenol A), glycidyl-polyether af 2,2-bis(4-hydroxy-phenyl)-methan (bisphenol F) og glycidyl-polyether af novolakharpikser og anilin eller substituerede aniliner, fortrinsvis P-aminophenol eller 4,4'-diamino-diphenyl-methan.

9. Epoxyharpikssammensætning ifølge ethvert af kravene 6 til 8, **kendetegnet ved, at** biguanider, fortrinsvis ortho-tolylbiguanid (OTB), methylendianilin (MDA, DDM), para-amino-cyclohexyl-metan (PACM), 3,3'- eller 4,4'-diamino-diphenyl-sulfon (DDS), polyetheraminer, dicyandiamid (DCD), adipinsyre- eller sebacinsyre-dihydrazider, pyromellitsyre, trimellitsyre- eller phthalsyreanhydrider, phenol-novolakker eller cresol-novolakker eller blandinger deraf, er indeholdt som varmeaktiverbar hærder.