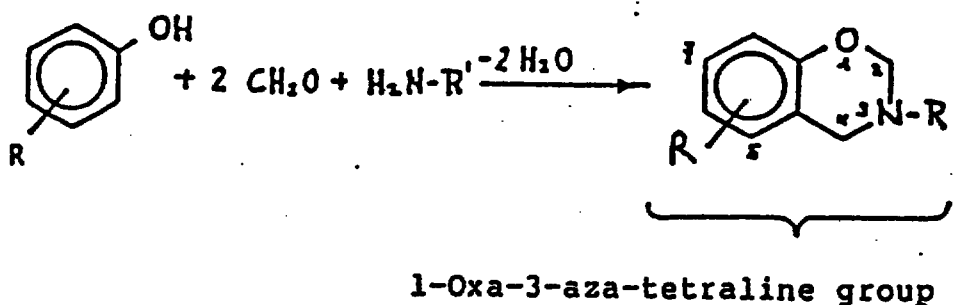


The invention relates to a novel chemically hardenable resin from compounds containing 1-oxa-3-aza tetraline groups and/or from prepolymers thereof and cycloaliphatic epoxy resins having epoxide groups anellated in a cycloaliphatic ring.

Compounds containing 1-oxa-3-aza tetraline groups, and prepolymers thereof, are known from, for example, Swiss Patents 574,978, 579,113 and 606,169. They can be obtained, for example, from phenols by reaction with formaldehyde and an amine, as in accordance with the formula:

(a)



or else by other methods resulting in homologous products. R is, for example, hydrogen, halogen, alkyl or alkoxy, and R' is an aliphatic or aromatic group.

Unlike other known condensation reactions of phenols, amines and formaldehyde, in the above reaction phenolic OH groups are consumed. Using equation (a) it is thus possible to establish the quantity of the synthesized 1-oxa-3-aza tetraline groups from the analytic determination of said OH groups in the reaction mixture.

Compounds having more than one 1-oxa-3-aza tetraline group in the molecule are used in accordance with the invention.

It is also known from the above-mentioned patents that these compounds containing 1-oxa-3-aza tetraline groups can be cured with epoxide resins, including cycloaliphatic epoxide resins.

The products concerned that have been obtained up to now are in themselves useful plastics, but their heat stability is limited. The Martens heat stability of the hardened resins obtained up to now is between 120 and 135°C, with peak values of 160 and 170°C.

For many areas of application far greater heat stability is necessary. For example, electric insulating materials with high heat resistance are in constant demand in the electrical engineering industry. Plastics reinforced with glass, quartz or carbon fibres will probably be suitable for many new areas of application if the heat resistance of the plastic can be substantially increased.

It has surprisingly been found that plastics with especially outstanding heat stability combined with very good mechanical characteristics are obtained by curing mixtures of compounds having more than one 1-oxa-3-aza tetraline group in the molecule and/or prepolymers thereof and certain cycloaliphatic epoxide resins having epoxide groups anellated in the cycloaliphatic ring.

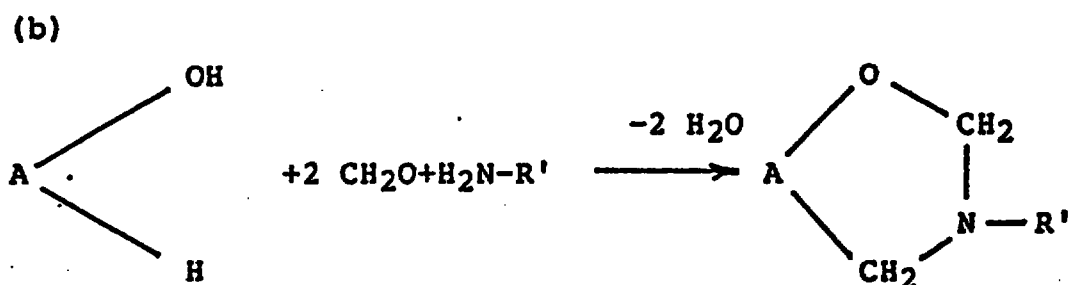
The heat stability of such plastics usually exceeds 200°C. Martens temperature and glass transition temperature reach values of 280°C. In addition these plastics are characterized by their low brittleness and high flexural and impact strength.

One object of the invention is the chemically hardenable resin from compounds containing 1-oxa-3-aza tetraline groups and cycloaliphatic epoxide resins containing anellated epoxide groups, and a method for preparing and

hardening them. A further object of the invention is the use of the resin mixtures and the hardened resins.

The chemically hardenable resin according to the present invention contains compounds having more than one 1-oxa-3-aza tetraline group in the molecule, and/or prepolymers thereof, and cycloaliphatic epoxide resins, and is characterized in that the epoxide resin contains at least two epoxide groups in the molecule, at least one of which is anellated in a cycloaliphatic ring and the remainder are likewise anellated in such a ring or directly connected to such a ring.

Compounds having more than 1-oxa-3-aza tetraline group in the molecule can be obtained from polyvalent phenols and/or amines in accordance with one of the following reaction schemes (b) or (c), or by other methods resulting in homologous products:



wherein:

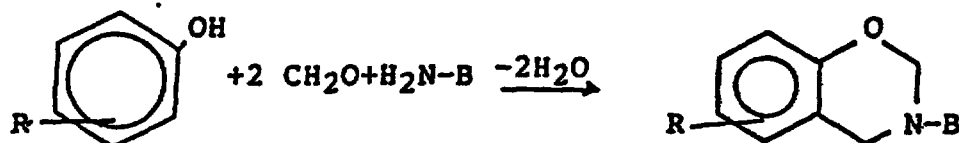
$\begin{array}{c} \text{OH} \\ \diagup \\ \text{A} \\ \diagdown \\ \text{H} \end{array}$
 is the nth part of a phenol with n phenol OH groups;

A
 is the group resulting from $\begin{array}{c} \text{OH} \\ \diagup \\ \text{A} \\ \diagdown \\ \text{H} \end{array}$
 after splitting off of OH and H in ortho position;

R' is an aliphatic or, preferably, an aromatic group; and

n is a number greater than 1, preferably less than 6, more preferably from about 1.5 to about 3.

(c)



B is the m th part of an m -valent aliphatic or, preferably, aromatic group, which may also contain hetero atoms, especially oxygen or nitrogen, or may be substituted by R ;

R is hydrogen, halogen, alkyl or alkoxy with 1 to 6 carbon atoms;

m is a number greater than 1, preferably smaller than 6, and especially 1.5 to 3.

The phenolic nuclei may also be part of a condensed ring system.

Values of n or m that are not integers signify mixtures of functionally different phenols or amines with average values n or m .

Also suitable for use in accordance with the invention as 1-oxa-3-aza tetraline compounds are reaction products prepared, for example, in accordance with Swiss Patent

606,169 from phenols, amines and formaldehyde in non-stoichiometric ratios. However, the molar ratios must be chosen so as to allow formation of more than one 1-oxa-3-aza tetraline group per molecule on average.

Prepolymers of the 1-oxa-3-aza tetraline compounds are also claimed under the invention. Since the 1-oxa-3-aza tetraline groups may react during polymerization these prepolymers may contain fewer 1-oxa-3-aza tetraline groups. It is, however, essential that the intermediately formed or hypothetical monomeric reaction product contain more than one 1-oxa-3-aza tetraline group per molecule. This can easily be calculated by a person skilled in the art from the functionality and the proportions of the starting materials. A 1-oxa-3-aza tetraline compound according to the invention or the prepolymer thereof is, for example, formed when per mole of multifunctional phenol or amine more than two moles of formaldehyde and more than one mole of monofunctional amine or phenol are reacted and the molar ratios remain within the limit defined in Swiss Patent 606,169.

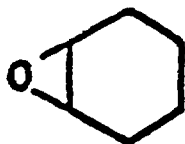
The starting materials or parent substances for the 1-oxa-3-aza tetraline compound are phenol and phenol derivatives, amines and formaldehyde.

Examples of suitable phenols include monovalent phenols such as phenol itself and m- and p-cresol, m- and p-ethyl phenol, m- and p-isopropyl phenol, m and p-methoxy phenol, m and p-ethoxy phenol, m and p-isopropoxy phenol, m and p-chloro phenol and β -naphthol. The meta-substituted phenols are preferred, because they do not include any blocked reactive sites. Bivalent phenols such as 4,4'-dihydroxy-diphenyl methane, 3,3'-dihydroxy-diphenyl methane, 2,2-bis-(4-hydroxyphenyl)-propane, 4,4'-dihydroxy stilbene, hydroquinone, pyrocatechin and resorcin may be

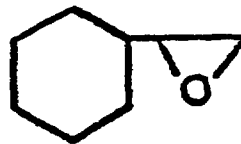
used. Low-condensed phenol and formaldehyde novolak resins can be used, mixed with a phenol if required.

Examples of especially suitable amines include aniline, o-, m- and p-phenylene diamine, benzidine, 4,4'-diaminodiphenyl methane and 2,2-bis-(aminophenyl)-propane.

Special structural requirements are set for the second component of the chemically hardenable resin, the epoxide. In order to obtain final products with outstanding heat resistance that are markedly superior in quality to hitherto known comparable resins, the second component has to be bivalent or polyvalent cycloaliphatic epoxide resins containing at least one anellated epoxide group, the remaining epoxide groups likewise being anellated or connected directly to a cycloaliphatic group:



anellated



directly connected

Especially preferred are epoxide resins having an equivalent weight between 70 and about 250, preferably 120 and 200. The preferred epoxide resins are as follows:

2-(3,4-epoxy)cyclohexyl-5,5-spiro(3,4-epoxy)cyclohexane-m-dioxane, 1 to 4 times methylated 2-(3,4-epoxy)cyclohexyl-5,5-spiro(3,4-epoxy) cyclohexane-m-dioxane, 4-(1,2-epoxyethyl)-1,2-epoxycyclohexane, 1,2,8,9-diepoxy-p-methane, 2,2-bis(3,4-epoxycyclohexyl)propane, bis-(2,3-epoxycyclopentyl) ether, 1,2,5,6-diepoxy-4,7-hexahydro-

methanoindane, bis-(3,4-epoxy-cyclohexylmethyl) adipate, bis(3,4-epoxy-6-methylcyclohexylmethyl) adipate, bis-(3,4-epoxy-cyclohexylmethyl) terephthalate, bis-(3,4-epoxy-6-methyl-cyclohexylmethyl)-terephthalate, 3,4-epoxy-cyclohexane carboxylic acid-(3,4-epoxy-cyclohexylmethyl) ester, 3,4-epoxy-6-methylcyclohexanecarboxylic acid-(3,4-epoxy-6-methylcyclohexylmethyl) ester, 1,2-bis-(5(1,2-epoxy)-4,7-hexahydromethanoindane oxy)-ethane 1,1,1-tris ((5-(1,2-epoxy)-4,7-hexahydromethanoindane oxy)-methyl)-propane and 4,5-epoxyhexahydrophthalic acid-bis-(3,4-epoxy-cyclohexylmethyl) ester.

Especially good resins are those where the proportion of compounds containing 1-oxa-3-aza tetraline groups and epoxide resin is from 0.2 to 2, preferably from 0.8 to 1.5, expressed as the molar ratio of the epoxide group to the 1-oxa-3-aza tetraline group. For the purposes of calculating equivalent ratios, the number of 1-oxa-3-aza tetraline groups contained is based on the amount of primary amine reacted; irrespective of whether the latter actually is incorporated as a 1-oxa-3-aza tetraline group. It is further assumed that for each mole of formaldehyde that is reacted, one mole of water will be split off. Thus, for example, in Experiment 6 (see page 13) the theoretical equivalent weight of the 1-oxa-3-aza tetraline compound is based on the following calculation:

1 gram equivalent Novolak (equiv. weight = 100)	=100 g
+0.8 mole analine	=74.4 g
+1.5 mole formaldehyde	=45 g
-1.5 mole water	<u>=-27 g</u>
	=192.4g

$$N\text{-equivalent weight} = 192.4 : 0.8 = 240.5$$

If when the 1-oxa-3-aza tetraline compounds are prepared no nitrogen compounds other than the primary amines are added, the equivalent weight may then also be calculated from the nitrogen content, for example in known manner employing the method of Kjeldahl. Compounds having more than 1-oxa-3-aza tetraline group per molecule are those where the N-equivalent weight is less than the average molecular weight.

Especially preferred epoxide resins for the reaction with the 1-oxa-3-aza tetraline derivatives are: 2-(3,4-epoxy)-cyclohexyl-5,5-spiro(3,4-epoxy)cyclohexane-m-dioxane, 1 to 4 times methylated 2-(3,4-epoxy)cyclohexyl-5,5-spiro(3,4-epoxy)cyclohexane-m-dioxane, bis(3,4-epoxy-cyclohexyl-methyl)adipate, bis(3,4-epoxy-6-methylcyclohexylmethyl)-adipate, 3,4-epoxy-cyclohexane carboxylic acid-(3,4-epoxy-cyclohexylmethyl)-ester and 3,4-epoxy-6-methylcyclohexane carboxylic acid-(3,4-epoxy-6-methylcyclohexylmethyl)ester.

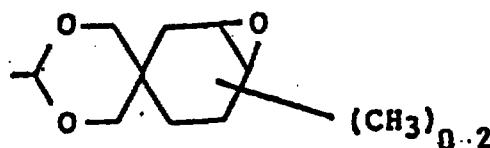
The most preferred epoxide resins may be defined by the general formula



wherein:

X is a 3,4-epoxycyclohexyl group or a mono- or di-methyl substituted 3,4-epoxycyclohexyl group; and

Y is a group of the formula



epoxyethyl of the formula



or a group of the formulae $\text{-COO-CH}_2\text{-X}$ or $\text{-CH}_2\text{-Z-CH}_2\text{-X}$

wherein Z is the acid residue of an aliphatic, cycloaliphatic or aromatic dicarboxylic acid, especially of adipic acid, terephthalic acid or 4,5-epoxy-hexahydrophthalic acid.

The invention furthermore relates to the preparation of a resin characterized by preparing and curing mixtures of a compound containing more than one 1-oxa-3-aza tetraline group in the molecule, and/or a prepolymer thereof, and a cycloaliphatic epoxide resin containing at least two epoxide groups in the molecule, at least one of said epoxide groups being anellated in a cycloaliphatic ring and the remainder likewise being anellated in such a ring or connected directly to such ring.

The method is further characterized in that the components are mixed in molar ratios of epoxide to 1-oxa-3-aza tetraline groups of from 0.2 to 2, preferably from 0.8 to 1.5.

Curing is carried out at a temperature of 50 to 300°C, preferably 100 to 250°C, and especially 140 to 230°C.

For many applications it is advantageous to carry out the curing process in at least two steps, producing a solid or high-viscosity, but still soluble or fusible synthetic resin as an intermediate product. Prepolymerization can take place when the 1-oxa-3-aza tetraline compound is prepared, before mixing, during mixing or after mixing. The

final curing step is then carried out by heating to about 140 to 230°C.

The final curing step can be improved by the addition of a catalyst to accelerate the reaction. In particular, this is a way of shortening the curing time.

Examples of suitable catalysts for this purpose include acids, Friedel-Crafts catalysts, amines, phosphines or quaternizing agents for tertiary amines, particularly alkyl, aralkyl and aryl halides such as benzyl chloride, chlorobenzol, iodobenzol, iodoform, bromoform, methyl iodide or methyl sulphate.

The curing step may include the addition of standard additives such as fillers, colourants, reinforcing fibres, plasticizers and the like. It is also possible to combine the products of the invention with other plastics, synthetic resins or compounds polymerizable thereto, especially aldehyde condensation resins such as, preferably, phenol formaldehyde resins and other epoxide resins and their curing agents.

Additives that are miscible with the resins of the invention or soluble therein should not exceed 50% of the mixture, preferably 10 to 20%.

The synthetic resins of the present invention can be used for many different purposes, including casting, laminating, impregnating, coating, gluing, painting, binding or insulating resins, or as embedding, pressing, injection moulding, extruding, sand mould binding, foam and ablative compounds.

The novel synthetic resins are above all suitable for use in applications demanding extremely high heat stability. Thus, for example, the use of heat-stable insulating resins in, say, electrical windings, enables higher

voltages or reduced wire diameters to be used. Apart from allowing far more economical electric motors to be made, heat-resistant insulating resins generally permit electrical devices and constructional elements to be miniaturized.

The novel highly heat-resistant synthetic resins are especially useful and advantageous in plastics reinforced with glass, quartz, carbon or aramide fibres, because here the supporting material is far more heat-resistant than the synthetic resin. The increase in heat stability of such fibre-reinforced plastics enables them to be used in more applications than was hitherto possible. They allow metals or ceramic materials to be replaced in many more applications involving heat-stressed constructional elements. In these applications the high flexural and impact strength of the synthetic resins obtained in accordance with the invention is also particularly advantageous.

Therefore one object of the invention is also the use, as electrical insulating materials, mouldings, laminates, printed circuit boards or foamed materials, in plastics compounds reinforced with glass, quartz, carbon or amide and aramide fibres, and as adhesive, coating and sealing compounds, of cured mixtures of compounds having more than one 1-oxa-3-aza tetraline group in the molecule, or prepolymers thereof, and cycloaliphatic epoxide resins, where the epoxide resin contains at least two epoxide groups in the molecule, at least one of said epoxide groups being anellated in a cycloaliphatic ring, and the remainder likewise being anellated in such a ring or connected direct to such ring.

Examples

1. Preparation of Condensates containing 1-oxa-3-aza Tetraline Groups

EXPERIMENT 1

210 g of 30% formaldehyde (2.1 moles) are put into a stirrer vessel equipped with a reflux condenser and a melt comprising 94 g of phenol (1 mole) and 99 g of 4,4'-diaminodiphenyl methane (0.5 mole) is added in 15 minutes at 80°C. The mixture is then allowed to settle, the top aqueous layer, smelling slightly of formaldehyde, is removed, and the remaining water is distilled off in a vacuum at about 100°C. The resinous 1-oxa-3-aza tetraline compound has an N-equivalent of 217.

EXPERIMENT 2

Under the same conditions as for Experiment 1, 4.1 moles of formaldehyde are condensed with 2 moles of aniline, 1 mole of phenol and 0.5 mole of bisphenol A (= 2,2-bis(4-hydroxyphenyl)-propane).

N-equivalent = 221.

EXPERIMENT 3

Under the conditions used for Experiment 1, the condensation product is prepared from formaldehyde, phenol and 1,4-diaminobenzol in a molar ratio of 2:1:0.5.

N-equivalent = 172.

EXPERIMENT 4

PREPARATION OF A NOVOLAK

A mixture comprising 37.6 kg (400 moles) of phenol, 15 kg (200 moles) of 40% formaldehyde and 2 kg of 10% sulphuric acid is heated to 40°C in a stirrer vessel equipped with a reflux condenser. Evolution of reaction heat causes the

mixture to heat to 96°C under slight cooling. It is then stirred for some 30 minutes longer at this temperature. After the mixture has cooled and settled the aqueous layer is removed. The lower layer consists of a phenol and novolak mixture with an average of 2 nuclei (calculated by weighing), and containing 15% water and 22% phenol. Accordingly, the phenol equivalent is 117.7.

EXPERIMENT 5

The mixture of 117.7 g novolak from Experiment 4 containing 1 mole of phenolic hydroxy groups and 93 g (1 mole) of aniline is stirred together with 157.5 g (2.1 moles) of 40% formaldehyde containing 5 millimoles of potassium hydroxide for 7 minutes and then boiled for 30 minutes under refluxing conditions. The mixture is then allowed to settle and as much of the aqueous layer is removed as possible. The remaining water is removed from the resin by distillation under a vacuum, the temperature finally being raised as far as 123°C.

N-equivalent weight = 217.

EXPERIMENT 6

Under the same conditions as for Experiment 5, a resin containing an average of 1.6 1-oxa-3-aza tetraline groups per molecule is prepared from 1.5 moles of formaldehyde, 1 gram equivalent of novolak from Experiment 4, and 0.8 mole of aniline.

N-equivalent = 240.

2. Epoxide Resins Suitable for the Present Invention

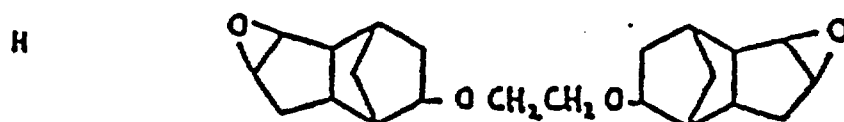
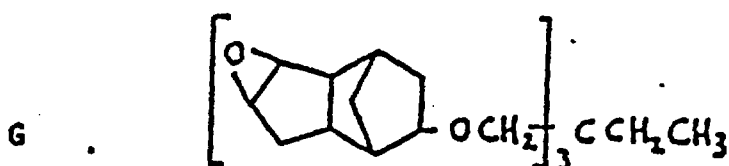
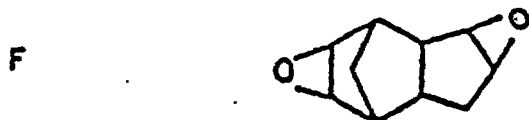
Table 1

Symbol	Chemical Name of the Epoxide Resin
A	4-(1,2-epoxyethyl)-1,2-epoxycyclohexane
B	1,2,8,9-diepoxyp-methane
C	2,2-bis-(3,4-epoxycyclohexyl)-propane
D	Bis-(2,3-epoxycyclopentyl)ether (liquid form)
E	Bis-(2,3-epoxycyclopentyl)ether (isomer crystalline form)
F	1,2,5,6-diepox-4,7-hexahydromethanoindane
G	1,1,1-tris((5-(1,2-epoxy)-4,7-hexahydromethanoindane oxy) methyl)-propane
H	1,2-bis(5(1,2-epoxy) 4,7-hexahydromethoindane oxy)-ethane
I	3,4-epoxycyclohexane carboxylic acid-(3,4-epoxycyclohexylmethyl) ester
K	3,4-epoxy-6-methylcyclohexane carboxylic acid-(3,4-epoxy-6-methylcyclohexylmethyl) ester
L	2-(3,4-epoxy) cyclohexyl-5,5-spiro(3,4-epoxy)-cyclohexane-m-dioxane
M	2-(3,4-epoxy-4-methylcyclohexyl-5,5-spiro(3,4-epoxy) cyclohexane-m-dioxane
N	2-(3,4-epoxy) cyclohexyl-5,5-spiro(3,4-epoxy)-4-methylcyclohexane-m-dioxane
O	2-(3,4-epoxy-4-methylcyclohexyl)-5,5-spiro(3,4-epoxy)-4-methyl cyclohexane-m-dioxane
P	2-(3,4-epoxy)-4,6-dimethylcyclohexyl-5,5-spiro-(3,4-epoxy)-4-methylcyclohexane-m-dioxane
Q	2-(3,4-epoxy)-4,6-dimethylcyclohexyl-5,5-spiro-(3,4-epoxy)-4,6-dimethylcyclohexane-m-dioxane

TABLE 1 (Cont'd)

R	Bis-(3,4-epoxy-6-methylcyclohexylmethyl) adipate	
S	Bis-(3,4-epoxycyclohexylmethyl) adipate	
T	Bis-(3,4-epoxy-cyclohexylmethyl)-terephthalate	
U	Bis-(3,4-epoxy-6-methylcyclohexylmethyl)-terephthalate	
V	4,5-epoxy-hexahydrophthalic epoxy-cyclohexylmethyl) ester	acid-bis-(3,4-

Structural formulae of epoxide resins F, G, H and L



3. Preparation of the Resins

EXAMPLE 1

100 parts of the condensate from Experiment 1 are mixed at 140°C with 100 parts of 3,4-epoxycyclohexane carboxylic acid-(3,4-epoxycyclohexylmethyl)ester and poured in a vacuum into a mould for a plate 10 mm thick. The mixture is cured for 1 hour at 180°C, one hour at 200°C and two hours at 220°C. Test pieces prepared from the plate show no decomposition even at 250°C. They have a bending strength of 115 MPa, an E-modulus of 4800 MPa, an electrical volume resistance of $< 10^{15}$ ohms and a loss factor of $>10^{-2}$. The glass transition temperature is 230°C.

The glass transition temperature is used here to denote the temperature at which the specific heat and thermal expansion coefficient show a sharp rise and the mechanical characteristics exhibit a sharp fall.

EXAMPLES 2 to 17

Using the method described in Example 1, cast resin plates are prepared from the resin mixtures given in Table 2. The epoxide resins used are listed in Table 1, along with other epoxide resins suitable for the purpose according to the invention. The characteristics of the cured resins can be taken from Table 2. See page 18 for Table 2.

EXAMPLE 18

75 g of epoxide resin L (Table 1) are mixed *in vacuo* at 120°C with 100 g of the 1-oxa-3-aza tetraline compound from Experiment 1 and 200 g of quartz powder and poured into a mould. The cast piece is cured for 1 hour at 200°C

and one hour at 220°C. It exhibits a bending strength of 60 MPa and shows no deformation at 250°C.

EXAMPLE 19

A glass cloth with a glycidyl-propyl silane finish and a unit weight of 120 g per sq. m. is impregnated with a 60% solution of the resin mixture from Example 15 and dried in a two-step hot air duct at 100-140°C. Eight layers of the Prepreg are pressed between layers of copper foil for one hour at 180°C to form a plate. The laminate shows no delamination in the solder bath test at 260°C. The electrical volume resistance is $> 10^{15}$ ohm-cm, the loss factor below 0.01. Bending strength is 500 MPa.

4. Comparative Tests 1 to 3

Cast resin plates are prepared from resin mixtures from Table 3 that do not conform to the definition according to the invention. Comparative tests 1 and 2 use other types of cycloaliphatic epoxide resins, and comparative test 3 a monofunctional 1-oxa-3-aza tetraline as disclosed in Swiss Patent 579,113, Example 1. All products of the comparative tests show markedly worse heat stability or lower glass transition temperatures.

TABLE 2

Example No.	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17		
1-Oxa-3-aza-tetra- line compound from Experiment No.	S	S	S	S	S	S	S	S	S	S	2	3	6	S	S	S		
N-equivalent weight 1)	217	217	217	217	217	217	217	217	217	217	231	172	240	217	217	217		
Quantity g	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100		
Epoxide compound as in Table 1	K	S	L	L	L	L	L	L	I	O	R	I	L	R + L	K + A	A		
Epoxide equivalent weight	140 ³⁾	183 ³⁾	160 ²⁾							126 ³⁾	147 ³⁾	197 ³⁾	126 ³⁾	160 ³⁾	-	-	70 ³⁾	
Quantity g	100	100	100	20	40	66	75	150	100	100	100	100	50	50+50	80+20	26		
Equivalent ratio EP/N	1.55	1.18	1.36	0.27	0.54	0.9	1.0	2.0	1.7	1.5	1.2	1.36	0.75	-	-	0.8		
Curing cycle	6) 180°C 6) 200°C 6) 220°C															7) 140°C 8) 200°C	7) 140°C 8) 160°C 8) 200°C	
Recuring			9) 250°C															
Behaviour at 220° C 250° C	4) 4)	4) 4)	4) 4)	4) 4)	4) 4)	4) 4)	4) 4)	4) 4)	4) 5)	4) 4)	4) 4)	4) 4)	4) 4)	4) 4)	4) 4)	4) 5)		
Bending resistance 25° C 220° C 250° C MPa		115		100-110 65 50					115									
Glass transition temperature, C°	220°	190°	250°	280°	210°	250°	>260°	>260°	>260°	230°	220°	200°	240°	180°	220°	220°	170°	

1) Calculated from production

- 1) Calculated from production.
- 2) Analytically determined.
- 3) Calculated from theoretical formula.
- 4) Unchanged
- 5) Cracks and bubbles observed.

- 6) 1 hour at
- 7) 24 hours at
- 8) 2 hours at
- 9) 3 hours at

TABLE 3 COMPARATIVE TESTS

No.	1	2	3
1-Oxa-3-aza-tetraline compound from Exprmnt. No.	5	5	N-Phenyl-1-oxa-3-aza-tetraline
N-equivalent 1)			211
Quantity g.	100	100	100
Epoxide compound as in Table 1	Tetrahydrophthalic acid diglycidylester	Hexahydrophthalic acid diglycidylester	1
Epoxide equivalent			140 ³⁾
Quantity g.	100	100	40
Equivalent ratio EP/N			0.60
Curing cycle	2 hrs. at 180°C 1 hr. at 200°C	2 hrs. at 180°C 1 hr. at 200°C	2 hrs. at 160°C 1 hr. at 200°C
Behaviour at 220°C	5)	5)	4)
Glass transition temperature, °C.			110°C

See Table 2 for footnotes.

In comparison to the structurally closest previously known resins, the properties of which are well known, the resins obtained in the examples of the invention exhibit generally far higher heat stability, along with very good mechanical characteristics, especially high bending and impact strength.

This observation is borne out by the comparative tests.



Claims

1. Chemically hardenable resin containing compounds having more than one 1-oxa-3-aza tetraline group in the molecule, and/or prepolymers thereof and cycloaliphatic epoxide resins, characterized in that the epoxide resin contains at least two epoxide groups in the molecule, at least one of which is anellated in a cycloaliphatic ring and the remainder likewise being anellated in such a ring or connected direct to such a ring, the proportion of compounds containing 1-oxa-3-aza tetraline groups and epoxide resin being between 0.2 and 2, expressed as the molar ratio of epoxide groups to 1-oxa-3-aza tetraline groups.

2. The resin according to Claim 1, characterized in that the equivalent weight of the epoxide resin is between 70 and about 250, preferably 120 and 200.

3. The resin according to Claim 1, characterized by containing as the epoxide resin:

2-(3,4-epoxy)cyclohexyl-5,5-spiro(3,4-epoxy)cyclohexane-m-dioxane, 1 to 4 times methylated 2-(3,4-epoxy)cyclohexyl-5,5-spiro(3,4-epoxy) cyclohexane-m-dioxane, 4-(1,2-epoxyethyl)-1,2-epoxycyclohexane, 1,2,8,9-diepoxy-p-methane, 2,2-bis(3,4-epoxycyclohexyl)propane, bis-(2,3-epoxycyclopentyl) ether, 1,2,5,6-diepoxy-4,7-hexahydro-methanoindane, bis-(3,4-epoxy-cyclohexylmethyl) adipate, bis(3,4-epoxy-6-methylcyclohexylmethyl) adipate, bis-(3,4-epoxy-cyclohexylmethyl) terephthalate, bis-(3,4-epoxy-6-methyl-cyclohexylmethyl)-terephthalate, 3,4-epoxy-cyclohexane carboxylic acid-(3,4-epoxy-cyclohexylmethyl) ester, 3,4-epoxy-6-methylcyclohexanecarboxylic acid-(3,4-epoxy-6-methylcyclohexylmethyl) ester, 1,2-bis-(5(1,2-epoxy)-4,7-hexahydromethanoindane oxy)-ethane 1,1,1-tris ((5-(1,2-epoxy)-4,7-hexahydromethanoindane oxy)-methyl)-propane or 4,5-epoxyhexahydrophthalic acid-bis-(3,4-epoxy-cyclohexylmethyl) ester.



4. The resin according to Claim 3, characterized by containing as the epoxide resin:

2-(3,4-epoxy)cyclohexyl-5,5-spiro(3,4-epoxy) cyclohexane-m-dioxane, 1 to 4 times methylated 2-(3,4-epoxy)cyclohexyl-5,5-spiro (3,4-epoxy)cyclohexane-m-dioxane, bis(3,4-epoxy-cyclohexylmethyl)adipate, bis(3,4-epoxy-6-methylcyclohexylmethyl)adipate, 3,4-epoxy-cyclohexane-carboxylic acid-(3,4-epoxy-cyclohexylmethyl) ester or 3,4-epoxy-6-methylcyclohexane carboxylic acid-(3,4-epoxy-6-methylcyclohexylmethyl) ester.

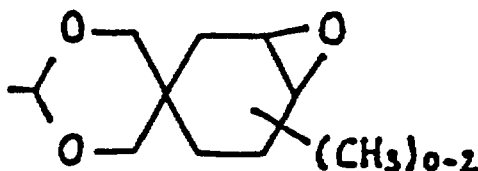
5. The resin according to Claim 1, characterized by containing an epoxide resin of general formula



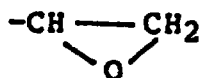
wherein:

X is a 3,4-epoxycyclohexyl group or a mono- or di-methyl substituted 3,4-epoxycyclohexyl group; and

Y is a group represented by the formula



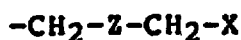
epoxy ethyl group of the formula



or a group of the formula



or





wherein Z represents the acid residue of an aliphatic, cycloaliphatic or aromatic dicarboxylic acid.

6. The resin according to Claims 1 to 5, characterized in that the proportion of compounds containing 1-oxa-3-aza tetraline groups and epoxide resin is between 0.8 and 1.5, expressed as the molar ratio of epoxide groups to 1-oxa-3-aza tetraline groups.

7. The resin according to Claims 1 to 6, characterized in that the 1-oxa-3-aza tetraline groups are aromatically substituted at the nitrogen atom.

8. Method for preparing a resin, characterized by preparing and curing mixtures of a compound containing more than one 1-oxa-3-aza tetraline group in the molecule, and/or a prepolymer thereof, and a cycloaliphatic epoxide resin containing at least two epoxide groups in the molecule, at least one of said epoxide groups being anellated in a cycloaliphatic ring and the remainder likewise being anellated in such a ring or connected directly to such ring, the mixing ratio of epoxide to 1-oxa-3-aza tetraline groups, expressed as the molar ratio of epoxide groups to 1-oxa-3-aza tetraline groups, being between 0.2 and 2.

9. The method for preparing a resin according to Claim 8, characterized by using as the epoxide resin

2-(3,4-epoxy)cyclohexyl-5,5-spiro(3,4-epoxy)cyclohexane-m-dioxane, 1 to 4 times methylated 2-(3,4-epoxy)cyclohexyl-5,5-spiro(3,4-epoxy) cyclohexane-m-dioxane, 4-(1,2-epoxyethyl)-1,2-epoxycyclohexane, 1,2,8,9-diepoxyp-methane, 2,2-bis(3,4-epoxycyclohexyl)propane, bis-(2,3-epoxycyclopentyl) ether, 1,2,5,6-diepox-4,7-hexahydro-methanoindane, bis-(3,4-epoxy-cyclohexylmethyl) adipate, bis(3,4-epoxy-6-methylcyclohexylmethyl) adipate,



bis-(3,4-epoxy-cyclohexylmethyl) terephthalate, bis-(3,4-epoxy-6-methyl-cyclohexylmethyl)-terephthalate, 3,4-epoxy-cyclohexane carboxylic acid-(3,4-epoxy-cyclohexylmethyl) ester, 3,4-epoxy-6-methylcyclohexanecarboxylic acid-(3,4-epoxy-6-methylcyclohexylmethyl) ester, 1,2-bis-(5(1,2-epoxy)-4,7-hexahydromethanoindane oxy)-ethane 1,1,1-tris ((5-(1,2-epoxy)-4,7-hexahydromethanoindane oxy)-methyl)-propane or 4,5-epoxyhexahydrophthalic acid-bis-(3,4-epoxy-cyclohexylmethyl) ester.

10. The method according to Claim 8, characterized by using as the epoxide resin:

2-(3,4-epoxy)cyclohexyl-5,5-spiro(3,4-epoxy) cyclohexane-m-dioxane, 1 to 4 times methylated 2-(3,4-epoxy)cyclohexyl-5,5-spiro (3,4-epoxy)cyclohexane-m-dioxane, bis(3,4-epoxy-cyclohexylmethyl) adipate, bis(3,4-epoxy-6-methylcyclohexylmethyl) adipate, 3,4-epoxy-cyclohexane-carboxylic acid-(3,4-epoxy-cyclohexylmethyl) ester or 3,4-epoxy-6-methylcyclohexane carboxylic acid-(3,4-epoxy-6-methylcyclohexylmethyl) ester.



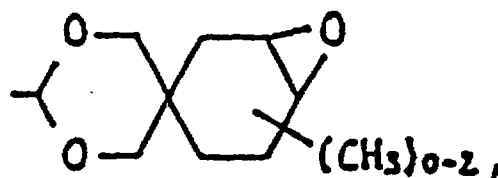
11. The method according to Claim 8, characterized by using an epoxide of the general formula



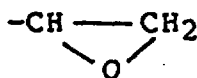
wherein:

X is a 3,4-epoxycyclohexyl group or a mono- or di-methyl substituted 3,4-epoxycyclohexyl group; and

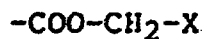
Y is a group represented by the formula



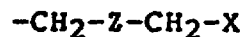
epoxy ethyl of the formula



or a group of the formula



or



wherein Z is the acid residue of an aliphatic, cycloaliphatic or aromatic dicarboxylic acid.

12. The method according to Claim 8, characterized by mixing the components in a molar ratio of epoxide groups to 1-oxa-3-aza tetraline groups of 0.8 to 1.5.



13. The method according to Claims 8 to 12, characterized in that the 1-oxa-3-aza tetraline groups are substituted at the nitrogen atom.

14. The method according to Claim 8, characterized in that curing is carried out at an elevated temperature.

15. The method according to Claim 14, characterized in that curing is carried out at temperatures from 50 to 300°C, preferably in the temperature range 100 to 250°C, especially 140 to 230°C.

16. The method according to Claim 10, characterized in that curing is carried out in the presence of a catalyst accelerating the reaction.

17. The use as casting, laminating, impregnating, coating, gluing, painting, binding or insulating resin, or as embedding, pressing, injection moulding, extruding, sand mould binding, foam and ablative compounds, of mixtures of compounds having more than one 1-oxa-3-aza tetraline group in the molecule, and/or prepolymers thereof, and cycloaliphatic epoxide resins, the epoxide resin containing at least two epoxide groups in the molecule, at least one of said epoxide groups being anellated in a cycloaliphatic ring and the remainder likewise being anellated in such a ring or connected direct to such ring.

18. The use as electrical insulating materials, mouldings, laminates or printed circuit boards in plastics compounds reinforced with glass, quartz, carbon or amide and aramide fibres, and as adhesive, coating and sealing compounds, of cured mixtures of compounds having more than one 1-oxa-3-aza tetraline group in the molecule, and/or prepolymers thereof, and cycloaliphatic epoxide resins,



the epoxide resin containing at least two epoxide groups in the molecule, at least one of said epoxide groups being anellated in a cycloaliphatic ring, and the remainder likewise being anellated in such a ring or connected direct to such ring.