(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 736 941 B9

(12) CORRECTED EUROPEAN PATENT SPECIFICATION

(15) Correction information:
Corrected version no 1 (W1 B1)
Corrections, see
Description Paragraph(s) 49

(48) Corrigendum issued on:
10.08.2016 Bulletin 2016/32

(45) Date of publication and mention
of the grant of the patent:
20.01.2016 Bulletin 2016/03

(21) Application number: **11738229.1**

(22) Date of filing: **29.07.2011**

(51) Int Cl.:
C08L 63/00 $^{(2006.01)}$
H01B 3/40 $^{(2006.01)}$
C08G 59/18 $^{(2006.01)}$
C08G 59/24 $^{(2006.01)}$
C08G 59/68 $^{(2006.01)}$

(86) International application number:
PCT/EP2011/063148

(87) International publication number:
WO 2013/017149 (07.02.2013 Gazette 2013/06)

---

(54) CURABLE EPOXY RESIN COMPOSITION

HÄRTBARE EPOXIDHARZZUSAMMENSETZUNG

COMPOSITION DE RÉSINE ÉPOXYDE DURCISSABLE

---

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

(43) Date of publication of application:
04.06.2014 Bulletin 2014/23

(73) Proprietor: **ABB Research Ltd.**
8050 Zürich (CH)

(72) Inventors:
- **HO, Chau-Hon**
4332 Stein (CH)
- **TZAVALAS, Spiros**
CH-5426 Lengnau (CH)

(74) Representative: **Zimmermann & Partner**
Patentanwälte mbB
Postfach 330 920
80069 München (DE)

(56) References cited:
WO-A1-82/04256
WO-A1-82/04437
GB-A- 1 402 899

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Printed by Jouve, 75001 PARIS (FR)

Description

Field of Invention

[0001] The present invention refers to a curable epoxy resin composition comprising a defined aromatic epoxy resin component and a defined latent catalyst system, and optionally further additives. Said curable composition being a volatile-free single epoxy resin composition having a prolonged pot life at a processing temperature within the range of 40°C to 70°C. Said curable epoxy resin composition on curing yields cured products with good electrical properties and is especially useful in the production of high voltage electrical insulations which require impregnation and/or wet winding applications as well as a low viscosity of the curable epoxy resin composition used therefore.

State of the Art

[0002] In the production of electrical insulations, in particular in the production of high voltage applications, epoxy resin compositions comprising a hardener component, such as an acid anhydride hardener component, are widely used due to their excellent electrical and mechanical properties. However, using acid anhydrides may cause health damages, especially when such compounds are industrially used in open processes, such as in open impregnation or wet winding applications.

[0003] In order to minimize such health damages it has been proposed to use epoxy resin compositions which are free of compounds which generate emission of highly volatile organic compounds during processing, i.e. which are volatile-free, specifically which are free of acid anhydrides and volatile diluents such as styrene or methyl methacrylate, and which are cured in the presence of a catalyst. Such epoxy resin compositions contain a latent catalyst, said latent catalyst comprising e.g. a metal acetylacetonate or a mixture of such compounds. The term latent catalyst means that the catalyst is present as an integral part within the composition.

[0004] For electrical insulation applications, especially for high voltage applications, however, essential requirements for material properties and processing parameters must be fulfilled. In case of impregnation applications, for example for impregnating mica tape wound coils for electrical machines or for the impregnation of paper wound conductors for bushings, or for filament wet winding applications, it is substantial that the curable epoxy resin composition has a long pot life, i.e. slow curing speed at processing temperature and a short gel time, i.e. fast cross-linking reaction resp. polymerization reaction, at curing temperature. Further, a low dielectric loss of the final cured insulating material within a wide temperature range is required, in particular for high voltage applications. However, the properties of a long pot life and a short gel time are contradictory. In general a long pot life goes along with a prolonged gel time, caused by the low reactivity and slow polymerization speed of the composition, whilst a short gel time goes along with a short pot life, caused by the elevated reactivity and elevated polymerization speed of the composition. This is especially relevant for the present invention which provides a composition with a prolonged pot life at an elevated temperature within the range of 40°C to 70°C combined with a short gel time above 100°C.

[0005] For most impregnation applications, such as impregnating or filament wet winding applications, a low viscosity is required for proper processing. In the absence of any hardener component or volatile diluents, the epoxy resin needs to be heated up for decreasing the viscosity. This heating up to elevated temperature, however, causes a viscosity increase and a shortened pot life. For vacuum pressure impregnation (VPI) of mica tape wound coils and wet winding processes for fibers, the resin in the tank or basin is used for several production runs and products. Thus, a long pot life at processing temperature with stable low viscosity is substantial for obtaining good impregnation quality and keeping production costs low, as e.g. vacuum pressure impregnation (VPI) and filament wet winding processes are continuous production processes using partially open tanks or basins.

[0006] Fast gelling in the curing oven, i.e. after impregnation or winding, is important in order to avoid the curable epoxy resin composition dripping off the impregnated or the wet wound parts before being cured. Thus, short gel times below 10-30 minutes at curing temperature are often required.

[0007] Epoxy resin formulations comprising an epoxy resin component and a catalyst system composed of a metal acetylacetonate and a phenolic compound are known, e.g. from GB1402899. Such catalytic systems are described as providing stability to the curable epoxy resin formulation at room temperature for a long period of time. Basically, the chemical activity of such catalytic systems is not limited to the type of epoxy resin. GB1402899 describes the activity of the catalytic system at elevated temperatures, such as 100°C to 160°C, whilst using epoxy resin compositions, especially cycloaliphatic compounds, which have a low viscosity at room temperature. Such low viscosity at room temperature allows to use these cycloaliphatic compounds in VPI and filament wet winding processes at room temperature. Also storage of said curable epoxy resin formulations was performed at room temperature whereby no gelation occurred. However, for producing electrical insulators from aromatic epoxy resin compounds, such as from diglycidylether of bisphenol A (DGEBA), due to the high viscosity of DGEBA at room temperature, the curable epoxy resin formulation must be kept at elevated temperature during processing, such as at about 50°C, for a longer period of time without gelling.

[0008] Therefore, there is a need for a curable epoxy resin composition having at the same time a long pot life within a temperature range of about 40°C to about 70°C, and a short gel time at temperature above 100°C and which on curing yields shaped articles with low dielectric loss values, especially for processes requiring impregnation and/or wet winding applications. Further, there is a need to use for these purposes epoxy compositions which comprise a conventional aromatic epoxy resin which is comparatively cheap and commercially available.

Summary of the Invention

[0009] It has now been found that curable epoxy resin compositions comprising a defined aromatic epoxy resin component and a defined latent catalyst system comprising at least one metal acetylacetonate and a phenolic compound fulfill the requirements of having a long pot life at a processing temperature within the range of about 40°C to 70°C and at the same time have a short gel time at a temperature above 100°C. The curable composition according to the present invention is a volatile-free single epoxy resin composition having a low and stable viscosity at processing resp. impregnation temperature resulting in a prolonged pot life. Said curable epoxy resin composition at the same time has a high reactivity at elevated curing temperatures and on curing yields cured products with good electrical properties, such as products with low dielectric loss values, and is especially useful in the production of high voltage electrical insulations which require impregnation and/or wet winding applications.

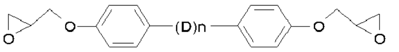
[0010] The prolonged pot life is at least one week, preferably at least three weeks, at a processing temperature within the range of about 40°C to 70°C, which is achieved by continuous resin replenishment, for example at a rate within the range of 10% to 30% of fresh resin per week, calculated to the total amount of resin present in the tank. With a resin replenishment rate of e.g. 20 % per week, the steady state viscosity is reached after about ten weeks.

[0011] Said curable epoxy resin composition polymerizing without the addition of a hardener component is also called a curable homopolymerizing epoxy resin composition or a curable single epoxy resin composition and is especially useful in producing high voltage electrical insulations requiring impregnation and/or wet winding applications.

Description of the Invention

[0012] The present invention is defined in the claims. The present invention refers to a curable epoxy resin composition comprising a defined aromatic epoxy resin component and a defined latent catalyst system, and optionally further additives, said curable composition being a volatile-free single epoxy resin composition having a prolonged pot life at a processing temperature within the range of 40°C to 70°C, wherein:

(a) the epoxy resin component is a compound of formula (I) in monomeric form or in a low polymeric form thereof, or is a mixture of such compounds:



(I)

D = $-CH_2-$, $-C(CH_3)_2-$, -S-, -O-, $-SO_2-$, -CO-

n = zero or one

said epoxy resin component having an inherent viscosity within the range of 80 mPas to 300 mPas, measured at a temperature of 50°C;

(b) the latent catalyst system comprises at least one metal acetylacetonate and at least one phenolic compound, wherein

(b1) the metal acetylacetonate is selected from known metal acetylacetonate compounds, or is a mixture of these compounds, and is present in a concentration of 0.1 phr to 1.0 phr (parts per hundred parts) of the epoxy resin component; and

(b2) the phenolic compound is a dihydroxybenzene or a trihydroxybenzene or any mixture thereof, and is present in a concentration of 2.0 phr to 4.0 phr (parts per hundred parts) of the epoxy resin component;

characterized in that, said curable epoxy resin composition is kept at a temperature within the range of 40°C to 70°C and the prolonged pot life at said temperature is provided to the composition by continuous resin replenishment with fresh resin at a rate within the range of 10% to 30% of fresh resin per week, preferably at a rate of 20% of fresh resin per week, calculated to the total amount of resin present in the tank, said fresh resin having an inherent viscosity within the range of 80 mPas to 300 mPas, measured at a temperature of 50°C.

[0013] The present invention further refers to the use of said curable epoxy resin composition for producing high voltage electrical insulations using impregnation and/or wet winding application techniques. Such application techniques preferably are impregnating mica tape wound coils for electrical machines or impregnating paper wound conductors for bushings, or filament wet winding applications.

[0014] The present invention also refers to the use of said curable epoxy resin composition in vacuum pressure impregnation (VPI) applications for mica tape wound coils and wet winding processes for fibers or tapes, at the given temperature range, especially where the resin in the tank or basin is used for several runs and products.

[0015] The present invention further refers to a shaped article in the form of an electrical insulator being made from said curable epoxy resin composition, at the given temperature range, especially by shaping and subsequently curing said curable epoxy resin composition to form the cured solid electrical insulator.

[0016] The present invention further refers to electrical articles comprising an electrical insulator made from a composition according to the present invention.

[0017] The present invention further refers to a method of producing a curable epoxy resin composition as defined herein above, said curable epoxy resin composition having a prolonged pot life at a processing temperature within the range of 40°C to 70°C, characterized in that fresh resin, having an inherent viscosity within the range of 80 mPas to 300 mPas, measured at 50°C, is continuously provided to the composition at said temperature range of 40°C to 70°C, by continuous resin replenishment at a rate within the range of 10% to 30% of fresh resin per week, preferably at a rate of 20% of fresh resin per week, calculated to the total amount of resin present in the tank.

[0018] The curable epoxy resin composition according to the present invention generally has a prolonged pot life, i.e. a viscosity increase of 100 %, of at least one week, preferably of at least three weeks, at an elevated processing temperature within the range of about 40°C to 70°C, e.g. at about 50°C, which can be prolonged for several more weeks by continuous resin replenishment at a rate of continuous resin replenishment within the range of 10% to 30% of fresh resin per week, such as a rate of 20% of fresh resin per week, calculated to the total amount of resin present in the tank.

[0019] The curable epoxy resin composition which is added to the pot preferably has an "initial" viscosity which is lower than the "steady state" viscosity of the curable epoxy resin composition in the pot, so that the curable composition in the pot can be used for at least ten weeks or more when continuously replenished at the mentioned rate, e.g. of about 20%, with the curable epoxy resin composition with the "initial" viscosity.

[0020] The curable epoxy resin composition which is added to the pot has an "initial" viscosity preferably within the range of about 80 mPas to about 120 mPas, preferably within the range of about 100 mPas to about 110 mPas, measured at 50°C.

[0021] The "steady state" viscosity of the curable epoxy resin composition, within the context of the present invention, means the viscosity range reached after subsequent replenishment at the given rate, e.g. of about 20% per week, keeping the resin composition at "elevated processing temperature", i.e. at a temperature within the range of 40°C to 70°C, preferably within the range of 45°C to 60°C, and preferably at about 50°C.

[0022] The "steady state" viscosity of the curable epoxy resin composition reached within the pot is preferably within the range of about 260 mPas to about 300 mPas, preferably within the range of about 270 mPas to about 280 mPas, measured at 50°C.

[0023] The curable epoxy resin composition within the pot has generally a viscosity within the range of about 80 mPas to about 300 mPas, preferably within the range of about 100 mPas to about 280 mPas, preferably within the range of about 110 mPas to about 270 mPas, and preferably within the range of about 120 mPas to 260 mPas, measured at 50°C.

[0024] This means that by using a base aromatic epoxy resin component as defined herein with a starting low initial viscosity within the range of about 80 mPas to about 300 mPas, with the preferred ranges as given above, curable epoxy resin compositions with a stable steady state viscosity as defined herein can be obtained at a temperature within the range of 40°C to 70°C, preferably within the range of 45°C to 60°C, and preferably at about 50°C, as required for processing.

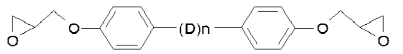
[0025] Said curable aromatic epoxy resin composition generally solidifies to a gel within 30 minutes at a maximum temperature of 165°C, i.e. has a short gel time of less than 30 minutes at a maximum temperature of 165°C. Preferred gelling temperatures are applied within the range of 100 °C to 165°C, preferably within the range of 120°C to 165°C, and preferably at about 165°C, whereby said gelling times are generally between 20 minutes and 40 minutes, and preferably less than 30 minutes. The composition is subsequently completely cured.

[0026] The cured epoxy resin composition obtained from the curable epoxy resin composition according to the present invention, further has a low electromagnetic permittivity (ε), measured in SI units (système international d'unites). It is a measure of how much resistance is encountered when forming an electric field in the medium. Said electromagnetic permittivity (ε) preferably is within the range of 1 to 5 between 40°C and 180°C and preferably within the range of 3 to 5 between 40°C and 180°C.

[0027] The cured epoxy resin composition obtained from the curable epoxy resin composition according to the present invention, further has low dielectric loss values, known as [$\tan(\delta)$]. These values are within the range of 0.001 to 0.100 between 40°C and 180°C and preferably within the range of 0.003 to 0.05 between 40°C and 180°C.

[0028] Said curable epoxy resin composition has no hardener component, in particular no acid anhydride component such as tetrahydrophthalic anhydride, hexahydrophthalic anhydride, methylhexahydrophthalic anhydride, methyltetrahydrophthalic anhydride, or methyl nadic anhydride, and preferably no volatile diluents such as reactive diluents, such as styrene, vinyl toluene, alphamethyl styrene, methacrylate or acrylate derivatives and, therewith, is a hardener free and preferably a diluent free epoxy resin composition having practically no emissions of volatile organic compounds.

[0029] The epoxy resin component of the present invention is based on compounds of formula (I):



(I)

D = $-CH_2-$, $-C(CH_3)_2-$, -S-, -O-, $-SO_2-$, -CO-

n = zero or one

and is present in monomeric form or polymeric form or as a mixture thereof. Preferred epoxy resin components according to the present invention are:

diglycidylether of bisphenol A [DGEBA; D = $-C(CH_3)_2-$, n = 1]; diglycidylether of bisphenol F [DGEBF; D = $-CH_2-$, n = 1]; and diglycidylether bisphenol S [DGEBS; D = -S-, n = 1] compounds, or mixtures thereof. Most preferred epoxy resin components are diglycidylether of bisphenol A [DGEBA] and diglycidylether of bisphenol F [DGEBF].

[0030] When producing these compounds, the monomeric compounds according to formula (I) as well as low polymeric (oligomeric) compounds derived therefrom are formed so that generally a mixture of these compounds is obtained. Further, when producing for example diglycidyl ether of bisphenol F (DGEBF), there is generally obtained a mixture of isomeric compounds such as a mixture of o,o'-, o,p'- and p,p'-bisglycidyloxyphenylmethane. This is known to the expert in the art.

[0031] These glycidyl compounds preferably have a molecular weight between 200 and 1200, especially between 200 und 1000 and have an epoxy value (equiv./kg) preferably at least three, preferably at least four and especially at about five, preferably about 5.0 to 6.5.

[0032] The latent catalyst system comprises at least a metal acetylacetonate and at least a phenolic compound. The metal acetylacetonate [component (b1)] corresponds to the chemical formulae (II), (III), (IV) and (V):

$$[CH_3\text{-}C(O)\text{-}CH{=}C(O^-)\text{-}CH_3].\ Me^+ \qquad (II)$$

or

$$[CH_3\text{-}C(O)\text{-}CH{=}C(O^-)\text{-}CH_3]_2.\ Me^{2+} \qquad (III)$$

or

$$[CH_3\text{-}C(O)\text{-}CH{=}C(O)\text{-}CH_3]_3.\ Me^{3+} \qquad (IV)$$

or

$$[CH_3\text{-}C(O)\text{-}CH{=}C(O^-)\text{-}CH_3]_4.\ Me^{4+} \qquad (V).$$

[0033] Basically, all known metal acetylacetonates can be used within the scope of the present invention. Preferred are metal acetylacetonates wherein Me^+ is selected from Li^+, Na^+ and K^+; Me^{2+} is selected from Cu^{2+}, Co^{2+}, Zn^{2+} and Ca^{2+}; Me^{3+} is selected from Al^{3+}, V^{3+} and Fe^{3+}; and Me^{4+} is selected from Zr^{4+}. Preferably Me^{2+} is Mg^{2+}, and Me^{3+} is selected from Al^{3+} and Fe^{3+}.

[0034] Preferred are aluminum acetylacetonate and zirconium acetylacetonate or a mixture of these compounds.

[0035] The metal acetylacetonate or the mixture of metal acetylacetonates is present in a concentration of 0.1 phr to 1.0 phr, preferably in a concentration of 0.2 phr to 1.0 phr and preferably in a concentration of 0.5 phr to 1.0 phr (parts per hundred parts) of the epoxy resin component.

[0036] The phenolic compound [compound (b2)] is a dihydroxybenzene or a trihydroxybenzene or any mixture thereof, preferably 1,2-dihydroxybenzene (catechol), 1,3-dihydroxybenzene (resorcinol) or 1,4-dihydroxybenzene (hydroquinone) or 1,2,3-trihydroxybenzene (pyrogallol) or 1,2,4-trihydroxybenzene or any mixture of these compounds, preferably catechol or resorcinol or hydroquinone or pyrogallol or any mixture thereof, preferably catechol or resorcinol or hydroquinone, or a mixture thereof. The phenolic compound is present in a concentration of 0.5 phr to 6.0 phr, preferably in a concentration of 1.0 phr to 5.0 phr, preferably in a concentration of 2.0 phr to 4.0 phr, (parts per hundred parts) of the epoxy resin component.

[0037] The ratio of the metal acetylacetonate compound [component (b1)] to the phenolic compound [component (b2)] is within the weight ratio of 4.0 : 1.0 to 1.0 : 1.0, preferably with the weight ratio of 3.0 : 1.0 to 1.0 : 1.0.

[0038] The present invention further refers to the use of said curable epoxy resin composition for producing high voltage electrical insulations requiring impregnation and/or wet winding applications. Impregnation processes such as vacuum pressure impregnation (VPI) applications for mica tape wound coils and wet winding processes for fibers wherein the filaments are preimpregnated with the curable composition followed by winding the impregnated fibers on a mandrel are known in the art and need no further explanation.

[0039] The curable composition of the present invention is made by mixing all the components, optionally under vacuum, in any desired sequence, whereby the latent catalyst [component (b)] is not stored separately but forms an integral part of the composition according to the present invention.

[0040] The curable epoxy resin composition of the present invention primarily is used for producing high voltage electrical insulations requiring impregnation and/or wet winding applications as mentioned herein above. However, the composition may also be used for other electrical insulating applications not requiring impregnation and/or wet winding applications.

[0041] Depending on the type of insulator to be produced, the curable composition may further contain optional additives selected from filler materials, wetting/dispersing agents, plasticizers, antioxidants, light absorbers, as well as further additives used in electrical applications.

[0042] Examples of filler materials are known inorganic filler such as silica and aluminum trihydrate (ATH), glass powder, chopped glass fibers, metal oxides such as silicon oxide (e.g. Aerosil, quartz, fine quartz powder), metal nitrides, metal carbides, natural and synthetic silicates, as known to the expert in the art. Also the average particle size distribution of such fillers and the quantity present within the composition as applied in electrical high voltage insulators are known in the art. Preferred filler materials are silica and aluminum trihydrate (ATH).

[0043] Plasticizers, antioxidants, light absorbers, as well as further additives used in electrical applications are known in the art.

[0044] Electrical insulation produced according to the present invention can be used for insulating electrical coils and in the production of electrical components such as transformers, bushings, insulators, switches, sensors, converters, cable end seals and high voltage surge arresters, as known to the expert in the art.

[0045] Preferred uses of the insulation system produced according to the present invention are also high-voltage insulations such as used in overvoltage protectors, in switchgear constructions, in power switches, dry-type transformers, and electrical machines, as coating materials for transistors and other semiconductor elements and/or to impregnate electrical components. The following example illustrates the invention.

Examples 1 to 5

[0046] The components as given in Example 1 (Table 1), in Example 2 (Table 2), Example 3 (Table 3), Example 4 (Table 4) and Example 5 (Table 5), were mixed at an internal temperature of about 50°C and kept in the pot at that temperature during processing. When manufacturing cured parts, e.g. plates of about 1 mm thickness, the applied mixtures were degassed in vacuum at 70°C before application, resp. curing. The mixed components were cast into a mold, said mold being preheated to a temperature of 80°C to 90°C. The mold was preheated in order to facilitate pouring of the curable resin composition and to avoid air bubbles being trapped during pouring. The compositions were then cured at 165°C for 24 hours in total. During curing time the resin was transformed into the final thermoset polymer and used as such in the final application of the product (electrical device). During gelling, the polymerization progressed to a highly viscous gel state of the resin, where the resin was not dripping out of the jar.

[0047] For pot life determination the resin was kept at suggested processing temperature and its viscosity was measured at regular time intervals.

[0048] Dielectric properties [relative permittivity (ε) and loss factor (tan δ)] were measured on square samples (38 mm x 38 mm) with 1.4 to 1.5 mm thickness. Results are shown at different frequencies and temperatures. Glass transition temperatures (Tg) were measured using differential scanning calorimetry (DSC) with 10 K/min heating rate, respectively.

Meaning of EP158, MY790-1, η, η^*, ε, tan δ

[0049]

- EP158: Bisphenol F based epoxy resin from Hexion with viscosity of 1-1.4 Pa·s (at 50°C) and an epoxy content of 6.3 equiv/kg
- MY790-1: Bisphenol A based epoxy resin from Huntsman with viscosity of 4-6.4 Pa·s (at 50°C) and epoxy content of 5.6-5.9 equiv/kg

- η = viscosity of the full formulation at 50°C [In the Examples, the initial viscosity and the time where the doubled initial viscosity (= 100 % increase) is reached are shown.]
- η^* = constant steady state viscosity at 50 °C reached after ca. 10 weeks obtained by resin replenishment with a rate of 20% addition of fresh resin per week. In brackets the total increase in % compared to initial viscosity is shown.
- ε = relative permittivity
- tan δ = dielectric loss

Example 1 (Table 1)

Components	Pot life at 50 °C	Gel time	T_g	Dielectric properties at 50 Hz		
				T [°C]	ε	tan δ
EP158 3 phr resorcinol 1 phr zirconium acetylacetonate	100 % η increase (130 → 260 mPas) after 3 weeks Steady state η^*: 250 mPas (62 %)	ca. 25 min at 165 °C	100 °C	40	3.82	0.0042
				60	3. 87	0.0048
				80	3.96	0.0072
				100	4.20	0.0177
				120	4.63	0.0265
				140	4.92	0.0171
				160	4.96	0.0104
				180	4.90	0.0129

Example 2 (Table 2)

Composition	Pot life at 50 °C	Gel time	T_g	Dielectric properties at 50 Hz		
				T [°C]	ε	tan δ
EP158 2 phr resorcinol 1 phr zirconium acetylacetonate	100 % η increase (125 → 250 mPas) after 5 weeks Steady state η^*: 200 mPas (60 %)	ca. 30 min at 165 °C	85 °C	40	3. 94	0.0045
				60	4.02	0.0063
				80	4.16	0.0135
				100	4.44	0.0275
				120	4.81	0.0248
				140	4.92	0.0143
				160	4.85	0.0173
				180	4.77	0.0509

Example 3 (Table 3)

Components	Pot life at 50 °C	Gel time	T_g	Dielectric properties at 50 Hz		
				T [°C]	ε	tan δ
EP158 3 phr resorcinol 1 phr hydroquinone 1 phr zirconium acetylacetonate	100 % η increase (130 → 260 mPas) after 5 weeks Steady state η*: 220 mPas (69 %)	ca. 25 min at 160 °C	95 °C	40	3.96	0.0046
				60	4.03	0.0062
				80	4.15	0.0111
				100	4.47	0.0257
				120	4.9	0.0276
				140	5.04	0.0206
				160	4.98	0.0519
				180	4.92	0.1958

Example 4 (Table 4)

Components	Pot life at 50 °C	Gel time	T_g	Dielectric properties at 50 Hz		
				T [°C]	ε	tan δ
EP158 2 phr resorcinol 2 phr hydroquinone 1 phr zirconium acetylacetonate	100 % η increase (130 → 260 mPas) after 4 weeks Steady state η*: 230 mPas (77 %)	ca. 25 min at 160 °C	110 °C	40	3. 86	0.0039
				60	3.90	0.0042
				80	3.96	0.0052
				100	4.09	0.0105
				120	4.47	0.0257
				140	4.92	0.0251
				160	5.04	0.0177
				180	4.98	0.0494

Example 5 (Table 5)

Components	Pot life at 50 °C	Gel time	T_g	Dielectric properties at 50 Hz		
				T [°C]	ε	tan δ
MY790-1 4 phr catechol 1 phr aluminium acetylacetonate	100 % η increase (350 → 700 mPas) after 3 weeks	ca. 20 min at 160 °C	140 °C	40	3. 91	0.0028
				60	3.94	0.0027
				80	3.95	0.0025
				100	3. 95	0.0026
				120	3.96	0.0035
				140	4.02	0.0066
				160	4.21	0.0141
				180	4.39	0.0130

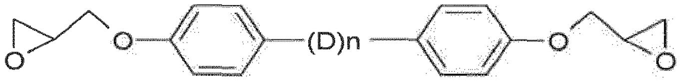
[0050] With a composition (using Bisphenol A based epoxy resins) as shown in Example 5 higher glass transition temperature as well as excellent dielectric properties (very low dielectric losses) can be achieved, especially suitable for high performance high voltage bushings.

[0051] In the Appendix Figure 1 illustrates the results of Example 1; Figure 2 illustrates the results of Example 2; Figure 3 illustrates the results of Example 3; and Figure 4 illustrates the results of Example 4.

Claims

1. Curable epoxy resin composition comprising a defined aromatic epoxy resin component and a defined latent catalyst system, and optionally further additives, said curable composition being a volatile-free single epoxy resin composition having a prolonged pot life at a processing temperature within the range of 40°C to 70°C, wherein:

   (a) the epoxy resin component is a compound of formula (I) in monomeric form or in a low polymeric form thereof, or is a mixture of such compounds:



(I)

$D = -CH_2-, -C(CH_3)_2-, -S-, -O-, -SO_2-, -CO-$

n = zero or one

   said epoxy resin component having an inherent viscosity within the range of 80 mPas to 300 mPas, measured at a temperature of 50°C;

   (b) the latent catalyst system comprises at least one metal acetylacetonate and at least one phenolic compound, wherein

      (b1) the metal acetylacetonate is selected from known metal acetylacetonate compounds, or is a mixture of such compounds, and is present in a concentration of 0.1 phr to 1.0 phr (parts per hundred parts) of the epoxy resin component; and

      (b2) the phenolic compound is a dihydroxybenzene or a tri-hydroxybenzene or any mixture thereof, and is present in a concentration of 2.0 phr to 4.0 phr (parts per hundred parts) of the epoxy resin component;

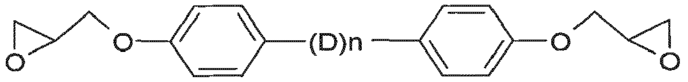
   characterized in that said curable epoxy resin composition is kept at a temperature within the range of 40°C to 70°C and the prolonged pot life at said temperature is provided to the composition by continuous resin replenishment with fresh resin at a rate within the range of 10% to 30% of fresh resin per week, preferably at a rate of 20% of fresh resin per week, calculated to the total amount of resin present in the tank, said fresh resin having an inherent viscosity within the range of 80 mPas to 300 mPas, measured at a temperature of 50°C.

2. Composition according to claim 1, **characterized in that** said composition has a pot life of at least one week, preferably of at least three weeks, at an elevated processing temperature within the range of about 40°C to 70°C, preferably at about 50°C, which can be prolonged for several more weeks by continuous resin replenishment at a rate of continuous resin replenishment within the range of 10% to 30% of fresh resin per week, preferably at a rate of 20% of fresh resin per week, calculated to the total amount of resin present in the tank.

3. Composition according to claim 1 or 2, **characterized in that** the curable epoxy resin composition which is added to the pot has a viscosity within the range of about 80 mPas to about 120 mPas, preferably within the range of about 100 mPas to about 110 mPas, measured at 50°C.

4. Composition according to any one of the claims 1-3, **characterized in that** the viscosity of the curable epoxy resin composition reached within the pot is within the range of about 260 mPas to about 300 mPas, preferably within the range of about 270 mPas to about 280 mPas, measured at 50°C.

5. Composition according to any one of the claims 1-3, **characterized in that** the epoxy resin component of the present invention is based on compounds of formula (I):



(I)

D = $-CH_2-$, $-C(CH_3)_2-$, -S-, -O-, $-SO_2-$, -CO-

n = zero or one

and is present in monomeric form or polymeric form or as a mixture thereof,
further **characterized in that** the epoxy resin components is preferably diglycidylether of bisphenol A, diglycidylether of bisphenol F, or diglycidylether bisphenol S, or a mixture thereof, preferably is diglycidylether of bisphenol A or diglycidylether of bisphenol F or a mixture thereof.

6. Composition according to claim 5, **characterized in that** the glycidyl compounds have a molecular weight between 200 and 1200, preferably between 200 und 1000 and have an epoxy value (equiv./kg) of at least three, preferably at least four and preferably about 5.0 to 6.5.

7. Composition according to any one of the claims 1-6, **characterized in that** the metal acetylacetonate [component (b1)] corresponds to the chemical formulae (II), (III), (IV) and (V):

$$[CH_3\text{-}C(O)\text{-}CH{=}C(O)\text{-}CH_3].\ Me^{+} \qquad (II)$$

or

$$[CH_3\text{-}C(O)\text{-}CH{=}C(O^{-})CH_3]_2.\ Me^{2+} \qquad (III)$$

or

$$[CH_3\text{-}C(O)\text{-}CH{=}C(O^{-})\text{-}CH_3]_3.\ Me^{3+} \qquad (IV)$$

or

$$[CH_3\text{-}C(O)\text{-}CH{=}C(O^{-})\text{-}CH_3]_4.\ Me^{4+} \qquad (V),$$

wherein Me^+ is selected from Li^+, Na^+ and K^+; Me^{2+} is selected from Cu^{2+} Co^{2+}, Zn^{2+} and Ca^{2+}; Me^{3+} is selected from Al^{3+}, V^{3+} and Fe^{3+}; and Me^{4+} is selected from Zr^{4+}, further **characterized in that** Me^{2+} is preferably Mg^{2+}, and Me^{3+} is preferably selected from Al^{3+} and Fe^{3+}, still further **characterized in that** preferably the metal acetylacetonate is aluminum acetylacetonate or zirconium acetylacetonate or a mixture thereof, and further **characterized in that** preferably the metal acetylacetonate or the mixture of metal acetylacetonates is present in a concentration of 0.1 phr to 1.0 phr, preferably in a concentration of 0.2 phr to 1.0 phr and preferably in a concentration of 0.5 phr to 1.0 phr (parts per hundred parts) of the epoxy resin component.

8. Composition according to any one of the claims 1-7, **characterized in that** the phenolic compound is selected from 1,2-dihydroxybenzene (catechol), 1,3-dihydroxybenzene (resorcinol) or 1,4-dihydroxybenzene (hydroquinone) or 1,2,3-trihydroxybenzene (pyrogallol) or 1,2,4-trihydroxybenzene or ia a mixture of these compounds, preferably is catechol or resorcinol or hydroquinone or pyrogallol or a mixture thereof, preferably catechol or resorcinol or hydroquinone, or a mixture thereof.

9. Composition according to any one of the claims 1-8, **characterized in that** the phenolic compound is present in a concentration of 0.5 phr to 6.0 phr, preferably in a concentration of 1.0 phr to 5.0 phr, preferably in a concentration of 2.0 phr to 4.0 phr, (parts per hundred parts) of the epoxy resin component.

10. Composition according to any one of the claims 1-9, **characterized in that** the ratio of the metal acetylacetonate compound to the phenolic compound is within the weight ratio of 4.0 : 1.0 to 1.0 : 1.0, preferably with the weight ratio of 3.0 : 1.0 to 1.0 : 1.0.

11. Composition according to any one of the claims 1-10, **characterized in that** the composition contains additives selected from filler materials, wetting/dispersing agents, plasticizers, antioxidants, light absorbers, as well as further additives used in electrical applications.

12. The use of the curable epoxy resin composition according to any one of the claims 1-11 for producing high voltage electrical insulations using impregnation and/or wet winding application techniques.

13. Shaped article in the form of an electrical insulator being made from a curable epoxy resin composition as defined in any one of the claims 1-11.

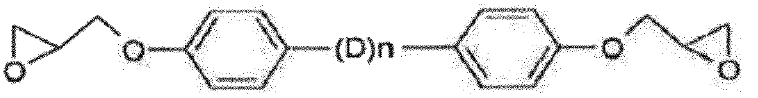
14. Electrical articles comprising an electrical insulator made from a curable epoxy resin composition according to any one of the claims 1-11.

15. Method of producing a curable epoxy resin composition according to any one of the claim 1-11, **characterized in that** fresh resin, having an inherent viscosity within the range of 80 mPas to 300 mPas, preferably within the range of about 80 mPas to about 120 mPas, preferably within the range of about 100 mPas to about 110 mPas, measured at 50°C, is continuously provided to the composition in the pot at a temperature range of 40°C to 70°C, by continuous resin replenishment at a rate within the range of 10% to 30% of fresh resin per week, preferably at a rate of 20% of fresh resin per week, calculated to the total amount of resin present in the tank.

Patentansprüche

1. Härtbare Epoxidharz-Zusammensetzung, umfassend einen definierten aromatischen Epoxidharz-Bestandteil und ein definiertes latentes Katalysator-System, und optional weitere Zusätze, wobei die härtbare Zusammensetzung eine volatil-freie Einzel-Epoxidharz-Zusammensetzung ist, die eine verlängerte Topfzeit bei einer Verarbeitungstemperatur im Bereich von 40 °C bis 70 °C aufweist, wobei:

(a) der Epoxidharz-Bestandteil ein Stoff mit der Formel (I) in monomerer Form oder in einer niedrigen polymeren Form davon ist, oder eine Mischung solcher Stoffe ist:



(I)

D = $-CH_2-$, $-C(CH_3)_2-$, -S-, -O-, $-SO_2-$, -CO-

n = 0 oder 1

wobei der Epoxidharz-Bestandteil eine inhärente Viskosität im Bereich von 80 mPas bis 300 mPas aufweist, gemessen bei einer Temperatur von 50 °C;

(b) das latente Katalysator-System wenigstens ein Metall-Azetylazetonat und wenigstens einen Phenol-Stoff umfasst, wobei

(b1) das Metall-Azetylazetonat aus bekannten Metall-Azetylazetonat-Stoffen ausgewählt ist, oder eine Mischung solcher Stoffe ist, und in einer Konzentration von 0.1 phr bis 1.0 phr (Teile pro 100 Teile) des Epoxidharz-Bestandteils vorhanden ist; und

(b2) der Phenol-Stoff ein Dihydroxybenzol oder ein Trihydroxybenzol oder eine beliebige Mischung davon ist, und in einer Konzentration von 2.0 phr bis 4.0 phr (Teile pro 100 Teile) des Epoxidharz-Bestandteils vorhanden ist;

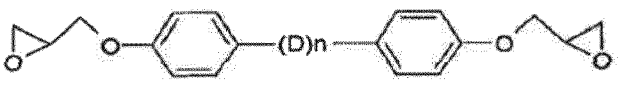
dadurch gekennzeichnet, dass die härtbare Epoxidharz-Zusammensetzung bei einer Temperatur im Bereich von 40 °C bis 70 °C gehalten wird und die verlängerte Topfzeit bei dieser Temperatur für die Zusammensetzung bereitgestellt ist durch einen kontinuierlichen Harz-Nachschub mit frischem Harz bei einer Rate im Bereich von 10 % bis 30 % frischem Harz pro Woche, vorzugsweise bei einer Rate von 20 % frischem Harz pro Woche, berechnet bezüglich der Gesamtmenge des im Tank vorhandenen Harzes, wobei das frische Harz eine inhärente Viskosität im Bereich von 80 mPas bis 300 mPas aufweist, gemessen bei einer Temperatur von 50 °C.

2. Die Zusammensetzung nach Anspruch 1, **dadurch gekennzeichnet, dass** die Zusammensetzung eine Topfzeit von wenigstens einer Woche aufweist, vorzugsweise von wenigstens drei Wochen, bei einer erhöhten Verarbeitungstemperatur im Bereich von 40 °C bis 70 °C, vorzugsweise bei etwa 50 °C, was für einige weitere Wochen verlängert werden kann durch kontinuierlichen Harz-Nachschub bei einer Rate des kontinuierlichen Harz-Nachschubs im Bereich von 10 % bis 30 % frischem Harz pro Woche, vorzugsweise bei einer Rate von 20 % frischem Harz pro Woche, berechnet bezüglich der Gesamtmenge des im Tank vorhandenen Harzes.

3. Die Zusammensetzung nach Anspruch 1 oder 2, **dadurch gekennzeichnet, dass** die härtbare Epoxidharz-Zusammensetzung, die dem Topf zugeführt wird, eine Viskosität im Bereich von etwa 80 mPas bis etwa 120 mPas aufweist, vorzugsweise im Bereich von etwa 100 mPas bis etwa 110 mPas, gemessen bei 50 °C.

4. Die Zusammensetzung nach einem der Ansprüche 1-3, **dadurch gekennzeichnet, dass** die im Topf erreichte Viskosität der härtbaren Epoxidharz-Zusammensetzung im Bereich von etwa 260 mPas bis etwa 300 mPas ist, vorzugsweise im Bereich von etwa 270 mPas bis etwa 280 mPas, gemessen bei 50 °C.

5. Die Zusammensetzung nach einem der Ansprüche 1-3, **dadurch gekennzeichnet, dass** der Epoxidharz-Bestandteil der vorliegenden Erfindung auf Stoffen der Formel (I) basiert:



(I)

$D = -CH_2-, -C(CH_3)_2-, -S-, -O-, -SO_2-, -CO-$

$n = 0$ oder 1

und in einer monomeren Form oder einer polymeren Form oder als Mischung davon vorhanden ist, weiter **dadurch gekennzeichnet, dass** der Epoxidharz-Bestandteil vorzugsweise Diglycidylether von Bisphenol A, Diglycidylether von Bisphenol F oder Diglycidylether Bisphenol S oder eine Mischung davon ist, und vorzugsweise Diglycidylether von Bisphenol A oder Diglycidylether von Bisphenol F oder eine Mischung davon ist.

6. Die Zusammensetzung nach Anspruch 5, **dadurch gekennzeichnet, dass** die Glycidyl-Stoffe ein Molekulargewicht zwischen 200 und 1200 aufweisen, vorzugsweise zwischen 200 und 1000, und einen Epoxidwert (equiv./kg) von wenigstens 3, vorzugsweise wenigstens 4 und vorzugsweise etwa 5.0-6.5 aufweisen.

7. Die Zusammensetzung nach einem der Ansprüche 1-6, **dadurch gekennzeichnet, dass** das Metall-Azetylazetonat [Bestandteil (b1)] den chemischen Formeln (II), (III), (IV) und (V) entspricht:

$$[CH_3\text{-}C(O)\text{-}CH{=}C(O^-)\text{-}CH_3].\ Me^+ \qquad \text{(II)}$$

oder

$$[CH_3\text{-}C(O)\text{-}CH{=}C(O^-)\text{-}CH_3]_2.\ Me^{2+} \qquad \text{(III)}$$

oder

$$[CH_3\text{-}C(O)\text{-}CH{=}C(O)\text{-}CH_3]_3.\ Me^{3+} \qquad \text{(IV)}$$

oder

$$[CH_3\text{-}C(O)\text{-}CH{=}C(O^-)\text{-}CH_3]_4.\ Me^{4+} \qquad \text{(V),}$$

wobei Me^+ ausgewählt ist aus Li^+, Na^+ und K^+; Me^{2+} ausgewählt ist aus Cu^{2+}, Co^{2+}, Zn^{2+} und Ca^{2+}; Me^{3+} ausgewählt ist aus Al^{3+}, V^{3+} und Fe^{3+}; und Me^{4+} ausgewählt ist aus Zr^{4+},
weiter **dadurch gekennzeichnet, dass** Me^{2+} vorzugsweise Mg^{2+} ist, und Me^{3+} vorzugsweise aus Al^{3+} und Fe^{3+} ausgewählt ist,
weiter **dadurch gekennzeichnet, dass** das Metall-Azetylazetonat vorzugsweise Aluminium-Azetylazetonat oder Zirkonium-Azetylazetonat oder eine Mischung davon ist,
und weiter **dadurch gekennzeichnet, dass** das Metall-Azetylazetonat oder die Mischung der Metall-Azetylazetonate in einer Konzentration von 0.1 phr bis 1.0 phr, vorzugsweise in einer Konzentration von 0.2 phr bis 1.0 phr und vorzugsweise in einer Konzentration von 0.5 phr bis 1.0 phr (Teile pro 100 Teile) des Epoxidharz-Bestandteils vorhanden ist.

8. Die Zusammensetzung nach einem der Ansprüche 1-7, **dadurch gekennzeichnet, dass** der Phenol-Stoff ausgewählt ist aus 1,2-Dihydroxybenzol (Brenzkatechin), 1,3-Dihydroxybenzol (Resorcin) oder 1,4-Dihydroxybenzol (Hydrochinon) oder 1,2,3-Trihydroxybenzol (Pyrogallol) oder 1,2,4-Trihydroxybenzol oder eine Mischung dieser Stoffe ist, vorzugsweise Brenzkatechin oder Resorcin oder Hydrochinon oder Pyrogallol oder eine Mischung davon ist, und vorzugsweise Brenzkatechin oder Resorcin oder Hydrochinon oder eine Mischung davon ist.

9. Die Zusammensetzung nach einem der Ansprüche 1-8, **dadurch gekennzeichnet, dass** der Phenol-Stoff in einer Konzentration von 0.5 phr bis 6.0 phr, vorzugsweise in einer Konzentration von 1.0 phr bis 5.0 phr, und vorzugsweise in einer Konzentration von 2 phr bis 4.0 phr (Teile pro 100 Teile) des Epoxidharz-Bestandteils vorhanden ist.

10. Die Zusammensetzung nach einem der Ansprüche 1-9, **dadurch gekennzeichnet, dass** das Verhältnis des Metall-Azetylazetonat-Stoffs zum Phenol-Stoff im Gewichtsverhältnis von 4.0 : 1.0 bis 1.0 : 1.0 ist, und vorzugsweise mit dem Gewichtsverhältnis von 3.0 : 1.0 bis 1.0 : 1.0.

11. Die Zusammensetzung einem der Ansprüche 1-10, **dadurch gekennzeichnet, dass** die Zusammensatzung Zusatzstoffe enthält, die ausgewählt sind aus Füllmaterialien, Benetzungs-/Dispergiermitteln, Weichmacher, Antioxidantien, Lichtabsorbern, als auch weiteren Zusatzstoffen, die in elektrischen Anwendungen verwendet werden.

12. Die Verwendung der härtbaren Epoxidharz-Zusammensetzung nach einem der Ansprüche 1-11 zum Herstellen von elektrischer Hochspannungsisolation unter Verwendung von Imprägnierung und/oder Nassläufer-Anwendungstechniken.

13. Ein geformte Artikel in der Gestalt eines elektrischen Isolators, der aus der härtbaren Epoxidharz-Zusammensetzung besteht, wie sie in einem der Ansprüche 1-11 definiert ist.

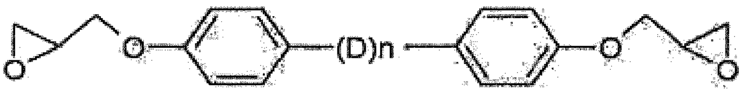
14. Ein elektrischer Artikel, umfassend einen elektrischen Isolator, der aus der härtbaren Epoxidharz-Zusammensetzung besteht, wie sie in einem der Ansprüche 1-11 definiert ist.

15. Verfahren zum Herstellen einer härtbaren Epoxidharz-Zusammensetzung nach einem der Ansprüche 1-11, **dadurch gekennzeichnet, dass** frisches Harz, das eine inhärente Viskosität im Bereich von 80 mPas bis 300 mPas aufweist, vorzugsweise im Bereich von etwa 80 mPas bis etwa 120 mPas, vorzugsweise im Bereich von etwa 100 mPas bis etwa 110 mPas, gemessen bei 50 °C, kontinuierlich der Zusammensetzung im Topf bei einem Temperaturbereich von 40 °C bis 70 °C zugeführt wird, durch kontinuierlichen Harz-Nachschub bei einer Rate im Bereich von 10 % bis 30 % frischem Harz pro Woche, vorzugsweise bei einer Rate von 20 % frischem Harz pro Woche, berechnet bezüglich der Gesamtmenge des im Tank vorhandenen Harzes.

Revendications

1. Composition de résine époxyde durcissable comprenant un composant à base de résine époxyde aromatique défini et un système de catalyseur latent défini, et optionnellement d'autres additifs, ladite composition durcissable étant une composition de résine époxyde unique non volatile ayant une durée de conservation prolongée à une température de traitement de l'ordre de 40°C à 70°C, dans laquelle:

   (a) le composant de résine époxyde est un composé de la formule (I) sous forme de monomère ou sous forme de polymère à faible concentration, ou est un mélange de tels composés :



(I)

$D = -CH_2-, -C(CH_3)_2-, -S-, -O-, -SO_2-, -CO-$

n = zero ou un

   ledit composant de résine époxyde ayant une viscosité inhérente de l'ordre de 80 mPas à 300 mPas, mesurée à une température de 500C;

   (b) le système de catalyseur latent comprend au moins un acétylacétonate de métal et au moins un composé phénolique, où

      (b1) l'acétylacétonate de métal est choisi parmi les composés à base d'acétylacétonate de métal connus, ou est un mélange de tels composés, et est présent à une concentration de 0,1 phr à 1,0 phr (parts pour cent parts) du composant de résine époxyde; et

      (b2) le composé phénolique est un dihydroxybenzène ou un trihydroxybenzène ou tout mélange de ces derniers, et est présent à une concentration de 2,0 phr à 4,0 phr (parts pour cent parts) du composant de résine époxyde ;

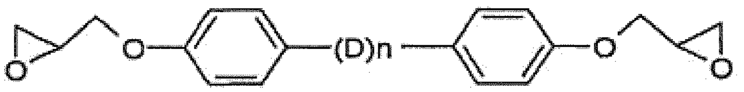
caractérisée par le fait que ladite composition de résine époxyde durcissable est maintenue à une température de l'ordre de 40°C à 70°C et que la durée de conservation prolongée à ladite température est conférée à la composition par remplissage de résine en continu par de la résine fraîche à un taux de l'ordre de 10% à 30% de résine fraîche par semaine, de préférence à un taux de 20% de résine fraîche par semaine, calculé sur la quantité totale de résine présente dans le réservoir, ladite résine fraîche ayant une viscosité inhérente de l'ordre de 80 mPas à 300 mPas, mesurée à une température de 50°C.

2. Composition selon la revendication 1, **caractérisée par le fait que** ladite composition présente une durée de conservation d'au moins une semaine, de préférence d'au moins trois semaines, à une température de traitement élevée de l'ordre d'environ 40°C à 70°C, de préférence à environ 50°C, qui peut être prolongée pendant plusieurs semaines additionnelles par remplissage de résine en continu à un taux de remplissage de résine en continu de l'ordre de 10% à 30% de résine fraîche par semaine, de préférence à un taux de 20% de résine fraîche par semaine, calculé sur la quantité totale de résine présente dans le réservoir.

3. Composition selon la revendication 1 ou 2, **caractérisée par le fait que** la composition de résine époxyde durcissable qui est ajoutée à la cuve a une viscosité de l'ordre d'environ 80 mPas à environ 120 mPas, de préférence de l'ordre d'environ 100 mPas à environ 110 mPas, mesurée à 50°C.

4. Composition selon l'une quelconque des revendications 1 à 3, **caractérisée par le fait que** la viscosité de la composition de résine époxyde durcissable atteinte dans la cuve est de l'ordre d'environ 260 mPas à environ 300 mPas, de préférence de l'ordre d'environ 270 mPas à environ 280 mPas, mesurée à 50°C.

5. Composition selon l'une quelconque des revendications 1 à 3, **caractérisée par le fait que** le composant de résine époxyde de la présente invention est basé sur les composés de la formule (I);



(I)

D = $-CH_2-$, $-C(CH_3)_2-$, $-S-$, $-O-$, $-SO_2-$, $-CO-$

n = zéro ou un

et est présent sous forme de monomère ou de polymère ou d'un mélange de ces derniers,
caractérisée par ailleurs par le fait que le composant de résine époxyde est de préférence l'éther diglycidylique de bisphénol A, l'éther diglycidylique de bisphénol F, ou l'éther diglycidylique de bisphénol S, ou un mélange de ces derniers, est de préférence l'éther diglycidylique de bisphénol A ou le diglycidyléther de bisphénol F ou un mélange de ces derniers.

6. Composition selon la revendication 5, **caractérisée par le fait que** les composés glycidyliques présentent un poids moléculaire compris entre 200 et 1200, de préférence entre 200 et 1000 et présentent une valeur d'époxyde (équiv. / Kg) d'au moins trois, de préférence d'au moins quatre et de préférence d'environ 5,0 à 6,5.

7. Composition selon l'une quelconque des revendications 1 à 6, **caractérisée par le fait que** l'acétylacétonate de métal [composant (b1)] correspond aux formules chimiques (11), (111), (IV) et (V):

$[CH_3\text{-}C(O)\text{-}CH{=}C(O^-)\text{-}CH_3].\ Me^+$ (11)

ou

$[CH_3\text{-}C(O)\text{-}CH{=}C(O^-)\text{-}CH_3]_2.\ Me^{2+}$ (111)

ou

$[CH_3\text{-}C(O)\text{-}CH{=}C(O^-)\text{-}CH_3]_3.\ Me^{3+}$ (IV) ou

$[CH_3\text{-}C(O)\text{-}CH=C(O^-)\text{-}CH_3]_4 . Me^{4+}$ (V)

où Me^+ est choisi parmi Li^+, Na^+ et K^+ ; Me^{2+} est choisi parmi Cu^{2+}, $C0^{2+}$, zn^{2+} et Ca^{2+}; Me^{3+} est choisi parmi Al^{3+}, V^{3+} et Fe^{3+}, et Me^{4+} est choisi parmi Zr^{4+},
caractérisée par ailleurs par le fait que Me^{2+} est de préférence Mg^{2+} et Me^{3+} est de préférence choisi parmi Al^{3+} et Fe^{3+},
caractérisée par ailleurs encore par le fait que, de préférence, l'acétylacétonate de métal est l'acétylacétonate d'aluminum ou l'acétylacétonate de zirconium ou un mélange de ces derniers,
et **caractérisée par** ailleurs par le fait que, de préférence, l'acétylacétonate de métal ou le mélange d'acétylacétonates de métal est présent à une concentration de 0,1 phr à 1,0 phr, de préférence à une concentration de 0,2 phr à 1.0 phr et de préférence à une concentration de 0,5 phr à 1,0 phr (parts pour cent parts) du composant de résine d'époxyde.

8. Composition selon l'une quelconque des revendications 1 à 7, **caractérisée par le fait que** le composé phénolique est choisi parmi le 1,2-dihydroxybenzène (pyrocatéchol), le 1,3-dihydroxybenzène (résorcinol) ou le 1,4-dihydroxybenzène (hydroquinone) ou le 1,2,3-trihydroxybenzène (pyrogallol) ou le 1,2,4-trihydroxybenzène ou est un mélange de ces composés, est de préférence le catéchol ou le résorcinol ou l'hydroquinone ou le pyrogallol ou un mélange de ces derniers, de préférence le catéchol ou le résorcinol ou l'hydroquinone, ou un mélange de ces derniers.

9. Composition selon l'une quelconque des revendications 1 à 8, **caractérisée par le fait que** le composé phénolique est présent à une concentration de 0,5 phr à 6,0 phr, de préférence à une concentration de 1,0 phr à 5,0 phr, de préférence à une concentration de 2,0 phr à 4,0 phr (parts pour cent parts) du composant de résine époxyde.

10. Composition selon l'une quelconque des revendications 1 à 9, **caractérisé par le fait que** le rapport entre le composé à base d'acétylacétonate de métal et le composé phénolique est de l'ordre du rapport en poids de 4,0 : 1,0 à 1,0 : 1,0, de préférence de l'ordre du rapport en poids de 3,0 : 1,0 à 1,0 : 1,0.

11. Composition selon l'une quelconque des revendications 1 à 10, **caractérisée par le fait que** la composition contient des additifs choisis parmi les matériaux de charge, les agents mouillants/de dispersion, les plastifiants, les antioxydants, les absorbeurs de lumière, ainsi que d'autres additifs utilisés dans les applications électriques.

12. Utilisation de la composition de résine époxyde durcissable selon l'une quelconque des revendications 1 à 11 pour la production d'isolants électriques à haute tension à l'aide des techniques d'application d'imprégnation et/ou d'enroulement en humide.

13. Article façonné sous forme d'un isolant électrique réalisé à partir d'une composition de résine époxy durcissable telle que définie dans l'une quelconque des revendications 1 à 11.

14. Articles électriques comprenant un isolant électrique réalisé à partir d'une composition de résine époxy durcissable selon l'une quelconque des revendications 1 à 11.

15. Procédé de production d'une composition de résine époxyde durcissable selon l'une quelconque des revendications 1 à 11, **caractérisé par le fait que** de la résine fraîche ayant une viscosité inhérente de l'ordre de 80 mPas à 300 mPas, de préférence de l'ordre d'environ 80 mPas à environ 120 mPas, de préférence de l'ordre d'environ 100 mPas à environ 110 mPas, mesurée à 50°C, est alimentée en continu vers la composition dans la cuve à une température de l'ordre de 40°C à 70°C, par remplissage de résine en continu à un taux de l'ordre de 10% à 30% de résine fraîche par semaine, de préférence à un taux de 20% de résine fraîche par semaine, calculé sur la quantité totale de résine présente dans le réservoir,

Figure 1

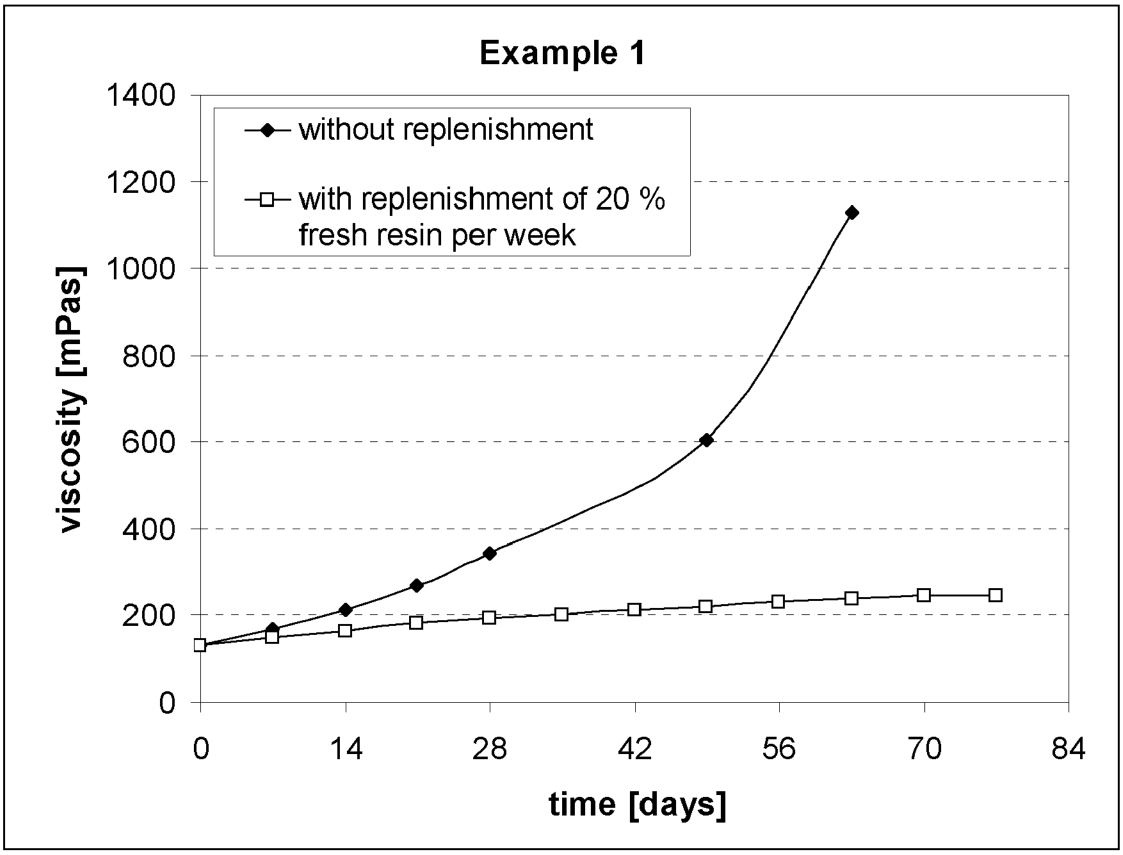

Example 1
viscosity [mPas]
0
200
400
600
800
1000
1200
1400
time [days]
0
14
28
42
56
70
84
without replenishment
with replenishment of 20 % fresh resin per week

Figure 2

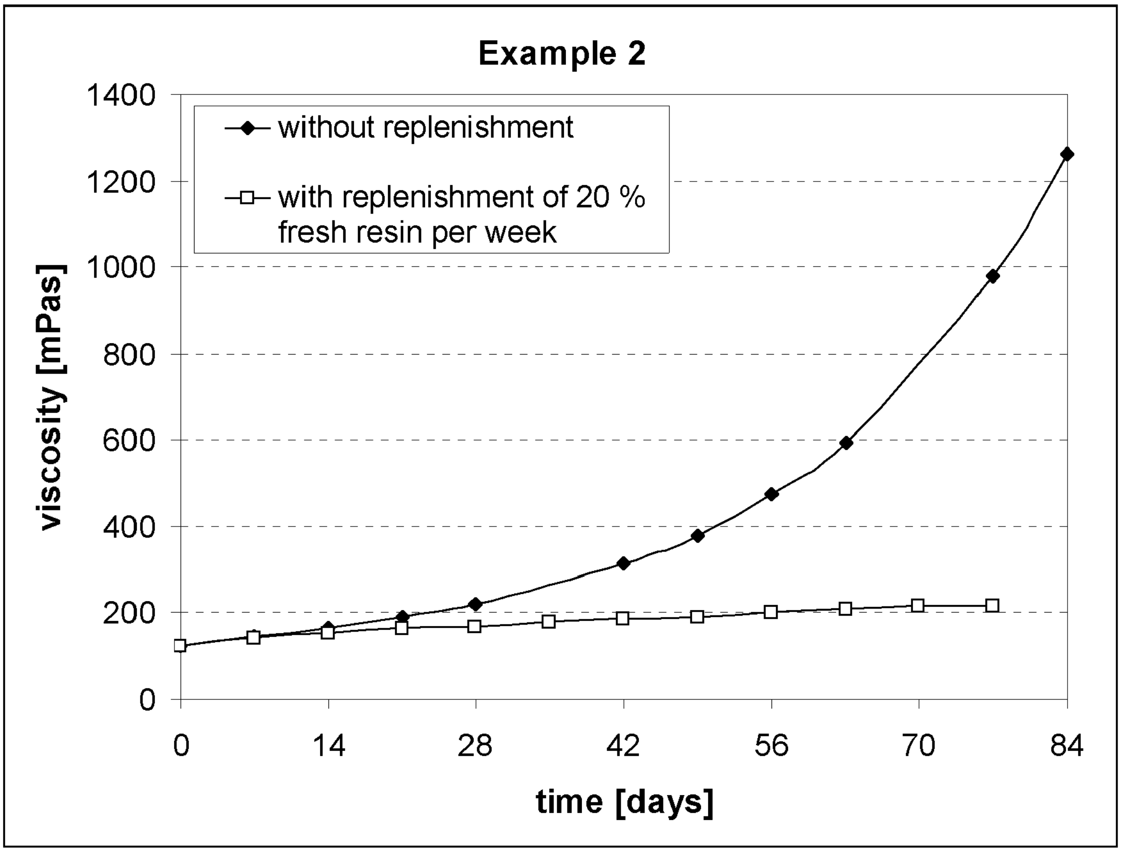

Example 2
without replenishment
with replenishment of 20 % fresh resin per week
viscosity [mPas]
0
200
400
600
800
1000
1200
1400
time [days]
0
14
28
42
56
70
84

Figure 3

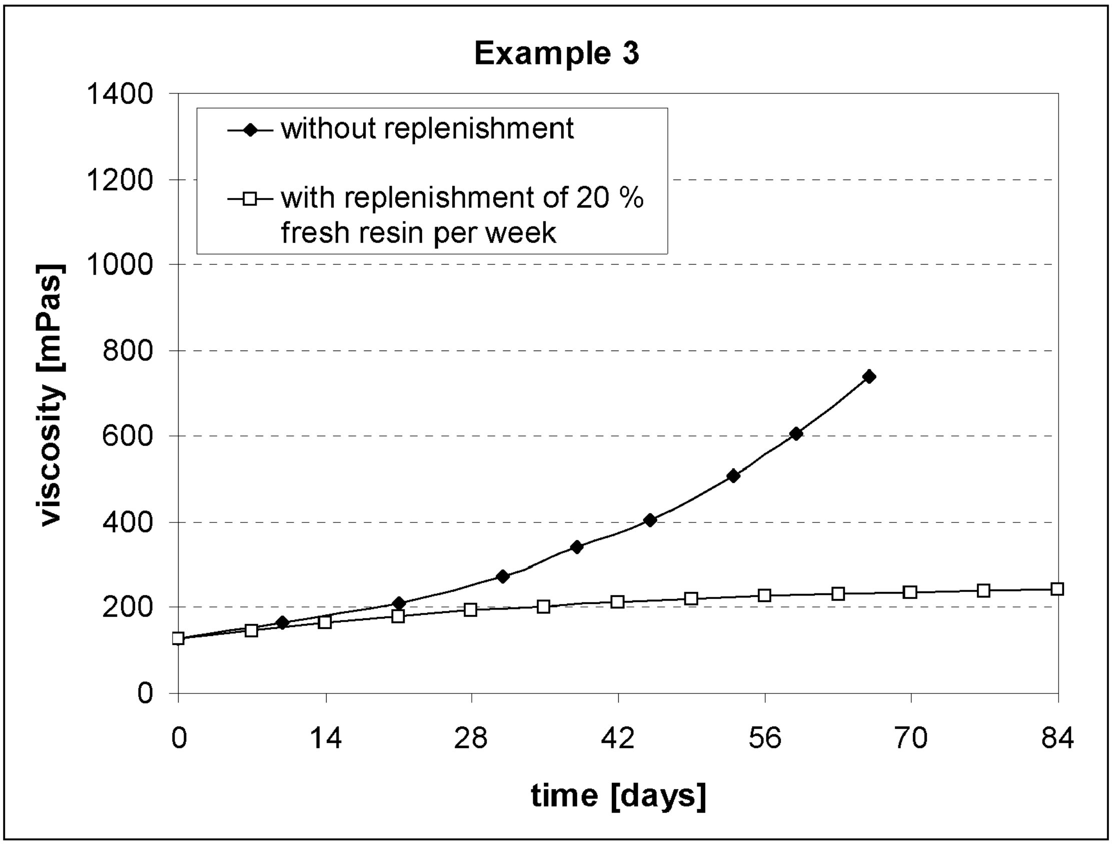
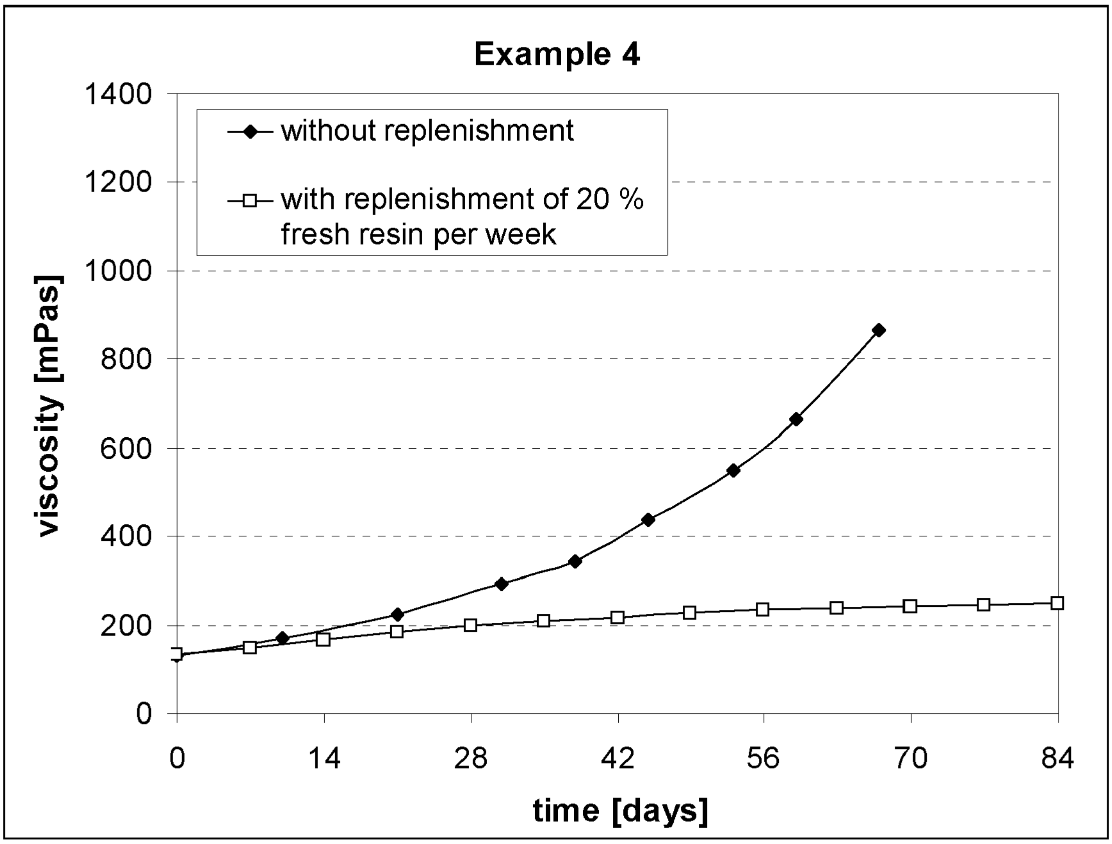

Example 3
1400
1200
1000
800
600
400
200
0
viscosity [mPas]
0
14
28
42
56
70
84
time [days]
without replenishment
with replenishment of 20 % fresh resin per week

Figure 4


Example 4
1400
1200
1000
800
600
400
200
0
viscosity [mPas]
0
14
28
42
56
70
84
time [days]
without replenishment
with replenishment of 20 % fresh resin per week

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- GB 1402899 A **[0007]**