Title: CURABLE SOL-GELO COMPOSITION

Abstract: Curable sol-gel composition useful for modifying the surface of a conventional electrical insulation system and providing said surface with an improved tracking and erosion resistance, characterized in that said sol-gel composition comprises: (a) cyclo-aliphatic epoxy resin compound containing at least two 1,2-epoxy groups per molecule [component (a)]; (b) a glycidoxypropyltri (C1-4) alkoxysilane [component (b)]; (c) a gamma-aminopropytri (C1-4) alkoxysilane [component (c)]; (d) a mineral filler material [component (d)]; and (e) a hydrophobic compound [component (e)] or a mixture of such hydrophobic compounds being selected from the group comprising fluorinated or chlorinated hydrocarbons or organopolysiloxanes; wherein the ratio of the epoxy equivalents of component (a) to the epoxy equivalents of component (b) is from 9:1 to 6:4; the molar ratio of component (c) to the epoxy equivalents of the sum of [component (a)] and [component (b)] is from about 0.9 to 1.1; the mineral filler material [component (d)] is present in a quantity of about 55% by weight to about 85% by weight, calculated to the total weight of the cured composition; the hydrophobic compound [component (e)] is present in a quantity of about 1.0% by weight to about 10% by weight, calculated to the total weight of the cured composition; whereby the curable sol-gel composition optionally contains further additives; electrical insulation system comprising said cured composition.
Curable sol-gel composition

The present invention refers to a curable sol-gel composition useful for modifying the outer surface of a conventional electrical insulation system and providing said surface with an improved tracking and erosion resistance. This is achieved by applying the curable sol-gel composition to the outer surface of the electrical insulation system and curing the applied sol-gel composition, whereby a thin cured coating composition is formed which provides said electrical insulation system with an improved tracking and erosion resistance. The present invention also refers to a surface modified electrical insulation system the outer surface of said electrical insulation system being coated with a thin coating composition made from a selected cured sol-gel composition as described herein.

Electrical insulations often are exposed to surface discharges in service. The temperature of such surface discharges generally is higher than 1000°C (>1000°C). In the case of electrical insulation systems based on synthetic polymers filled with a filler composition, these high discharge temperatures lead to erosion and carbonization (also called tracking) of the surface of the insulation material since the degradation temperature of polymeric insulation material typically is much lower than 1000°C, and generally lower than 400°C. Epoxy resin compositions generally start to degrade at temperatures around 250°C.

State of the art
In US 6,541,118 an electrical insulator with a molding made of a ceramic and a hydrophobic coating applied to the ceramic surface is disclosed. The hydrophobic coating comprises a plasma polymer having been applied directly to the ceramic. Ceramic materials are very stable having a high dimensional stability and a great resistance to heat. It is therefore possible to coat the ceramic surface with a plasma polymer coating by applying said plasma coating directly to the ceramic surface.
Electrical indoor insulations very often are based on synthetic polymers such as epoxy resin compositions, polyester compositions or polyurethane compositions. Electrical indoor insulations based on epoxy resin compositions generally are made from cycloaromatic epoxy resin compounds. However, cured epoxy resin compositions comprising aromatic moieties undergo degradation due to UV-radiation and their outdoor use therefore is limited. Epoxy resin compositions based on cycloaliphatic epoxy resin compounds, therefore, generally are used for electrical outdoor insulations.

The resistance of electrical insulators to electrical surface discharges without degradation is measured with the (International Electrotechnical Commission) IEC 60587 inclined plane tracking standard test. Indoor epoxy (IEP) compositions based on cycloaromatic epoxy resin compounds and polyurethane (PU) compositions repeatedly fail the 3.5 kV level of the inclined tracking and erosion test (class 1A3.5 according to standard IEC 60587). Therefore, there is a need to increase the time during which such polymeric insulation can withstand exposure to the high temperatures of surface discharges without degradation.

Description of the invention
It has now been found that an electrical insulation system made from a conventional synthetic polymer composition, such as a cycloaromatic or a cycloaliphatic epoxy resin composition or a polyurethane composition, can be coated with a thin coat as defined herein, so that the insulation system passes the 3.5 kV level of the inclined tracking and erosion test (class 1A3.5 according to standard IEC 60587). Said thin coat is an electrically non-conductive hydrophobic polymeric material which is obtained by applying a selected sol-gel composition as defined herein to the surface, and especially to the outer surface, of the electrical insulation system and curing said sol-gel composition. This allows the production of low cost coatings for comparatively low-cost electrical insulator compositions and
provides these electrical insulators with a superior tracking and erosion resistance even compared to the commonly used outdoor insulators based on cycloaliphatic epoxy resin compositions. Further, the cured coating composition has a high hydrophobicity and high adhesion to the basic outer surface of the electrical insulator.

The present invention is defined in the claims. The present invention specifically refers to a curable sol-gel composition useful for modifying the surface of a conventional electrical insulation system and providing said surface with an improved tracking and erosion resistance, characterized in that said sol-gel composition comprises:

(a) a cyclo-aliphatic epoxy resin compound containing at least two 1,2-epoxy groups per molecule [component (a)];
(b) a glycidoxypropane-tri(C_{1-4})alkoxysilane [component (b)];
(c) a gamma-aminopropyl-tri(C_{1-4})alkoxysilane [component (c)];
(d) a mineral filler material [component (d)];
(e) and a hydrophobic compound [component (e)] or a mixture of such hydrophobic compounds being selected from the group comprising fluorinated or chlorinated hydrocarbons or organopolysiloxanes;

wherein
- the ratio of the epoxy equivalents of component (a) to the epoxy equivalents of component (b) is from 9:1 to 6:4;
- the molar ratio of component (c) to the epoxy equivalents of the sum of [component (a)] and [component (b)] is from about 0.9 to 1.1;
- the mineral filler material [component (d)] is present in a quantity of about 55% by weight to about 85% by weight, calculated to the total weight of the cured composition;
- the hydrophobic compound [component (e)] is present in a quantity of about 1.0% by weight to about 10% by weight, calculated to the total weight of the cured composition;

whereby the curable sol-gel composition optionally contains further additives.
The present invention further refers to a method of making said curable sol-gel composition. The present invention further refers to the use of said curable sol-gel composition for modifying the surface of an electrical insulation system said insulation system being made from a hardened or cured conventional synthetic polymer composition, to yield an electrical insulation system with improved tracking and erosion resistance.

The present invention further refers to an electrical insulation system wherein the surface of said electrical insulation system, and especially the outer surface of said electrical insulation system, is coated with a thin coating composition as defined in the present invention.

The present invention further refers to a method of producing an electrical insulation system being coated with a thin coating composition as defined in the present invention, comprising the steps of applying an uncured sol-gel composition as defined in the present invention to the surface of an electrical insulation system, especially applying to the outer surface of an electrical insulation system, as a thin coating, and subsequently curing said sol-gel composition.

Conventional electrical insulation systems are generally made from a synthetic polymer composition comprising a cycloaromatic and/or a cycloaliphatic epoxy resin composition or a polyester, for example poly(methyl-methacrylate) or poly(alkylacrylo-nitrile), or a polyurethane composition. Such compositions are known. According to the present invention, the surface of any of such conventional electrical insulation system may be covered with a the coating as defined in the present invention.

Component (a) of the sol-gel composition is a cyclo-aliphatic epoxy resin compound containing at least two 1,2-epoxy groups per molecule. Cycloaliphatic epoxy resin compounds useful for the
present invention comprise unsubstituted glycidyl groups and/or glycidyl groups substituted with methyl groups. These glycidyl compounds have an epoxy value (equiv./kg) preferably of at least three, preferably at least four and especially at about five or higher, preferably about 5.0 to 6.1. Preferred are for example optionally substituted epoxy resins of formula (I):

\[
\begin{align*}
\text{D} &= -\text{O}, -\text{SO}_2-, -\text{CO}_2-, -\text{CH}_2-, -\text{C(CH}_3)_2-, -\text{C(CF}_3)_2- \\
n &= \text{zero or 1}
\end{align*}
\]

Compounds of formula (I) wherein D is \(-\text{(CH}_3\text{-)}\) or \([-\text{C(CH}_3)_2\text{-}]\) are preferred. Further cycloaliphatic epoxy resins [component (a)] to be used within the scope of the present invention are for example hexahydro-o-phthalic acid-bis-glycidyl ester, hexahydro-m-phthalic acid-bis-glycidyl ester or hexahydro-p-phthalic acid-bis-glycidyl ester.

Preferred cycloaliphatic epoxy resin compounds are liquid at room temperature or when heated to a temperature of up to about 65°C. Preferred cycloaliphatic epoxy resin compounds are for example Araldite® CY 184 (Huntsman Advanced Materials Ltd.), a cycloaliphatic epoxy resin compound (diglycidylester) having an epoxy content of 5.80-6.10 (equiv/kg). Preferred are cycloaliphatic epoxy resin compounds based on a diglycidyl ester of hexahydrophthalic acid.

Component (b) is preferably glycidoxypropane-trimethoxysilane (GPTMS).

The ratio of the epoxy equivalents of component (a) to the epoxy equivalents of component (b) is from 9:1 to 6:4, preferably from 8:1 to 6:4, and preferably at about 7:3.
Component (c) is preferably gamma-aminopropyl-triethoxysilane (GAPES). The molar ratio of component (c) to the epoxy equivalents of the sum of [component (a)] and [component (b)] is from about 0.9 to 1.1, preferably from 0.95 to 1.05, and preferably about 1:1.

The mineral filler material is preferably selected from silicone oxides (silica, quartz), known silicates such as sodium/potassium silicates and/or aluminosilicates, preferably layered silicates, aluminium oxide, aluminium trihydrate [ATH], titanium oxide or dolomite [CaMg(CO₃)₂], metal nitrides, such as silicon nitride, boron nitride and aluminium nitride or metal carbides, such as silicon carbide. Preferred are layered silicates, silica and quartz, the silica and quartz having a minimum SiO₂-content of about 95-97% by weight.

The mineral filler compound or the mixture of such compounds have a preferred average grain size (at least 50% of the grains) in the range of from about 100 nm to 200μm, preferably in the range of from 500 nm to 100μm, preferably in the range of from 5μm to 100μm, preferably in the range of from 5μm to 40μm, and especially in the range of from 5μm to 35μm. The filler material may be surface treated, for example silanized.

The mineral filler material is present in a quantity of about 55% by weight to about 85% by weight, preferably 65% by weight to 80% by weight, preferably 70% by weight to 80% by weight, calculated to the total weight of the cured composition.

The filler material optionally may be present in a „porous“ form. As a porous filler material, which optionally may be coated, is understood, that the density of said filler material is within the range of 60% to 80%, compared to the real density of the non-porous filler material. Such porous filler materials have a higher total surface area than the non-porous material. Said surface area is higher than 0.3 m²/g (BET m²/g) and preferably
higher than 0.4 m²/g (BET) and preferably is within the range of 0.4 m²/g (BET) to 100 m²/g (BET), preferably within the range of 0.4 m²/g (BET) to 80 m²/g (BET).

The hydrophobic compound or the mixture of hydrophobic compounds is selected from the group comprising fluorinated or chlorinated hydrocarbons or cyclic, linear or branched organopolysiloxanes. Preferably the hydrophobic compound is a flowable compound.

Fluorinated or chlorinated hydrocarbons are compounds containing -CH₂-units, -CHF-units, -CF₃-units, -CF₂-units, -CHCl-units, -C(Cl)₂-units, -C(Cl)₃-units, or mixtures thereof. The fluorinated or chlorinated hydrocarbon is preferably a flowable compound. The organopolysiloxane may be a cyclic, linear or branched organopolysiloxane and is preferably a flowable compound. Said hydrophobic compound or said mixture of said compounds may be present in encapsulated form.

The hydrophobic compound preferably has a viscosity in the range from 50 cSt to 10,000 cSt, preferably in the range from 100 cSt to 10,000 cSt, preferably in the range from 500 cSt to 3000 cSt, measured in accordance with DIN 53 019 at 20°C.

Preferably the hydrophobic compound comprises a compound, or a mixture of compounds, of the general formula (II):

```
R₂-Si-O-Si-O-Si-O-Si-R₂
R₂-Si-O-Si-O-Si-O-Si-R₂
```

wherein

R₁ independently of each other is an unsubstituted or chlorinated or fluorinated alkyl radical having from 1 to 8 carbon atoms, (C₁₋₈-alkyl)aryl, or is aryl;

R₂ independently at each other has one of the definitions of R₁ or R₃, it being possible for two terminal substituents R₂
attached to different Si-atoms, being taken together to be an oxygen atom (= cyclic compound);

\( R_3 \) has one of the definitions of \( R_1 \), or is hydrogen or a residue \(-\text{CH}_2\text{-(CH-CH}_2\text{(O)})\) or \(-\text{C}_2\text{H}_4\text{-(CH-CH}_2\text{(O)})\);

\( m \) is on average from zero to 5000;

\( n \) is on average from zero to 100;

the sum of \([m+n]\) for non-cyclic compounds being at least 20, and the sequence of the groups \(-[\text{Si}(R_1)(R_1)\text{O}]^-\) and \(-[\text{Si}(R_2)(R_2)\text{O}]^-\) in the molecule being arbitrary.

The formula \(-\text{CH-CH}_2\text{(O)}\) has the meaning the epoxy substituent.

Preferred is the compound of the formula (II), wherein \( R_1 \) independently of each other is an unsubstituted or fluorinated alkyl radical having from 1 to 4 carbon atoms or is phenyl; \( m \) is on average from 20 to 5000; \( n \) is on average from 2 to 100; the sum of \([m+n]\) for non-cyclic compounds being on average in the range from 20 to 5000, and the sequence of the groups \(-[\text{Si}(R_1)(R_1)\text{O}]^-\) and \(-[\text{Si}(R_2)(R_2)\text{O}]^-\) in the molecule being arbitrary.

Preferred is the compound of the formula (II), wherein \( R_1 \) independently of each other is 3,3,3-trifluoropropyl, monofluoromethyl, difluoromethyl, or alkyl having 1-4 carbon atoms; \( m \) is on average from 50 to 1500; \( n \) is on average from 2 to 20; the sum of \([m+n]\) for non-cyclic compounds being on average in the range from 50 to 1500, and the sequence of the groups \(-[\text{Si}(R_1)(R_1)\text{O}]^-\) and \(-[\text{Si}(R_2)(R_2)\text{O}]^-\) in the molecule being arbitrary. Most preferred is a compound of the formula (II) wherein each \( R_1 \) is methyl.

Preferred cyclic compounds of formula (II) are those comprising 4-12, and preferably 4-8, \(-[\text{Si}(R_1)(R_1)\text{O}]^-\) units or \(-[\text{Si}(R_2)(R_2)\text{O}]^-\) units or a mixture of these units.

The hydrophobic compound [component (e)] is present in a quantity of about 1.0% by weight to about 10% by weight, preferably from
3% by weight to 8% by weight, preferably from 4% by weight to 7% by weight and preferably from 5% by weight to 6% by weight, calculated to the total weight of the cured composition.

The coating applied with the sol-gel composition according to the present invention using a sol-gel technique has preferably a thickness within the range of about 0.5 µm to about 4 mm; preferably within the range of about 1.0 µm to about 3 mm, whereby the thickness is not critical.

The curable sol-gel composition may optionally contain further additives. Such optional additive may be a curing catalyst; a flexibilizer; a solvent/diluent such as methanol, ethanol or propanol; a fluoroalkylsilane or fluoroalkoxysilane; pigments, antioxidants, light stabilizers and polymeric modifiers. Such additives are known.

The curing catalyst, such as such as 1-methylimidazole, is added preferably in an amount of 2% to 4% by weight, calculated to the amount of the sum of component (a) and component (b).

The flexibilizer, such as 2,2-dimethyl-1,3-propanediol, is added preferably in an amount of 12% to 14% by weight, calculated to the amount of the sum of component (a) and component (b).

The solvent such as methanol, ethanol or propanol, may be added in order to achieve a sol-gel formulation with a low enough viscosity so that the sol-gel formulation can be easily applied to the surface of the electrical insulator. The solvent is evaporating on curing the sol-gel formulation. The solvent usually is added in an amount of 5% to 10%, preferably about 5.5% to 7.7% by weight, calculated to the total weight of the sol-gel composition.

The antioxidant is optionally added, preferably in a concentration of up to 1.5 % by weight calculated to the total weight
of the composition. Preferably phenolic or amine antioxidants are used such as 2,6-tert.-butyl-p-cresol, N,N'-diphenyl-p-phenylene diamine.

The present invention further refers to a method of making said curable sol-gel composition. For making the sol-gel composition according to the present invention all the components are well mixed together. Preferably the optional catalyst is added at the end and just before applying the sol-gel composition to the surface of the insulator, i.e. before polymerization between the components (a), (b) and (c) begins.

The application of the sol-gel composition to the substrate preferably is made in two steps. Initially component (a), component (b), component (c), and component (e) are mixed in the presence of a solvent, followed by the addition of component (d). At this point the dominant reaction is the fast hydrolysis of the alkoxy silane groups which occurs assisted by the presence of atmospheric water vapor (open flask conditions).

Once hydrolyzed, in a subsequent step, this mixture is coated onto the substrate, i.e. the surface of the electrical insulator, which preferably is an epoxy substrate, where upon the mixture condenses and cross-links.

The condensation/curing reaction generally is slower than the hydrolysis and at these conditions is generally completed within about one to five hours of curing. Finally, during the curing step, besides the condensation of the hydrolyzed alkoxy silanes, the epoxy ring opening polymerization takes place, preferably in the presence of a curing catalyst. The final product is expected to comprise the cross-linked components (b) and (c) via =Si-O-Si= bonds and cross-linked components (a), (b), (c) and (d) via the epoxy ring opening polymerization reaction.

The total curing of the sol-gel composition after being applied to the surface of an insulator can be conducted over a wide range
of temperature and time and preferably is conducted at about
110°C for about eight hours.

The method of producing an electrical insulation system being
covered with the coating composition of the present invention,
comprises the steps of (i) hydrolyzing the alkoxy silane contained
in the sol-gel composition as defined herein and (ii) applying
the hydrolysed uncured sol-gel composition to the surface of an
electrical insulation system as a thin coating, especially
applying to the outer surface of an electrical insulation system,
and subsequently curing said sol-gel composition.

Preferred uses of the surface modified electrical insulation
system as defined in the present invention are in power trans-
mission and distribution applications, such as electrical insula-
tions, especially in the field of impregnating electrical coils
and in the production of electrical components such as transfor-
mers, embedded poles, bushings, high-voltage insulators for
indoor and outdoor use, especially for outdoor insulators
associated with high-voltage lines, as long-rod, composite and
cap-type insulators, sensors, converters and cable end seals as
well as for base insulators in the medium-voltage sector, in the
production of insulators associated with outdoor power switches,
measuring transducers, lead-throughs, and over-voltage
protectors, in switchgear construction.

The following examples illustrate the invention

Example 1

Typical formulations, i.e. compositions, were prepared by mixing
all the components besides the filler as given in Table 1 in a
vessel fitted with a magnetic stirrer for two hours at room
temperature. After the addition of the filler, the formulation
was further mixed with a Eurostar IKA Labortechnik mixer at room
temperature for thirty minutes.
Table 1:

<table>
<thead>
<tr>
<th>Components:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclo-aliphatic epoxy resin (a)</td>
<td>100 parts</td>
</tr>
<tr>
<td>Glycidoxypropane-trimethoxy silane (b)</td>
<td>60-70 phr</td>
</tr>
<tr>
<td>Gamma-aminopropyl-triethoxysilane (c)</td>
<td>150-160 phr</td>
</tr>
<tr>
<td>Silanized ultra-fine, Filler (d)</td>
<td>392-1710 phr</td>
</tr>
<tr>
<td>Silicone oil (e)</td>
<td>10.8-181 phr</td>
</tr>
<tr>
<td>Optional additives:</td>
<td></td>
</tr>
<tr>
<td>Fluoroalkylsilane</td>
<td>0.15-25 phr</td>
</tr>
<tr>
<td>1-methylimidazol</td>
<td>2-4 phr</td>
</tr>
<tr>
<td>2,2-dimethyl-1,3-propandiol</td>
<td>0.12-14 phr</td>
</tr>
</tbody>
</table>

5 phr = parts per hundred
(a) Cyclo-aliphatic epoxy resin, based on diglycidyl ester of hexahydro-phthalic acid (Huntsman CY184)
(b) GPTMS, Z-6040, Dow Corning Corp.
(c) GAPES, A110, Momentive Corp.
(d) Filler: W12EST, Quarzwerke AG, 55-77% by weight, calculated to the total weight of components (a), (b), (c) and (e)
(e) silicone oil: AK50 of Wacker Chemie AG, 1-10% by weight, calculated to the weight of the total composition
Fluoroalkylsilane: Dynasylan F8261, Evonik Degussa
1-methylimidazol: DY 070, Huntsman Corp.
2,2-dimethyl-1,3-propandiol: NPG, Fluka

Example 2
Components (a), (b), (c), and (e) are mixed in the presence of the solvent, followed by the addition of component (d) as described in Example 1. Hydrolysis of the alkoxy silanes is achieved by the presence of atmospheric water vapor (open flask conditions) whereby the condensation reaction is completed in a later stage during curing.
These formulations are applied via spin coating to cured plates of cured indoor epoxy resin compositions of dimensions 12cm x 5cm x 0.6cm. The samples are cured for eight hours at 110°C and tested with the inclined tracking and erosion testing at 3.5 kV.

The substrate formulation was degassed for 10-15 minutes at 4 mbar and cured at 90°C for two hours followed by curing at 110°C for 24 hours.

The basic formulation used as a substrate is described in the following Table 2:

<table>
<thead>
<tr>
<th>Component</th>
<th>Function</th>
<th>Name</th>
<th>phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>DER 331 (Dow)</td>
<td>Epoxy Resin</td>
<td>Diglycidyl ether of Bisphenol A</td>
<td>100</td>
</tr>
<tr>
<td>MTHPA NT (Lonza)</td>
<td>Hardener</td>
<td>Methyl-tetrahydro-phthalic anhydride</td>
<td>85</td>
</tr>
<tr>
<td>DY 062 (Huntsman)</td>
<td>Catalyst</td>
<td>Benzyl-N,N-dimethylamine</td>
<td>0.9</td>
</tr>
<tr>
<td>W12 (65%) (Quarzwerke)</td>
<td>Filler</td>
<td>Silica</td>
<td>345</td>
</tr>
</tbody>
</table>
An example of two different sol-gel formulations that led to samples that passed the 3.5 kV level of the inclined tracking and erosion test is presented in the following Table 3. The use of a higher amount of silicone oil in the Formulation 2 took place to counteract the lack of fluoroalkylsilane (liquid) as well as of the flexibilizer (solid). When using a higher amount of silicone oil the fluoroalkylsilane and the flexibilizer are not required and the viscosity remains sufficiently low leading to easy processing of the formulation without the need of additional amounts of solvent.

According to the inclined tracking and erosion test (class 1A3.5, IEC 60587) a sample is considered to have successfully passed the test when the leakage current does not overcome 60 mA for more than 2 seconds in a period of 6 hours. The samples of Formulations 1 and 2 (of Table 3) fulfilled the above criteria. In addition, for various samples of Formulation 1 the measurement was repeated until the failure of the sample. The average time of failure, in the case of Formulation 1, was found to 13.2 ± 3.6 hours, more than 100% higher than the 6 hour period necessary for the tracking and erosion test to be considered successful.

### Table 3

<table>
<thead>
<tr>
<th>Component</th>
<th>Function</th>
<th>Formulation 1</th>
<th>Formulation 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>%</td>
<td>phr</td>
</tr>
<tr>
<td>CY184</td>
<td>Epoxy resin</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>GTM6</td>
<td>Epoxy-silane</td>
<td>65.4</td>
<td></td>
</tr>
<tr>
<td>GAPE5</td>
<td>Amino-silane</td>
<td>153.8</td>
<td></td>
</tr>
<tr>
<td>DY070</td>
<td>Catalyst</td>
<td>2.15</td>
<td></td>
</tr>
<tr>
<td>F8261</td>
<td>Fluoro-silane</td>
<td>15.4</td>
<td></td>
</tr>
<tr>
<td>NPG</td>
<td>Flexibilizer</td>
<td>12.7</td>
<td></td>
</tr>
<tr>
<td>AK50</td>
<td>Silicone oil</td>
<td>4.9%</td>
<td>92.2</td>
</tr>
<tr>
<td>W1ZEST</td>
<td>Filler</td>
<td>76.5%</td>
<td>1440</td>
</tr>
<tr>
<td>Ethanol</td>
<td>Solvent</td>
<td>7.3%</td>
<td>148.4</td>
</tr>
</tbody>
</table>
Claims

1. Curable sol-gel composition useful for modifying the surface of a conventional electrical insulation system and providing said surface with an improved tracking and erosion resistance, characterized in that said sol-gel composition comprises:
   (a) cyclo-aliphatic epoxy resin compound containing at least two 1,2-epoxy groups per molecule [component (a)];
   (b) a glycidoxypropane-tri(C$_3$-4)alkoxysilane [component (b)];
   (c) a gamma-aminopropyl-tri(C$_3$-4)alkoxysilane [component (c)];
   (d) a mineral filler material [component (d)]; and
   (e) a hydrophobic compound [component (e)] or a mixture of such hydrophobic compounds being selected from the group comprising fluorinated or chlorinated hydrocarbons or organopolysiloxanes;

wherein
   - the ratio of the epoxy equivalents of component (a) to the epoxy equivalents of component (b) is from 9:1 to 6:4;
   - the molar ratio of component (c) to the epoxy equivalents of the sum of [component (a)] and [component (b)] is from about 0.9 to 1.1;
   - the mineral filler material [component (d)] is present in a quantity of about 55% by weight to about 85% by weight, calculated to the total weight of the cured composition;
   - the hydrophobic compound [component (e)] is present in a quantity of about 1.0% by weight to about 10% by weight, calculated to the total weight of the cured composition;

whereby the curable sol-gel composition optionally contains further additives.

2. Composition according to claim 1, characterized in that the cycloaliphatic epoxy resin compound comprises unsubstituted glycidyl groups and/or glycidyl groups substituted with methyl groups having an epoxy value (equiv./kg) of at least three, preferably at least four, preferably about 5.0 to 6.1.
3. Composition according to claim 2, characterized in that the cycloaliphatic epoxy resin is a compound of formula (I):

\[
\begin{array}{c}
\text{O} \quad \text{O} \\
\text{(D)n} \quad \text{O} \\
\text{O}
\end{array}
\]

\[ \text{D} = -\text{O}, -\text{SO}_2-, -\text{CO}_2-, -\text{CH}_2-, -\text{C(CH}_3\text{)}_2-, -\text{C(CF}_3\text{)}_2-
\]

\[ n = \text{zero or 1} \]

wherein D preferably is \(-\text{CH}_3\)- or \([-\text{C(CH}_3\text{)}_2\]-\.

4. Composition according to claim 2, characterized in that the cycloaliphatic epoxy resin is a hexahydro-o-phthalic acid-bis-glycidyl ester, hexahydro-m-phthalic acid-bis-glycidyl ester or hexahydro-p-phthalic acid-bis-glycidyl ester.

5. Composition according to any one of the claims 1-4, characterized in that component (b) is glycidoxypropane-trimethoxy-silane (GPTMS).

6. Composition according to any one of the claims 1-5, characterized in that the ratio of the epoxy equivalents of component (a) to the epoxy equivalents of component (b) is from 8:1 to 6:4, and preferably at about 7:3.

7. Composition according to any one of the claims 1-6, characterized in that component (c) is gamma-aminopropyl-triethoxy-silane (GAPES).

8. Composition according to any one of the claims 1-7, characterized in that the molar ratio of component (c) to the epoxy equivalents of the sum of [component (a)] and [component (b)] is from about from 0.95 to 1.05, and preferably about 1:1.
9. Composition according to any one of the claims 1-8, characterized in that the mineral filler material [component (d)] is selected from silicone oxides (silica, quartz), known silicates such as sodium/potassium silicates and/or aluminosilicates, preferably layered silicates, aluminium oxide, aluminium tri-hydrate [ATH], titanium oxide or dolomite [CaMg(CO₃)₂], metal nitrides, such as silicon nitride, boron nitride and aluminium nitride or metal carbides, such as silicon carbide, preferably from layered silicates, silica and quartz.

10. Composition according to any one of the claims 1-9, characterized in that the mineral filler material is present in a quantity of 65% by weight to 80% by weight, preferably 70% by weight, calculated to the total weight of the cured composition.

11. Composition according to any one of the claims 1-10, characterized in that the density of said filler material is within the range of 60% to 80%, compared to the real density of the non-porous filler material.

12. Composition according to any one of the claims 1-11, characterized in that the hydrophobic compound or the mixture of hydrophobic compounds is selected from compounds, of the general formula (II):

\[
\begin{align*}
R_2 & \quad \text{Si-O-} \quad \text{Si-O-} \quad \text{Si-O-} \quad \text{Si-O-} \quad \text{Si-O-} \quad \text{Si-O-} \quad \text{Si-O-} \\
R_2 & \quad \text{R}_1 \quad \text{R}_1 \quad \text{R}_2 \quad \text{R}_2 \quad \text{R}_2 \quad \text{R}_3 \quad \text{R}_2
\end{align*}
\]

wherein

- \( R_1 \) independently of each other is an unsubstituted or chlorinated or fluorinated alkyl radical having from 1 to 8 carbon atoms, \((C_1-C_4\text{-alkyl})\text{aryl}\), or is aryl;
- \( R_2 \) independently at each other has one of the definitions of \( R_1 \) or \( R_3 \), it being possible for two terminal substituents \( R_2 \) attached to different Si-atoms, being taken together to be an oxygen atom (= cyclic compound);
R₃ has one of the definitions of R₁, or is hydrogen or a residue -CH₂-[CH-CH₂(O)] or -C₂H₄-[CH-CH₂(O)];
m is on average from zero to 5000;
n is on average from zero to 100;
the sum of [m+n] for non-cyclic compounds being at least 20, and
the sequence of the groups -[Si(R₁)(R₁)O]- and -[Si(R₂)(R₂)O]- in
the molecule being arbitrary.

13. Composition according to claim 12, characterized in that the
compound of the formula (II), is a compound wherein R₁ inde-
dependently of each other is an unsubstituted or fluorinated alkyl
radical having from 1 to 4 carbon atoms or is phenyl; m is on
average from 20 to 5000; n is on average from 2 to 100; the sum
of [m+n] for non-cyclic compounds being on average in the range
from 20 to 5000, and the sequence of the groups -[Si(R₁)(R₁)O]-
and -[Si(R₂)(R₂)O]- in the molecule being arbitrary.

14. Composition according to claim 12, characterized in that the
compound of the formula (II), is a compound wherein R₁ indepen-
dently of each other is 3,3,3-trifluoropropyl, monofluoromethyl,
difluoromethyl, or alkyl having 1-4 carbon atoms, preferavly
methyl; m is on average from 50 to 1500; n is on average from
2 to 20; the sum of [m+n] for non-cyclic compounds being on
average in the range from 50 to 1500, and the sequence of the
groups -[Si(R₁)(R₁)O]- and -[Si(R₂)(R₂)O]- in the molecule being
arbitrary.

15. Composition according to claim 12, characterized in that the
cyclic compounds of formula (II) comprise 4-12, and preferably
4-8, -[Si(R₁)(R₁)O]-units or -[Si(R₂)(R₂)O]-units or a mixture of
these units.

16. Composition according to any one of the claims 1-15,
characterized in that the hydrophobic compound [component (e)] is
present in a quantity of from 3% by weight to 8% by weight,
preferably from 4% by weight to 7% by weight and preferably from
5% by weight to 6% by weight, calculated to the total weight of the cured composition.

17. Composition according to any one of the claims 1-16, characterized in that said composition further contains a curing catalyst; a flexibilizer; a solvent/diluent such as methanol, ethanol or propanol; a fluoroalkylsilane or fluoroalkoxysilane; pigments, antioxidants, light stabilizers and polymeric modifiers.

18. Composition according to claim 17, characterized in that said curing catalyst is 1-methylimidazole, and is present in an amount of 2% to 4% by weight, calculated to the amount of the sum of component (a) and component (b).

19. Composition according to claim 17, characterized in that the flexibilizer is 2,2-dimethyl-1,3-propanediol and is added in an amount of 12% to 14% by weight, calculated to the amount of the sum of component (a) and component (b).

20. Composition according to claim 17, characterized in that the solvent is methanol, ethanol and/or propanol, and is present in an amount of 5% to 10%, preferably 5.5% to 7.7% by weight, calculated to the total weight of the sol-gel composition.

21. Method of making the curable sol-gel composition according to any one of the claims 1-20, characterized in that all the components are well mixed together, whereby the optional catalyst is added at the end and just before applying the sol-gel composition to the surface of the insulator.

22. Method according to claim 21, characterized in that initially component (a), component (b), component (c), and component (e) are mixed in the presence of a solvent, followed by the addition of component (d) and the hydrolysis of the alkoxy silane
groups occurring in the presence of atmospheric water vapor, and in a subsequent step, this mixture is coated onto the substrate.

23. Method of producing an electrical insulation system being coated with the coating composition according to any one of the claims 1-20, comprising the steps of (i) preparing and hydrolyzing the sol-gel composition according to claim 21 or 22 and (ii) applying the hydrolysed uncured sol-gel composition to the surface of an electrical insulation system as a thin coating, preferably to the outer surface of an electrical insulation system, and subsequently curing said sol-gel composition.

24. Method according to claim 23, characterized in that said coating applied with the sol-gel composition has a thickness within the range of about 0.5 μm to about 4 mm; preferably within the range of about 1.0 μm to about 3 mm.

25. The use of a curable sol-gel composition according to any one of the claims 1-20 for modifying the surface of an electrical insulation system to yield an electrical insulation system with improved tracking and erosion resistance, wherein said insulation system is made from a hardened or cured conventional synthetic polymer composition.

26. Electrical insulation system wherein the surface of said electrical insulation system, preferably the outer surface, is coated with a thin coating composition as defined in any one of the claims 1-20, being used in power transmission and distribution applications, preferably in the field of impregnated electrical coils and in the production of electrical components such as transformers, embedded poles, bushings, high-voltage insulators for indoor and outdoor use, especially for outdoor insulators associated with high-voltage lines, as long-rod, composite and cap-type insulators, sensors, converters and cable end seals as well as for base insulators in the medium-voltage sector, in the production of insulators associated with outdoor
power switches, measuring transducers, lead-throughs, and over-voltage protectors, in switchgear construction.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08K3/34 H01B3/40

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08K H01B

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<td>WO 2009/046754 A1 (ABB RESEARCH LTD [CH]; CLIFFORD STEPHEN [CH]; SOYEUX FAUSTINE [FR]; KR) 16 April 2009 (2009-04-16) page 12; example 5; table 2</td>
<td>1-26</td>
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<tr>
<td>A</td>
<td>WO 98/32138 A1 (FURUKAWA ELECTRIC INST OF TECH [HU]; BANHEGYI GYOERGY [HU]; PINTER SZI) 23 July 1998 (1998-07-23) the whole document</td>
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<td>A</td>
<td>WO 2009/046755 A1 (ABB RESEARCH LTD [CH]; CLIFFORD STEPHEN [CH]; SINGH BANDEEP [CH]; KRIV) 16 April 2009 (2009-04-16) example 2</td>
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Further documents are listed in the continuation of Box C.

See patent family annex.

"A" document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the international search: 21 January 2010

Date of mailing of the international search report: 29/01/2010

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Marquis, Damien
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