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(54) Title: ELECTRICAL INSULATION SYSTEM WITH IMPROVED ELECTRICAL BREAKDOWN STRENGTH

(57) Abstract: Electrical insulation system with improved electrical breakdown strength, said electrical insulation system comprising a hardened polymer component having incorporated therein a conventional filler material and a selected pretreated filler material, wherein (a) the hardened polymer component is selected from epoxy resin systems, polyesters, polyamides, polybutylene terephthalate, polyurethanes and polydicyclopentadiene; (b) the conventional filler material is a known filler material having an average grain size distribution within the range of 1 µm- 500 µm, being present in a quantity within the range of 40 %- 65 % by weight, calculated to the total weight of the insulator system; and (c) the selected pretreated filler material is selected from silica, quartz, or a silicate, or is a mixture of these compounds, having an average grain size distribution within the range of 1 µm-500 µm, wherein said selected filler material has been pretreated with an intercalating compound and wherein said pretreated filler material is present in an amount of 1 %-30 % by weight, calculated to the weight of the conventional filler material present in the insulator system.

5 **Electrical insulation system with improved electrical breakdown strength**

The present invention refers to an electrical insulation system with improved electrical breakdown strength.

10

Electrical insulations for potting applications, for instance in embedded poles, instrument and distribution transformers or sensors, generally consist of an epoxy resin cured with an acid anhydride in the presence of an accelerator. The starting components usually are mixed together with a filler material, preferably silica flower, typically in the range of 60 to 65 % by weight of filler material, calculated to the total weight of the electrical insulator; the mixture is then cured. Alternative polymers can also be used such as polyesters, polyamides, polybutylene terephthalate, polyurethanes or polydicyclopentadiene. A large amount of filler generally decreases the overall price of the insulation, however, it also increases the stiffness, the fracture toughness, the thermal conductivity of the insulator and decreases its thermal expansion coefficient.

25

A key property for the reliability of an electrical insulation material is that it has a high electrical breakdown strength and therewith good insulating properties also at high electrical field strengths. WO 2006/008422 proposes the production of an electrical insulator for high voltage use comprising a mineral filler material wherein the mineral filler material is a combination of a filler material with an average grain size distribution within the micron size together with a selected filler material with an average grain size distribution within the nano size, i.e. less than 1 μm . However, such a combination, especially for industrial potting applications, e.g. in epoxy resins, has different disadvantages such as increased viscosity which reduces processability and possible not yet quantified impact of nanoparticles on health, safety and environment.

- 5 In the production of an electrical insulator for high voltage use generally a mineral micro filler material is used having an average grain size distribution within the range of 1 μm -500 μm , preferably within the range of 5 μm -100 μm .
- 10 It has now surprisingly been found that such micro filler material, when previously treated with an intercalating compound, for example with an alkyl ammonium compound, may be added to the untreated filler material in comparatively small quantities, thereby significantly improving the electrical
- 15 properties of the insulator system, especially its electrical breakdown strength. We could show that by adding about 5 parts by weight of such micro filler material, pretreated with an alkyl ammonium compound, to about 55 parts by weight of conventional micro silica, it is possible to improve the dielectric
- 20 breakdown strength of the polymeric insulation by up to 50% compared to the case where 60 parts by weight of micro silica only was used. Such pretreated filler material comprises for example silica, quartz and layered silicates.
- 25 The present invention is defined in the claims. The present invention specifically refers to an electrical insulation system with improved electrical breakdown strength, said electrical insulation system comprising a hardened polymer component having incorporated therein a conventional filler material and a
- 30 selected pretreated filler material, characterized in that
- (a) the hardened polymer component is selected from epoxy resin systems, polyesters, polyamides, polybutylene terephthalate, polyurethanes and polydicyclopentadiene, and preferably is a hardened epoxy resin system;
- 35 (b) the conventional filler material is a known filler material having an average grain size distribution within the range of 1 μm -500 μm , being present in a quantity within the range of 40 %-65 % by weight, calculated to the total weight of the insulator system; and

5 (c) the selected pretreated filler material is selected from
silica, quartz, or a silicate, preferably mica (glimmer),
kaolin or a layered silicate or talc, or is a mixture of
these compounds, having an average grain size distribution
within the range of 1 μm -500 μm , wherein said selected
10 filler material has been pretreated with an intercalating
compound and wherein said pretreated filler material is
present in an amount of 1 %-30 % by weight, calculated to
the weight of the conventional filler material present in
the insulator system.

15

The present invention also refers to the selected pretreated
filler material as defined as component (c) herein above having
an average grain size distribution within the range of 1 μm -500
 μm , preferably within the range of 5 μm -100 μm , having been
20 treated with an intercalating compound.

The present invention also refers to the mixture of the selected
pretreated filler material as defined as component (c) herein
above and the conventional non-treated filler material as
25 defined as component (b) herein above, wherein the selected
pretreated filler material is present in an amount of 1 %-30 %
by weight, calculated to the weight of the conventional filler
material, said selected pretreated filler material and said
conventional non-treated filler material having an average grain
30 size distribution within the range of 1 μm -500 μm .

The present invention also refers to a method of producing said
electrical insulation system with improved electrical breakdown
strength.

35

The present invention further refers to electrical articles com-
prising said electrical insulation system with improved
electrical breakdown strength.

5 An important feature of the present invention is that the
selected pretreated filler material has an average grain size
distribution within the range of 1 μm -500 μm . Said pretreated
filler material is selected from silica, quartz, or a silicate,
preferably mica, kaolin or a layered silicate, or talc or is a
10 mixture or these compounds. Preferred are two-layered or three-
layered silicates selected from phyllosilicates, preferably
selected from montmorillonite, hectorite, saponite, vermiculite,
smectite, illite, sepiolite, palygorskite, muscovite,
allewardite, amesite, fluorohectorite, beidellite, talcum,
15 nontronite, stevensite, bentonite, glimmer, fluorovermiculite,
halloysite, hydrotalcite or mixtures of these compounds.
Preferred are montmorillonite, hectorite, saponite, vermiculite,
smectite, illite; most preferred are montmorillonite, hectorite,
vermiculite, smectite, illite.

20

Different compounds can be used to pretreat the selected filler
material, thereby modifying the surface properties of the
selected filler material. It is understood that the modified
surface properties of the pretreated micro filler material
25 disperse remarkably well in the epoxy, thereby surprisingly
improving the dielectric strength as well as the mechanical
properties of the insulator system. The invention, however, is
not bound to this explanation.

30 Preferred compounds for modifying the surface properties of the
selected filler material are known per se. These compounds are
also named intercalating compounds. Preferred such compounds are
for example protonated primary, secondary or tertiary amines,
protonated basic heterocyclic compounds such as protonated
35 imidazole compounds, or quaternary ammonium compounds, substi-
tuted by at least one alkyl residue or at least one functiona-
lized alkyl residue. Preferred is the treatment with substituted
ammonium compounds, or with 2-hydroxyalkyl-substituted imidazole
compounds. Most preferred is the treatment with alkyl-substitu-

5 ted or hydroxyalkyl-substituted ammonium compounds, such as
dimethyl-dihydrogenated tallow-quaternary ammonium and related
hydroxyalkyl-containing compounds. There are many more inter-
calating compounds known in the art for the treatment of layered
silicates and other inorganic layered compounds, such as
10 metallic salts of aromatic, aliphatic, araliphatic and cyclo-
aliphatic carbonic acids as well as other acids. Examples are
alkali salts (lithium, sodium or potassium salts) of formic
acid, acetic acid, oxalic acid, gluconic acid, ethyleneglykol,
and of other diols. These compounds can also be used within the
15 scope of the present invention.

The conventional filler material as well as the selected pre-
treated filler material, both independent of each other,
preferably have an average grain size distribution within the
20 range of 5 μm -100 μm , preferably within the range of 5 μm -50 μm ,
preferably within the range of 5 μm -30 μm . Preferably at least
70 % of the particles, preferably at least 80 % of the
particles, have a particle size within the range indicated.

25 The conventional filler material may be selected independently
from the selected pretreated filler material and may also be the
same inorganic filler material as listed above for the pre-
treated filler material selected from silica, quartz, or talc or
a silicate, preferably mica, kaolin or a layered silicate. In
30 addition the conventional filler may also be chosen from other
known filler compounds such as aluminium oxide, aluminium tri-
hydrate [ATH, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, corresponding to $\text{Al}(\text{OH})_3$], titanium
oxide or dolomite [$\text{CaMg}(\text{CO}_3)_2$], metal nitrides, such as silicon
nitride, boron nitride and aluminium nitride or metal carbides,
35 such as silicon carbide. Mica (glimmer) and kaolin are aluminium
silicates substantially composed of SiO_2 and Al_2O_3 .

The conventional filler material may be surface treated with a
coupling agent known per se. The coupling agent is preferably

5 selected from the group comprising silanes and siloxanes and preferably is a silane, for example 3-glycidoxypropyl-trimethoxysilane or 3-glycidoxypropyldimethoxymethylsilane.

The method of producing the selected pretreated filler material
10 with an intercalating compound is characterized in that the selected filler material is brought in contact with the intercalating compound, optionally in the presence of a suitable solvent and under stirring, within the temperature range of 20°C to 150°C, preferably at room temperature up to 60°C, and for a
15 time long enough so that the intercalating compound modifies the surface of the selected filler material. This time is generally between one hour and three days depending on the temperature used. Preferred is room temperature and a reaction time of about one to three days. The suitable solvent is usually water but a
20 low molecular alcohol may also be used. The concentration of the intercalation compound in the solvent is not critical and is preferably within the range of 0.1 mol to 5.0 mol per liter of solvent. The suspension is then filtered off, washed with the solvent, preferably with water, and dried for several hours,
25 preferably for about 10 to 24 hours, at a temperature within the range of 50°C to 80°C, preferably at about 60°C.

The conventional filler material preferably is present within the insulator system in a quantity within the range of 50 %-60 %
30 by weight, preferably in a quantity of about 55 % by weight, calculated to the total weight of the insulator system.

The selected pretreated filler material having been pretreated with an intercalating compound preferably is present in an
35 amount of 2 %-20 % by weight, preferably in an amount of 2 %-10 % by weight, calculated to the weight of the conventional filler material present in the insulator system.

5 The electrical insulation system with improved electrical break-
down strength according to the present invention comprises a
filler containing hardened polymer component. Said hardened
polymer component is selected from epoxy resin systems, poly-
esters, polyamides, preferably nylon, polybutylene terephtha-
10 late, polyurethanes and polydicyclopentadiene, and preferably is
a hardened epoxy resin system.

Filler containing epoxy resin systems, polyesters, polyamides,
polybutylene terephthalate, polyurethanes and polydicyclo-
15 pentadiene have been described in the literature. When a special
filler composition according to the present invention is used,
i.e. a mixture of a conventional filler material as defined
herein above as component (b) and a selected pretreated filler
material as defined herein above as component (c), said filler
20 components of said filler composition can be incorporated into
the respective monomeric starting material of component (a) as
defined herein above, in an analogous manner as described in the
literature for other filler materials. This is within the know-
ledge of the expert. Regularly the filler material is incorpo-
25 rated into the monomeric starting materials of the respective
polymer by known methods so as to be uniformly dispersed
therein. The non-hardened composition, resp. dispersion, thus
obtained, e.g. the non-hardened epoxy resin composition, can for
example be processed using conventional vacuum casting and/or
30 automated pressure gelation (APG) manufacturing processes. The
dispersion is formed into the desired shape using known methods,
optionally with the help of a molding tool, and then hardened
out, optionally using post-curing.

35 The present invention also refers to a method of producing an
electrical insulation system with improved electrical breakdown
strength, characterized in that a conventional filler material
[as defined herein above as component (b)] and a selected
pretreated filler material [as defined herein above as component

5 (c)], are incorporated into the monomeric starting material of the respective polymer of the component (a) as defined herein above, so as to be uniformly dispersed therein, the dispersion is then formed into the desired shape, optionally with the help of a molding tool, and then hardened and optionally post-cured.

10

As optional additives the composition may comprise further components selected from wetting/dispersing agents, plasticizers, antioxidants, light absorbers, and from further additives generally used in electrical applications.

15

Preferred epoxy resins used within the context of the present invention are aromatic and/or cycloaliphatic compounds. These compounds are known per se. Epoxy resins are reactive glycidyl compounds containing at least two 1,2-epoxy groups per molecule. Preferably a mixture of polyglycidyl compounds is used such as a mixture of diglycidyl- and triglycidyl compounds.

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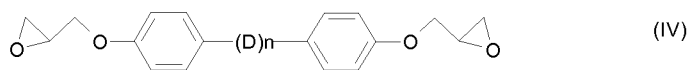
Epoxy compounds useful for the present invention comprise unsubstituted glycidyl groups and/or glycidyl groups substituted with methyl groups. These glycidyl compounds preferably have a molecular weight between 200 and 1200, especially between 200 and 1000 and may be solid or liquid. The epoxy value (equiv./100 g) is preferably at least three, preferably at least four and especially at about five, preferably about 4.9 to 5.1. Preferred are glycidyl compounds which have glycidyl ether- and/or glycidyl ester groups. Such a compound may also contain both kinds of glycidyl groups, e.g. 4-glycidylloxy-benzoic acidglycidyl ester. Preferred are polyglycidyl esters with 1 to 4 glycidyl ester groups, especially diglycidyl ester and/or triglycidyl esters.

25

30

35 Preferred glycidyl esters may be derived from aromatic, araliphatic, cycloaliphatic, heterocyclic, heterocyclic-aliphatic or heterocyclic-aromatic dicarbonic acids with 6 to 20, preferably 6 to 12 ring carbon atoms or from aliphatic dicarbonic acids with 2 to 10 carbon atoms. Preferred are for example optionally

5 substituted epoxy resins of formula (IV) :

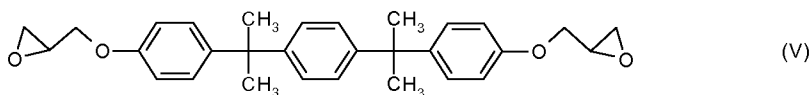


D = -O-, -SO₂-, -CO-, -CH₂-, -C(CH₃)₂-, -C(CF₃)₂-

n = zero or 1

or formula (V) :

10



Examples are glycidyl ethers derived from Bisphenol A or Bisphenol F as well as glycidyl ethers derived from Phenol-Novolak-resins or cresol-Novolak-resins.

15

Cycloaliphatic epoxy resins 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. Also aliphatic epoxy resins, for example 1,4-butane-diol diglycidyl-ether, may be used as a component for the composition of the present invention.

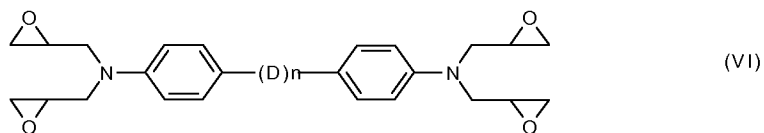
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Preferred within the present invention are also aromatic and/or cycloaliphatic epoxy resins which contain at least one, preferably at least two, aminoglycidyl group in the molecule. Such epoxy resins are known and for example described in WO 99/67315. Pre

25

30

5 ferred compounds are those of formula (VI):



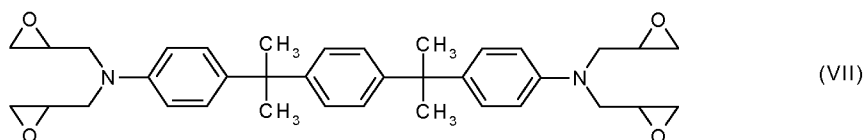
D = -O-, -SO₂-, -CO-, -CH₂-, -C(CH₃)₂-, -C(CF₃)₂-

n = Zero or 1

Especially suitable aminoglycidyl compounds are N,N-diglycidyl-
 10 aniline, N,N-diglycidyltoluidine, N,N,N',N'-tetraglycidyl-1,3-
 diaminobenzene, N,N,N',N'-tetraglycidyl-1,4-diaminobenzene,
 N,N,N',N'-tetraglycidylxylylendiamine, N,N,N',N'-tetraglycidyl-
 4,4'-diaminodiphenylmethane, N,N,N',N'-tetraglycidyl-3,3'-di-
 ethyl-4,4'-diaminodiphenylmethane, N,N,N',N'-tetraglycidyl-3,3'-
 15 diaminodiphenylsulfone, N,N'-Dimethyl-N,N'-diglycidyl-4,4'-di-
 aminodiphenylmethane, N,N,N',N'-tetraglycidyl- α,α' -bis(4-
 aminophenyl)-p-diisopropylbenzene and N,N,N',N'-tetraglycidyl-
 α,α' -bis-(3,5-dimethyl-4-aminophenyl)-p-diisopropyl-
 benzene.

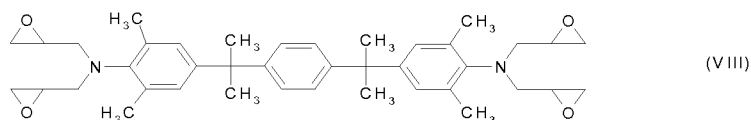
20

Preferred aminoglycidyl compounds are also those of formula
 (VII):



25

or of formula (VIII):



- 5 Further aminoglycidyl compounds which can be used according to the present invention are described in e.g. Houben-Weyl, Methoden der Organischen Chemie, Band E20, Makromolekulare Stoffe, Georg Thieme Verlag Stuttgart, 1987, pages 1926-1928.
- 10 Hardeners are known to be used in epoxy resins. Hardeners are for example hydroxyl and/or carboxyl containing polymers such as carboxyl terminated polyester and/or carboxyl containing acrylate- and/or methacrylate polymers and/or carboxylic acid anhydrides. Useful hardeners are further cyclic anhydrides of
- 15 aromatic, aliphatic, cycloaliphatic and heterocyclic polycarbonic acids. Preferred anhydrides of aromatic polycarbonic acids are phthalic acid anhydride and substituted derivatives thereof, benzene-1,2,4,5-tetracarboxylic acid dianhydride and substituted derivatives thereof. Numerous further hardeners are from
- 20 the literature.

The optional hardener can be used in concentrations within the range of 0.2 to 1.2, equivalents of hardening groups present, e.g. one anhydride group per 1 epoxide equivalent. However,

25 often a concentration within the range of 0.2 to 0.4, equivalents of hardening groups is preferred.

As optional additives the composition may comprise further at least a curing agent (accelerant) for enhancing the polymerization of the epoxy resin with the hardener, at least one

30 wetting/dispersing agent, plasticizers, antioxidants, light absorbers, as well as further additives used in electrical applications.

35 Curing agents for enhancing the polymerization of the epoxy resin with the hardener are for example tertiary amines, such as benzyldimethylamine or amine-complexes such as complexes of tertiary amines with boron trichloride or boron trifluoride; urea derivatives, such as N-4-chlorophenyl-N',N'-dimethylurea (Monu-

5 ron); optionally substituted imidazoles such as imidazole or 2-phenyl-imidazole. Preferred are tertiary amines. Other curing catalyst such as transition metal complexes of cobalt (III), copper, manganese, (II), zinc in acetylacetonate may also be used, e.g. cobalt acetylacetonate(III). The amount of catalyst
10 used is a concentration of about 50-1000 ppm by weight, calculated to the composition to be cured.

Wetting/dispersing agents are known per se for example in the form of surface activators; or reactive diluents, preferably
15 epoxy-containing or hydroxyl-containing reactive diluents; thixotropic agents or resinous modifiers. Known reactive diluents for example are cresylglycidylether, diepoxyethyl-1,2-benzene, bisphenol A, bisphenol F and the diglycidylethers thereof, diepoxydes of glycols and of polyglycols, such as neo-
20 pentylglycol-diglycidylether or trimethylolpropane-diglycidylether. Preferred commercially available wetting/dispersing agents are for example organic copolymers containing acidic groups, e.g. Byk® W-9010 having an acid value of 129 mg KOH/g). Such Wetting/dispersing agents are preferably used in amounts of
25 0.5 % to 1.0 % based on the filler weight.

Plasticizers, antioxidants, light absorbers, as well as further additives used in electrical applications are known in the art and are not critical.

30 The insulating composition made from epoxy resin is made simply by mixing all the components, optionally under vacuum, in any desired sequence and curing the mixture by heating. Preferably the hardener and the curing agent are separately added before
35 curing. The curing temperature is preferably within the range of 50°C to 280°C, preferably within the range of 100°C to 200°C. Curing generally is possible also at lower temperatures, whereby at lower temperatures complete curing may last up to several days, depending also on catalyst present and its concentration.

5

The non-hardened insulating resin composition is preferably applied by using vacuum casting or automated pressure gelation (APG) manufacturing processes, optionally under the application of vacuum, to remove all moisture and air bubbles from the coil and the insulating composition. The encapsulating composition may then be cured by any method known in the art by heating the composition to the desired curing temperature.

Preferred uses of the insulation produced according to the present invention are electrical insulations, especially in the field of impregnating electrical coils and in the production of electrical components such as transformers, bushings, insulators, switches, sensors, converters and cable end seals.

Preferred uses of the insulation system produced according to the present invention are also high-voltage insulations for indoor and outdoor use, especially for outdoor insulators associated with high-voltage lines, as long-rod, composite and cap-type insulators, and also for base insulators in the medium-voltage sector, in the production of insulators associated with outdoor power switches, measuring transducers, lead-throughs, and overvoltage protectors, in switchgear construction, 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 examples illustrate the invention.

Example 1 (Preparation of the pretreated filler material)

10 parts of montmorillonite (a layered silicate) with an average grain size distribution ($d_{50\%}$) of 16 μm are mixed with an aqueous solution of 120 ml water containing 20 parts of dimethyl-dihydrogenated-tallow-quaternary ammonium. The mixture is stirred for 3 days at room temperature. The montmorillonite is

5 filtered off, washed with 100 ml of pure water and then dried for 24 hours at 60°C in a closed vessel.

Example 2 (Preparation of an epoxy resin composition)

The epoxy resin compositions Formulation A and Formulation B are
 10 made from the components as given in Table 1. The compositions are prepared by thoroughly mixing the epoxy resin, the hardener, the accelerator and the filler material at a temperature of 80°C. Then the anhydride hardener and the catalyst are added under further stirring. Then the mixture is outgassed under
 15 vacuum and poured into a mold at 80°C. The mixture is then cured for ten hours at 140°C.

Definition of raw materials:

20 EPR 845 diglycidylether-bisphenol A (DGEBA) from Hexion Specialty Chemicals
 EPH 845 pre-reacted mixture of methyltetrahydrophthalic anhydride and neopentylglycol from Hexion Specialty Chemicals
 EPC 845 modified tertiary amine from Hexion Specialty Chemicals
 25 Silica W12 silica flower $d_{50\%}=16 \mu\text{m}$ from Quarzwerke GmbH
 (Example 1): montmorillonite type layered silicate modified with dimethyl-dehydrogenated-tallow-quaternaryammonium, prepared according to Example 1

Table 1:

	EPR 845	EPH 845	EPC 845	Silica W12	(Example 1)
Formulation A	100	82	2	276	-
Formulation B	100	82	2	267	9

30

Table 2: Weibull parameters of the dielectric breakdown strength distribution of Formulations A and Formulation B.

35

Table 2

	alpha	beta
Formulation A	61	3.8
Formulation B	93	5.9

5 Comparison between Formulation A and Formulation B

Formulation A corresponds to a standard electrical insulation formulation with 60 % by weight of microsilica. Replacing 5 % of microsilica with 5 % of a microfiller treated with alkylammonium according to Example 1 (i.e. Formulation B) increases the
10 electrical breakdown strength of the material by 50 % from 61 kVpeak/mm to 93 kVpeak/mm.

5 Claims

1. Electrical insulation system with improved electrical breakdown strength, said electrical insulation system comprising a hardened polymer component having incorporated therein a
10 conventional filler material and a selected pretreated filler material, characterized in that

(a) the hardened polymer component is selected from epoxy resin systems, polyesters, polyamides, polybutylene terephthalate, polyurethanes and polydicyclopentadiene, and preferably is a
15 hardened epoxy resin system;

(b) the conventional filler material is a known filler material having an average grain size distribution within the range of 1 μm -500 μm , being present in a quantity within the range of 40 %-65 % by weight, calculated to the total weight of
20 the insulator system; and

(c) the selected pretreated filler material is selected from silica, quartz, or a silicate, preferably mica (glimmer), kaolin or a layered silicate or talc, or is a mixture of these compounds, having an average grain size distribution
25 within the range of 1 μm -500 μm , wherein said selected filler material has been pretreated with an intercalating compound and wherein said pretreated filler material is present in an amount of 1 %-30 % by weight, calculated to the weight of the conventional filler material present in
30 the insulator system.

2. Electrical insulation system according to claim 1, characterized in that the conventional filler material [component (b)] as well as the selected pretreated filler material [component
35 (c)], both independent of each other, have an average grain size distribution within the range of 5 μm -100 μm , preferably within the range of 5 μm -50 μm , preferably within the range of 5 μm -30 μm .

5

3. Electrical insulation system according to claim 2, characterized in that at least 70 % of the particles, preferably at least 80 % of the particles, have a particle size within the range indicated in claim 2.

10

4. Electrical insulation system according to any one of the claims 1-3, characterized in that the conventional filler material [component (b)] is selected independently from the selected pretreated filler material [component (c)], and preferably is the same inorganic filler material as the pretreated

15

filler material.

20

5. Electrical insulation system according to any one of the claims 1-4, characterized in that the conventional filler material [component (b)] and the selected pretreated filler material [component (c)] independently of each other are selected from silica, quartz, or talc or a silicate, preferably mica, kaolin or a layered silicate.

25

6. Electrical insulation system according to any one of the claims 1-3, characterized in that the conventional filler [component (b)] is selected from aluminium oxide, aluminium trihydrate, titanium oxide or dolomite, metal nitrides, preferably silicon nitride, boron nitride and aluminium nitride, or metal

30

carbides, such as silicon carbide.

35

7. Electrical insulation system according to any one of the claims 1-3, characterized in that the conventional filler [component (b)] has been surface treated with a coupling agent, preferably selected from the group comprising silanes and siloxanes, preferably with 3-glycidoxypropyltrimethoxysilane or 3-glycidoxypropyldimethoxymethylsilane.

5 8. Electrical insulation system according to any one of the
claims 1-7, characterized in that the selected pretreated filler
material [component (c)] is a two-layered or three-layered
silicate selected from phyllosilicates, preferably selected from
montmorillonite, hectorite, saponite, vermiculite, smectite,
10 illite, sepiolite, palygorskite, muscovite, allevardite,
amesite, fluorohectorite, beidellite, talcum, nontronite,
stevensite, bentonite, glimmer, fluorovermiculite, halloysite,
hydrotalcite or a mixture of these compounds.

15 9. Electrical insulation system according to any one of the
claims 1-7, characterized in that the selected pretreated filler
material [component (c)] is selected from montmorillonite,
hectorite, saponite, vermiculite, smectite, illite; preferably
from montmorillonite, hectorite, vermiculite, smectite, illite.

20

10. Electrical insulation system according to any one of the
claims 1-9, characterized in that the selected pretreated filler
material [component (c)] has been pretreated with an intercala-
ting compound, preferably selected from the group comprising
25 protonated primary, secondary or tertiary amines; protonated
basic heterocyclic compounds, preferably as protonated imidazole
compounds, or quaternary ammonium compounds, substituted by at
least one alkyl residue or at least one functionalized alkyl
residue.

30

11. Electrical insulation system according to claim 10, charac-
terized in that the intercalating compound is selected from
substituted ammonium compounds, or from 2-hydroxyalkyl-substi-
tuted imidazole compounds, and preferably is an alkyl-substitu-
35 ted or hydroxyalkyl-substituted ammonium compounds, preferably
dimethyl-dihydrogenated tallow-quaternary ammonium and a related
hydroxyalkyl-containing compound.

5

12. Electrical insulation system according to any one of the claims 1-11, characterized in that the conventional filler material [component (b)] is present within the insulator system in a quantity within the range of 50 %-60 % by weight, preferably in a quantity of about 55 % by weight, calculated to the total weight of the insulator system.

13. Electrical insulation system according to any one of the claims 1-12, characterized in that the selected pretreated filler material [component (c)] is present in an amount of 2 %-20 % by weight, preferably in an amount of 2 %-10 % by weight, calculated to the weight of the conventional filler material present in the insulator system.

14. Electrical insulation system according to any one of the claims 1-13, characterized in that the hardened polymer component [component (a)] is selected from epoxy resin systems, polyesters, polyamides, preferably nylon, polybutylene terephthalate, polyurethanes and polydicyclopentadiene, and preferably is a hardened epoxy resin system.

15. Electrical insulation system according to any one of the claims 1-14, characterized in that the polymer composition comprises further additives selected from wetting/dispersing agents, plasticizers, antioxidants, light absorbers, and from further additives generally used in electrical applications.

16. Electrical insulation system according to any one of the claims 1-15, characterized in that component (a) is an epoxy resin composition is an aromatic and/or cycloaliphatic epoxy resin composition, preferably a mixture of polyglycidyl compounds, with an epoxy value (equiv./100 g) preferably at least three, preferably at least four and especially at about five, preferably about 4.9 to 5.1.

5 17. Method of producing the selected pretreated filler material
according to any one of the claims 1-16, characterized in that
the selected filler material is brought in contact with the
intercalating compound, optionally in the presence of a suitable
solvent and under stirring, within the temperature range of 20°C
10 to 150°C, preferably at room temperature up to 60°C, and for a
time long enough so that the intercalating compound modifies the
surface of the selected filler material, the suspension is then
filtered off, washed with the solvent, preferably with water,
and dried for several hours, preferably for about 10 to 24
15 hours, at a temperature within the range of 50°C to 80°C, pre-
ferably at about 60°C.

18. Method of producing the selected pretreated filler material
according to claim 17, characterized in that the pretreatment is
20 carried out at room temperature, the solvent being water or a
low molecular alcohol or a mixture of these compounds, the
concentration of the intercalation compound in the solvent being
within the range of 0.1 mol to 5.0 mol per liter of solvent.

25 19. The selected pretreated filler material as defined as
component (c) in any one of the claims 1-16.

20. The mixture of the selected pretreated filler material as
defined as component (c) and the conventional non-treated filler
30 material as defined in any one of the claims 1-16.

21. Method of producing an electrical insulation system accor-
ding to any one of the claims 1-16, characterized in that a con-
ventional filler material [component (b)] and a selected pre-
35 treated filler material [component (c)], are incorporated into
the monomeric starting material of the respective polymer of the
component (a), so as to be uniformly dispersed therein, the
dispersion is then formed into the desired shape, optionally

5 with the help of a molding tool, and then hardened and optionally post-cured.

22. Use of the electrical insulation system according to any one of the claims 1-16 in the field of impregnating electrical
10 coils and in the production of electrical components, high-voltage insulations for indoor and outdoor use, especially for outdoor insulators associated with high-voltage lines, as long-rod, composite and cap-type insulators, and also for base
15 insulators in the medium-voltage sector, in the production of insulators associated with outdoor power switches, measuring transducers, lead-throughs, and overvoltage protectors, in switchgear construction, in power switches, dry-type transformers, and electrical machines, as coating materials for transistors and other semiconductor elements and/or to im-
20 pregnate electrical components.

23. Electrical articles comprising an electrical insulation system as defined in any one of the claims 1-16.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2007/060504

A. CLASSIFICATION OF SUBJECT MATTER

INV. H01B3/40 C08K3/34 C08L63/00

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)

H01B C08K C08L

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

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2006/008422 A (AREVA T & D SA [FR]; BESSEDE JEAN-LUC [FR]; BEROUAL ABDERRAHMANE [FR];) 26 January 2006 (2006-01-26) cited in the application page 11, line 10 - page 13, line 30 page 25, line 12 - page 26, line 25 -----	1-3, 5-10, 12-16, 21-23.
A	US 6 238 790 B1 (SMITH JAMES D B [US] ET AL) 29 May 2001 (2001-05-29) examples 1,2; table 1 -----	1-16, 21-23

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

20 June 2008

Date of mailing of the international search report

26. 08. 2008

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2007/060504

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. As all required additional search fees were timely paid by the applicant, this international search report covers allsearchable claims.

2. As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-16, 21-23

Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-16, 21-23

Electrical insulation system comprising a) a hardened polymer component selected from epoxy resins, polyesters, polyamides, PBT, polyurethanes and polycyclopentadiene, b) 40 - 65 wt-% of an untreated filler material with a grain size distribution of 1 - 500 um and c) 1-30 wt-% (calculated against the filler content) a pretreated filler with an intercalating compound. Method for the production of the electrical insulation system, uses thereof and electrical articles thereof.

2. claims: 17-19

Pretreated filler material and method for its production

3. claim: 20

Mixture of an untreated conventional filler and a pretreated filler

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2007/060504

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2006008422 A	26-01-2006	EP 1769511 A1	04-04-2007
US 6238790 B1	29-05-2001	NONE	