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(54) Organogel for electrical cable insulating layer

(57) The present invention relates to an electric cable comprising at least one conductor (10), and an electrically insulating layer impregnated with a dielectric fluid (12), said insulating layer (12) surrounding said conductor (10), the dielectric fluid comprising an organogel including an oil and an organo-gelator, **characterized in that** the oil is a non-polar oil with a flash point inferior or equal to 200°C.

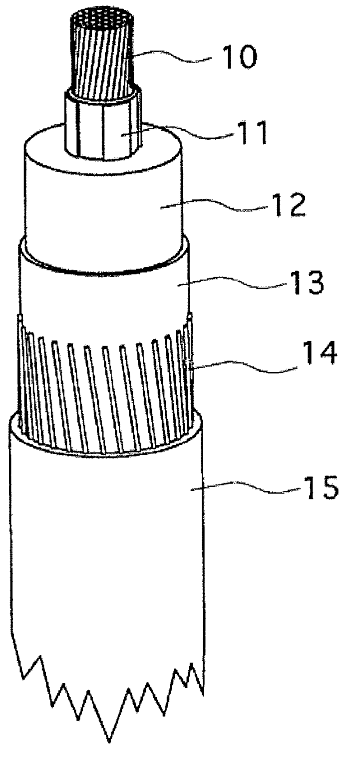

FIG.1

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Description

[0001] The present invention relates to an electric cable comprising an electrically insulating layer impregnated with a dielectric fluid including an organogel.

[0002] More particularly, the electric cable is a direct current transmission cable (DC transmission cable), more preferably a high voltage direct current cable (HVDC transmission cable) especially with a transmission capacity more than 1200 MW.

[0003] A typical DC transmission cable includes a conductor and an insulation system comprising a plurality of layers, such as an inner semi-conductive shield, an insulation body and an outer semi-conductive shield. The cable is also completed with casing, reinforcement, etc., to withstand water penetration and any mechanical wear or forces during production, installation and use. Almost all the DC cable systems supplied so far have been for submarine crossings or the land cable associated with them.

[0004] The insulation body is typically a wound body comprising an essentially all paper tape, i.e. a tape based on paper or cellulose fibers, but application of laminated tape materials, i.e. tape made of at least two layers adhered to each other, such as a laminated polypropylene paper tape, can be used as well. The wound body is typically impregnated with an electric insulation oil or mass.

[0005] The document WO 99/33068 describes a DC cable having at least one conductor and an electrically insulating layer impregnated with a dielectric fluid. The dielectric fluid comprises an oil and a gelling additive, wherein this gelling additive determines the viscosity and elasticity of the dielectric fluid.

[0006] The cable shall thus, in its impregnated insulating layer, comprise a dielectric fluid (i.e. oil plus gelling additive) with a sufficiently low viscosity at the (higher) impregnation temperature to ensure stable flow properties and flow behavior of this fluid, with a sufficiently high viscosity and elasticity at the (lower) operating temperature of the cable to ensure retention of the oil in the insulating layer, and with a sufficiently sharp viscosity increase on going from the impregnating to the operating temperature to enable the use of higher operating temperatures.

[0007] According to document WO 99/33068, the gelling additive molecule can be selected among a very large variety of compounds that are characterized by a polar part capable of forming hydrogen bonds, wherein said gelling additive together with an oil form a polymer gel when the gelling additive is a polymer, or an organogel when the gelling additive is a compound which is not a polymer. In the three examples of said document, three gelling additives are respectively used in combination with an unspecified naphthenic mineral oil.

[0008] However, the association of any gelling additive compound, as defined in WO 99/33068, with any unspecified naphthenic mineral oil does not provide a dielectric fluid with sufficiently stable dielectric properties within the electrically insulating layer. Typically, the described gelling additive and the oil will form a phase separated mixture, either because the gelling additive is not soluble in the oil resulting in a suspension of the additive in the oil, or because the gelling additive and the oil form a phase separated mixture of a gel phase and an oil phase (this is also called 'bleeding').

[0009] The present invention seeks to solve the above-mentioned problems of the prior art, and proposes to optimize the dielectric stability as well as the non-bleeding properties (i.e. the stability) of the dielectric fluid that is used to impregnate the electrically insulating layer of an electric cable.

[0010] An object of the present invention is to provide an electric cable comprising at least one conductor, and an electrically insulating layer impregnated with a dielectric fluid, said insulating layer surrounding said conductor, the dielectric fluid comprising an organogel including an oil and an organo-gelator, **characterized in that** the oil is a non-polar oil with a flash point inferior or equal to 200°C.

[0011] The non-polarity of the oil is essential to have satisfactory dielectric properties of the impregnated electrically insulating layer.

[0012] In a first variant according to the non-polarity properties of the oil, the non-polar oil has a low content of aromatics (C_A) according to the ASTM D 2140 standard, so that the weight percentage of C_A is preferably inferior to 12%, more preferably inferior to 10%, and even more preferably C_A is inferior to 6%.

[0013] In a second variant according to the non-polarity properties of the oil, and according to the IP 346 test, the non-polar oil has a low weight percentage that can be extracted from it with DMSO (a polar solvent), after the oil has been diluted with cyclohexane. Preferably, the DMSO-extractable weight percentage is inferior to 3%, preferably inferior to 2%, and more preferably inferior or equal to 1.5%.

[0014] In a third variant according to the non-polarity properties of the oil, the non-polar oil has a low content of aromatics (C_A) according to the ASTM D 2140 standard (first variant) and a low percentage of DMSO-extractibles according to the IP 346 test (second variant).

[0015] Advantageously, the combination of the organo-gelator with the specific oil of the invention provides clear and homogeneous organogels without any precipitate, with optimized stable dielectric properties (e.g. very high breakdown voltages), that do not exhibit bleeding phenomena.

[0016] According to the invention, the flash point of the oil indicates how volatile the oil is. The flash point is typically determined by the Pensky Marten (PM) closed cup method ASTM D 93 A, or similar tests such as the ASTM D92 or

ASTM D93 tests. The flash point is reached when the oil releases enough gases to make the gas mixture above the oil ignitable in the presence of an open flame. The flash point of the oil is preferably inferior or equal to 180°C and even more preferably inferior or equal to 160°C. The flash point of the oil is preferably superior or equal to 95°C, more preferably superior or equal to 110°C and even more preferably superior or equal to 120°C.

[0017] The non-polar oil can preferably be selected among a hydrocarbon oil, a silicon oil, a fluoro-oil and a natural oil (e.g. vegetable oils, terpene derived oils), or mixtures thereof, and is more preferably a hydrocarbon oil. Among hydrocarbon oils one can select a naphthenic oil, a paraffinic oil or an isoparaffinic oil, or mixtures thereof, where these may be mineral oils, semi-synthetic mineral oils (such as hydrotreated mineral oils) or synthetic oils (such as hydrogenated poly-alpha-olefines). Even more preferred are semi-synthetic hydrotreated mineral oils (either naphthenic, paraffinic or isoparaffinic).

[0018] The non-polar oil of the invention may be provided by any supplier or distributor, such as Nynas, Shell, Renkert Oil, Neste Oil, etc.

[0019] In a particular embodiment, the oil viscosity is inferior to 40 cSt (centistokes) at 40 °C, preferably inferior to 20 cSt at 40 °C, and more prefereably inferior to 10 cSt at 40 °C. The oil viscosity is determined in measuring the kinematic viscosity in cSt by Ubbelhode capillary according to ASTM D445 standard.

[0020] The non-polar oil used in the invention preferably contains molecules that are branched and/or cyclic. For example, heptamethylnonane is preferred over n-hexadecane, and decaline is preferred over n-dodecane. Other examples are (branched) alkyl cyclohexanes or (branched) alkyl decalines (i.e. these are hydrogenated alkyl benzenes and hydrogenated alkyl naphthalenes). Branching usually implies that various isomers are present in the oil, and this is preferred as the oil is preferably composed of a mixture of molecules. As a result, an oil composed of a mixture of primarily linear structures is also possible (i.e. paraffinic oils).

The organo-gelator

[0021] Organo-gelators are molecules that self-assemble in solution, by supramolecular interactions, usually by hydrogen bonding interactions and/or by π-π interactions. In solution, the organization of the organo-gelator molecules primarily takes place in one direction, so that long supramolecular structures are formed. Interactions between these structures, that become important as of a sufficiently high concentration of the organo-gelator molecules, cause the gelation of the solution. However, the supramolecular structure is not a polymer, or in other words, the organo-gelator is not a polymer, or a macromolecule, composed of repeating structural units (monomers) typically connected by covalent chemical bonds. Indeed, by heating the solution, the supramolecular structures disintegrate reversibly, giving a solution of individual molecules or very small aggregates of a few molecules, resulting in a sharp viscosity drop, and enabling easy processing at higher temperatures.

[0022] By way of example, the molecular weight of the organo-gelator is less than 5000 Dalton, more preferably less than 2000 Dalton, and even more preferably less than 1000 Dalton; more particularly, the molecular weight of the organo-gelator is from 200 to 800 Dalton.

[0023] In a preferred embodiment, the organo-gelator comprises a mixture of organo-gelators compounds, and more preferably a mixture of alike organo-gelators compounds. Hence, in this case, the organo-gelator cannot be composed of a single organo-gelator compound.

[0024] One can understand by the term "mixture", an organo-gelator composition comprising at least two different molecules, preferably from 2 up to 1000 different molecules, preferably from 2 up to 250, more preferably 4 up to 100, and most preferably from 6 up to 60 molecules. In said composition, the ratio in which the molecules are present may vary invariably. The most abundant species may preferably be present from 1 mol% up to 99 mol%, more preferably from 3 mol% up to 60 mol% and most preferably from 5 mol% up to 40%. The least abundant species is preferably present from 0.01 mol% to 49 mol%, preferably from 0.05 mol% to 25 mol%, and most preferably from 0.1 mol% to 15 mol%.

[0025] Examples of mixtures of organo-gelator compounds can be mixtures of enantiomers (i.e. racemates), mixtures of stereomers (e.g. mixtures of enantiomers and diastereomers), or mixtures of isomers.

[0026] One can understand by the term "a mixture of alike compounds", a mixture with compounds of the same chemical class or type. More particularly, the hydrogen bonding motif in the molecules of the mixture is the same, wherein the hydrogen bonding motif is defined as the hydrogen bonding functions (e.g. ureas or amides) and the spacer between these functions. This is further highlighted, explained and exemplified below.

[0027] In a particular embodiment according to the invention, the organo-gelator is selected among urea-based compounds, a mixture of urea-based compounds, amide-based compounds, and a mixture of amide-based compounds, or mixtures thereof.

[0028] Said organo-gelator is particularly suited to prepare stable organogels that are of interest in electrical cable insulation applications. Said organo-gelator, in combination with the oil according to the invention, is capable of producing clear, homogeneous and stable organogels.

[0029] Indeed, by far, most molecules are not organo-gelators, also not among molecules that bear a non-polar segment and that have a polar segment that can form hydrogen bonds. In addition, it is difficult to predict whether a molecular structure is capable of gelating an oil. Furthermore, some organo-gelators may be able to produce organogels, but these organogels may not be stable in time (precipitation or bleeding may occur).

[0030] In a preferred embodiment, the organo-gelator is selected among urea-based compounds or a mixture of urea-based compounds, and amide-based compounds or a mixture of amide-based compounds.

[0031] The mixtures according to the present invention are preferably composed of alike type of organo-gelator molecules, meaning that the hydrogen bonding motif in all molecules of the mixture is the same, where the hydrogen bonding motif is defined as the hydrogen bonding functions (preferably ureas or amides) and the spacer between these functions.

[0032] More particularly, mono-ureas can be mixed with other mono-ureas, aromatic tri-amides can be mixed with other aromatic tri-amides, etc. Even more particularly, for mixtures that contain multifunctional amide structures (or for mixtures that contain multifunctional urea structures), the spacer between the amide- or urea hydrogen bonding functions is preferably identical for all the mixed organo-gelator molecules.

[0033] For example:

- tri-alkyl benzene-1,3,5-tri-carboxamides are mixed with other tri-alkyl benzene-1,3,5-tricarboxamides; or
- 2,4-bis-urea toluenes are mixed with other 2,4-bis-urea toluenes; or
- metha-bis-urea benzenes are mixed with other metha-bis-urea benzenes; or
- di-amides with an n carbon atoms spacer between the two - NHCOR amides are mixed with other di-amides with an n carbon atoms spacer between the two -NHCOR amides; or
- 1,2-bis-urea (S,S)-cyclohexanes are mixed with other 1,2-bis-urea (S,S)-cyclohexanes.

[0034] Furthermore, when amides are considered, the orientation of the amide functions towards the spacer is preferably the same for the molecules (i.e. organo-gelator molecules) in the mixture. For example, all diamides in the mixture are R1-CONH-(Spacer)-NHCO-R2, or all diamides in the mixture are R1-NHCO-(Spacer)-NHCO-R2, or all diamides in the mixture are R1-NHCO-(Spacer)-CONH-R2, wherein R1 and R2 are just mentioned for the understanding of the amide functions orientation, and can be alkyl radicals or other kind of groups.

[0035] The mixtures of organo-gelators can be made by physically mixing a set of individually synthesized organo-gelators. For example, a particular, or several particular, 2,4-bis-(di-alkyl-ureido)-toluene(s) is/are physically mixed in a selected ratio with another, or with several other, 2,4-bis-(di-alkyl-ureido)-toluene(s).

[0036] Alternatively, the mixtures can also be synthesized by taking one specific multifunctional reactant, and allowing this building block to react with a mixture of mono-functional reactants. For example, 2,4-toluene di-isocyanate (the specific multifunctional reactant) is reacted with a mixture of primary amine reactants (the mono-functional reactants) to produce a mixture of 2,4-bis-(di-alkyl-ureido)-toluenes; or, in another example, (S,S)-1,2-diamino cyclohexane is reacted with a mixture of mono-isocyanates to produce a mixture of (S,S)-1,2-bis-urea cyclohexanes. The nature of the mono-functional reactants (e.g. linear alkyl, branched, cyclic, alkylaryl, etc.) and the ratio in which these reactants are present in the reactant mixture, are freely selected. Particular and well-suited mixtures of mono-functional reactants are racemates, such as for example racemates of primary amines, racemates of carboxylic acids or derivatives thereof, or racemates of isocyanates.

[0037] Thanks to the mixtures according to the invention, it is possible to surprisingly prepare an organo-gelator by mixing molecules that individually are not capable of gelating or thickening oils. In addition, said mixtures allow to optimize properties of the organogels (e.g. with respect to viscosity, gel point, stability, etc.), by altering the specific composition of the mixture.

Urea-based compounds

[0038] When referring to urea-based compounds, these urea functions can be regular ureas (-NH-CO-NH-), or thioureas (-NH-CS-NH-). Regular ureas are preferred.

[0039] When referring to urea-based compounds, both nitrogen atoms in one urea moiety can be substituted with hydrogens, or one of these nitrogen atoms can be alkylated or arylated. Preferably, both nitrogen atoms in the urea moiety are substitued with hydrogens, giving a -NH-CO-NH- urea moiety (or a -NH-CS-NH- thio-urea moiety) that is capable of engaging in hydrogen bonding interactions.

[0040] According to the urea-based compounds, these can be selected among mono-ureas or a mixture of mono-ureas, bis-ureas or a mixture of bis-ureas, and tris-ureas or a mixture of tris-ureas, and more preferably among mono-ureas or a mixture of mono-ureas, and bis-ureas or a mixture of bis-ureas. Most preferred are bis-ureas or a mixture of bis-ureas.

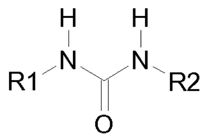
[0041] When the urea-based compound is substituted by at least two different R-groups, said compound is called an "asymmetric" urea-based compound. When all of the urea functions are substituted by identical R-groups, said compound is called a "symmetric" urea-based compound. R-groups are not spacer groups that connect different urea-functions.

[0042] In the cases where a mixture of urea-based compounds is considered, said mixture can comprise:

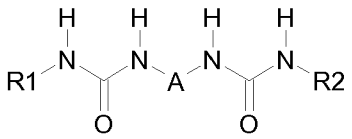
i. different symmetric urea-based compounds, or
ii. different asymmetric urea-based compounds, or
iii. at least one symmetric urea-based compound and at least one asymmetric urea-based compound.

[0043] The urea formulas as described hereafter concern regular ureas. However, thio-ureas (not represented) can be as well considered instead of regular ureas.

[0044] The mono-ureas (or a mixture of mono-ureas) or the bis-ureas (or a mixture of bis-ureas) can respectively comply with the following formulas Ia and Ib, respectively:



(I a)



(I b)

in which:

- R1 and R2 can be different or identical, and can be independently selected among hydrogen, a linear, branched or cyclic, saturated or unsaturated C_1-C_{24} alkyl, alkylaryl or arylalkyl carbon-based radicals, more particularly saturated alkyl based radicals, where these radicals may optionally contain from 1 to 3 heteroatoms chosen from O, S, F and N, so that e.g. ether, thio-ether, alcohol, amide, carboxylic acid, ester, urethane, tertiary amine and CF_x (x = 1, 2 or 3) groups may be included,
- A being a non-aromatic or aromatic spacer, preferably selected among a linear alkylene, a branched alkylene, a cyclohexylene (preferably a R,R- or S,S-1,2-cyclohexylene), a 4,4'-methylene-bis-cyclohexylene, a 4,4'-methylene-bis-phenylene, a 4,4'-oxy-bis-phenylene, a benzylene, a naphthalene, a phenylene, a tris-(2-ethylene)-amine, an isophoronylene, a para-menthylene and a lysine-derived spacer. Spacer A may also represent a direct covalent bond between the two nitrogen atoms.

[0045] More preferably, R1 and/or R2 are independently selected among 2-ethyl-hexyl; 1,5-dimethyl-hexyl; 3,7-dimethyl-octyl; 1-methyl-hexyl; other branched C_3-C_8 alkyls, linear C_4-C_{18} alkyls, benzyls, cyclohexyl, alkoxy alkyls and hydroxy-alkyls. In a more preferred way, R1 and/or R2 can be independently selected among 2-ethyl-hexyl; 1,5-dimethyl-hexyl; 1-methyl-hexyl; branched C_3-C_6 alkyls; and linear C_4-C_{10}, C_{16} and C_{18} alkyls. The most preferred is the 2-ethyl-hexyl radical.

[0046] In a particular embodiment, in cases where R1 and/or R2 groups contain stereocenters, these groups are preferably racemic groups (or more accurately stated, these R1 and/or R2 groups are then originated from racemic reactants, such as for example racemic primary amines, or racemic isocyanates).

[0047] In the cases where R1 is different from R2, an asymmetric urea compound is obtained.

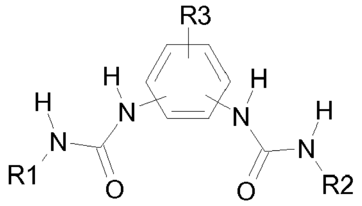
[0048] For structures Ia, in the cases where R1 is different from R2 in order to have an asymmetric mono-urea compound, R1 (or R2) can preferably be selected among aryl or benzyl derived C_6 to C_{15} carbon-based radicals, optionally containing from 1 to 3 heteroatoms chosen from O, S, F and N, and combinations thereof, and R2 (or R1) can be selected among hydrogen, linear, branched or cyclic, saturated or unsaturated C_1-C_{24} alkyl radicals optionally containing from 1 to 3 heteroatoms chosen from O, S, F and N.

[0049] For structures Ib, in the cases where R1 is different from R2 in order to have an asymmetric bis-urea-based compound, R1 (or R2) can preferably be selected among saturated or unsaturated, non-cyclic, branched C_3 to C_{15} carbon-based radicals, optionally containing from 1 to 3 heteroatoms chosen from O, S, F and N, and combinations thereof, and R2 (or R1) can be selected among hydrogen, linear, branched or cyclic, saturated or unsaturated C_1-C_{24} alkyl radicals optionally containing from 1 to 3 heteroatoms chosen from O, S, F and N.

[0050] In the cases where a mixture of mono-ureas according to formula Ia is considered, all the molecules in said mixture preferably have one specific identical R1-group, preferably a specific aryl-derived group, or a specific benzyl-derived group. For example, one can consider a mixture composed of only 1-benzyl-mono-ureas.

[0051] In the cases where a mixture of bis-ureas according to formula Ib is considered, all the molecules in said mixture preferably are alike and have the same spacer A. For example, the spacer A in all molecules of a mixture of structures Ib can be a R,R-1,2-cyclohexylene spacer; or can be a hexylene spacer.

[0052] In a preferred embodiment where the spacer A of the formula Ib is an aromatic spacer, the urea-based compound can be an aromatic bis-urea (or a mixture of aromatic bis-ureas) complying with the following formula II:

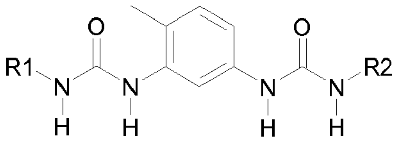


Aromatic bis-urea (II)

in which R1 and R2 are defined as above, and R3 is a hydrogen atom or a linear or branched C_1 to C_4 alkyl radical.

[0053] In the cases where a mixture of bis-ureas according to formula II is considered, in said mixture the urea groups in all molecules are preferably connected with the same aromatic spacer. For example, metha-bis-ureas are mixed with other metha-bisureas, para-bis-ureas are mixed with other para-bis-ureas and ortho-bis-ureas are mixed with other ortho-bis-ureas.

[0054] Preferably, the aromatic bis-urea can be a bis-urea substituted toluene (or a mixture of bis-urea substituted toluenes) complying with the following formula III:



Bis-urea substituted toluene (III)

in which R1 and R2 are defined as above.

[0055] When a mixture between structures II and III is considered, it is preferable that the urea groups in structures II are also metha-substituted onto the ring.

Amide-based compounds

[0056] When referring to amide-based compounds, these amide functions can be regular amides (-NH-CO-), or thio-amides (-NH-CS-). Regular amides are preferred.

[0057] When referring to amide-based compounds, the nitrogen atom in the amide moiety can be substituted with a hydrogen, giving -NH-CO-amide moiety (or -NH-CS- thio-amide moiety) that is capable of engaging in hydrogen bonding interactions.

[0058] According to the amide-based compounds, these can be selected among di-amides or a mixture of di-amides, tri-amides or a mixture of tri-amides, and tetra-amides or a mixture of tetra-amides.

[0059] When the amide-based compound is substituted by at least two different R-groups, said compound is called an "asymmetric" amide-based compound. When all of the amide functions are substituted by identical R-groups, said compound is called a "symmetric" amide-based compound. R-groups are not spacer groups that connect different amide functions.

[0060] In the cases where a mixture of amide-based compounds is considered, said mixture can comprise:

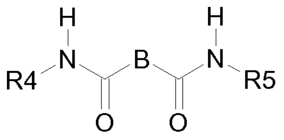
i. different symmetric amide-based compounds, or
ii. different asymmetric amide-based compounds, or

iii. at least one symmetric amide-based compound and at least one asymmetric amide-based compound.

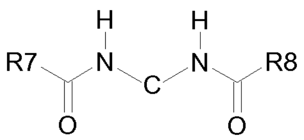
[0061] The amide formulas as described hereafter concern regular amides. However, thio-amides (not represented) can be as well considered instead of regular amides.

Di-amides

[0062] In a first example, the di-amide (or a mixture of di-amides) can comply with the following formulas IV or V:



(IV)



(V)

in which R4 and/or R5, and R7 and/or R8, can be different or identical, and can independently be selected among hydrogen, linear, branched or cyclic, saturated or unsaturated C_1-C_{36} alkyl, alkylaryl or arylalkyl carbon-based radicals, more particularly saturated alkyl based radicals, optionally containing from 1 to 3 heteroatoms chosen from O, S, F and N, so that e.g. ether, thio-ether, alcohol, carboxylic acid, ester, urethane, tertiary amine and CF_x (x= 1, 2 or 3) groups may be included.

[0063] For groups R4 and/or R5, these are preferably, and independently, selected among hydrogen, 2-ethyl-hexyl; 1,5-dimethyl-hexyl; 3,7-dimethyl-octyl; 1-methyl-hexyl; other branched C_3-C_8 alkyls, linear C_4-C_{18} alkyls, benzyls, cyclohexyl, alkoxy alkyls (e.g. 3-methoxypropyl) and hydroxy-alkyls.

[0064] For groups R7 and/or R8, these are preferably, and independently, selected among 1-ethyl-pentyl; 1-methyl-ethyl; 1-methyl-propyl; tert-butyl; 1-ethyl-propyl; 2,6-dimethyl-heptyl; other branched C_3-C_8 alkyls; C_9-C_{36} 1-alkyl-alkyls, linear C_4-C_{18} alkyls, benzyls, cyclohexyls, and alkoxy-alkyls.

[0065] In a particular embodiment, in cases where the R4 and/or R5 groups, or the R7 and/or R8 groups, contain stereocenters, these groups are preferably racemic groups. Or more accurately stated, are originated from racemic reactants, such as for example from racemic primary amine reactants (for IV) or from racemic carboxylic acid derived reactants (for V).

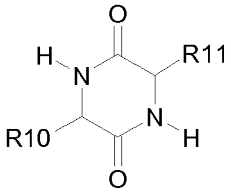
[0066] In the cases where R4 is different from R5 or R7 is different from R8, an asymmetric di-amide compound is obtained.

[0067] The moiety B is an non-aromatic or aromatic spacer, preferably selected among a linear alkylene, a branched alkylene, a cyclohexylene, a camphorylene, a phenylene, a bis-phenylene, a naphthalene, and a glutamic or aspartic acid derived spacer. Spacer B can also represent a direct covalent bond between the two carbons.

[0068] The moiety C is a non-aromatic or aromatic spacer, preferably selected among a linear alkylene, a branched alkylene, a cyclohexylene (preferably a R,R- or a S,S-1,2-cyclohexylene), a 4,4'-methylene-bis-cyclohexylene, a 4,4'-methylene-bis-phenylene, a 4,4'-oxy-bis-phenylene, a benzylene, a naphthalene, tris-(2-ethylene)-amine, an isophoronylene, a para-menthylene and a lysine-derived spacer. Spacer C can also represent a direct covalent bond between the two nitrogen atoms.

[0069] In the cases where a mixture of di-amides of the structure IV, or a mixture of di-amides of the structure V, is considered, all molecules in said mixtures preferably are alike and have the same spacer B (for the mixture of structures IV), or the same spacer C (for the mixture of structures V). For example, the spacer C in all molecules of a mixture of structures V can be a (R,R)-1,2-cyclohexylene spacer; or can be a hexylene spacer.

[0070] In a second example, the di-amide (or a mixture of di-amides), is a cyclic diamide, and can comply with the following formula VI:



(VI)

in which R10 and R11 can be different or identical, and can independently be selected among hydrogen, linear, branched or cyclic, saturated or unsaturated C_1-C_{24} alkyl, alkylaryl or arylalkyl carbon-based radicals, more particularly saturated alkyl based radicals, optionally containing from 1 to 3 heteroatoms chosen from O, S, F and N, so that e.g. ether, thioether, alcohol, amide, carboxylic acid, ester, urethane, tertiary amine and CF_x (x= 1, 2 or 3) groups may be included.

[0071] More preferably, R10 and R11 are derived from amino-acid residues, such as hydrogen, benzyl, alkyl, branched alkyl or alkyl residues containing alkyl-ester or alcohol groups.

[0072] In a particular embodiment, in cases where R10 and/or R11 groups contain stereocenters, these groups are preferably racemic groups.

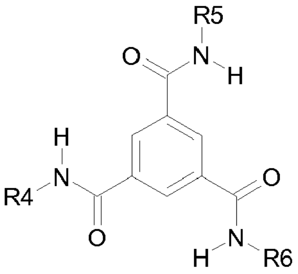
[0073] In the cases where R10 is different from R11, an asymmetric di-amide compound is obtained.

[0074] When a mixture of molecules of formula VI is considered, all molecules in this mixture preferably have the same configuration for the 6-membered ring, i.e. all molecules have the same R,R- or the same S,S-configuration, or the same R,S configuration.

Tri-amides

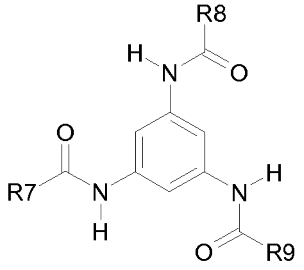
[0075] According to tri-amides, the amide-based compound can be an aromatic tri-amide.

[0076] In a first example, the aromatic tri-amide (or a mixture of aromatic tri-amides) is a benzene-1,3,5-tricarboxamide (BTA) (or a mixture of BTAs) complying with the following formula VII:



Benzene-1,3,5-tricarboxamide (BTA) (VII)

[0077] In a second example, the aromatic tri-amide (or a mixture of aromatic tri-amides) can comply with the following formula VIII:



Nitrogen centered benzene-1,3,5-tricarboxamide (nc-BTA) (VIII)

[0078] In the formula VII or VIII, R4, R5 and/or R6, and R7, R8 and/or R9 can be different or identical, and can be independently selected among hydrogen, linear, branched or cyclic, saturated or unsaturated C_1-C_{36} alkyl, alkylaryl or arylalkyl carbon-based radicals, more particularly saturated alkyl based radicals, optionally containing from 1 to 3 heteroatoms chosen from O, S, F and N, so that e.g. ether, thio-ether, alcohol, carboxylic acid, ester, urethane, tertiary amine and CF_x (x= 1, 2 or 3) groups may be included.

[0079] For groups R4, R5 and/or R6 of formula VII, these are preferably, and independently, selected among 2-ethylhexyl; 1,5-dimethyl-hexyl; 3,7-dimethyl-octyl; 1-methyl-hexyl; other branched C_3-C_8 alkyls, linear C_4-C_{18} alkyls, benzyls, cyclohexyl, alkoxy alkyls (e.g. 3-methoxy-propyl) and hydroxy-alkyls.

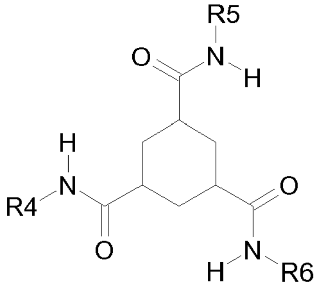
[0080] For groups R7, R8 and/or R9 of formula VIII, these are preferably, and independently, selected among 1-ethylpentyl; 1-methyl-ethyl; 1-methyl-propyl; tert-butyl; 1-ethyl-propyl; 2,6-dimethyl-heptyl; other branched C_3-C_8 alkyls; C_9-C_{36} 1-alkyl-alkyls, linear C_4-C_{18} alkyls, benzyls, cyclohexyls, and alkoxy-alkyls.

[0081] In a particular embodiment, in cases where the R4, R5 and/or R6 groups of formula VII, or the R7, R8 and/or R9 groups of formula VIII contain stereocenters, these groups are preferably racemic groups. Or more accurately stated, are originated from racemic reactants.

[0082] In the cases where at least one of the R group selected among R4, R5 and R6 is different from one of the two others, an asymmetric tri-amide compound is obtained.

[0083] In the cases where at least one of the R group selected among R7, R8 and R9 is different from one of the two others, an asymmetric tri-amide compound is obtained.

[0084] In a third example, the tri-amide (or a mixture of tri-amides) can comply with the following formula IX:



(IX)

in which R4, R5 and R6 are defined as above for structure VII.

[0085] In a particular embodiment, in cases where the R4, R5 and/or R6 groups of formula IX contain stereocenters, these groups are preferably racemic groups. Or more accurately stated, are originated from racemic reactants.

[0086] In the cases where at least one of the R group selected among R4, R5 and R6 is different from one of the two others, an asymmetric tri-amide compound is obtained.

[0087] When a mixture of molecules of formula IX is considered, all molecules in this mixture preferably are alike and have the same configuration for the 1,3,5-cyclohexylene ring, i.e. all molecules have the same axial and/or equatorial substitution pattern on this 1,3,5-cyclohexylene ring.

Tetra-amides

[0088] Tetra-amides can be pyromellitamide compounds or mixtures thereof, such as for example benzene-1,2,4,5-tetra-carboxamides.

[0089] Of the above mentioned formulas Ia, Ib, II, III, IV, V, VI, VII, VIII and IX, formulas Ia, Ib, III, V and VII are preferred. Most preferred are III and VII. In the present description, one notes that in the formulas I to IX the hydrogen bonding motif is drawn with attached R-radicals, i.e. the R-radicals are not part of the hydrogen bonding motif.

[0090] Furthermore, an organo-gelator that is a mixture of alike compounds is preferred, as opposed to an organo-gelator that is composed of a single compound. Mixtures of alike structures according to formula Ia, or to formula Ib, or to formula III, or to formulas II and III, or to formula V, or to formula VII are preferred. Most preferred are mixtures of alike structures according to formula III, according to formulas II and III, or according to formula VII.

[0091] It stems from the above that the present invention introduces a class of organo-gelators that can be used to effectively and stably thicken or gelate oils that are applied in electrical cable insulation.

Other type of organo-gelators

[0092] The concept of making organo-gelators from mixtures of alike molecules can further be applied to other type of molecular structures with (multiple) pendant alkyl groups, such as for example, metal-salts (e.g. mono- or di-nuclear metal diketonates or tetra carboxylic acids, di- or trivalent metal salts of fatty acids or phosphoric acids), sugar or poly-ol based compounds (e.g sorbitol derivatives, cholic acid derivatives), steroid derivatives (such as cholesterol derivatives), amino acid derivatives or oligopeptides, mellitic acid derivatives (e.g. mellitamides), systems that aggregate due to π-π-interactions (e.g. porphyrines, phthalocyanins, phenylenevinylidenes, fluorenes, azophenylenes, other dyes, anthraquinones), two-component systems (e.g acid-base systems, pyrimidine-barbituric acid systems, or similar systems based on melamines or triazines, systems based on cyclodextrins, donor-acceptor based systems), multivalent urethanes (e.g based on N-benzyl-3,4-dihydroxy-pyrrolidine), bola-amphiphilic structures, molecules with mesogenic groups (such as tri-alkyl gallic acid derivatives, 4-alkoxy benzoic acid derivatives).

The organogel

[0093] The dielectric fluid of the invention comprises the organo-gelator and the oil that both are described in detail above.

[0094] Contrary to a viscous solution, a fluid in a vial is considered as a gel when inverting the vial does not result in flowing of the fluid on the time scale of seconds or minutes, whereas a very viscous solution will flow slowly in seconds, and a low viscous solution will flow fast immediately.

[0095] The dielectric fluid of the invention, or more particularly the organogel, is preferably clear (or transparent), as opposed to being turbid or white. Additionally, it is preferably macroscopically homogeneous, as opposed to being a mixture having a precipitate (a suspension), or a mixture exhibiting any other type of phase separation, such as a mixture of a gel and a phase separated liquid.

[0096] An organogel is a visco-elastic solution, implying that it has both elastic (i.e. solid-like) and viscous (i.e. liquid-like) properties. The gel point (Tgel) of an organogel is the temperature below which the organogel has a more elastic or solid-like nature, and above which it has a more liquid-like behavior.

[0097] The gel point of an organogel can be determined by rheological measurements, or more particularly by complex viscosity measurements or by viscoelastic measurements. Rheological measurements are typically performed with a dynamic rheometer in oscillatory mode such as a Brookfield rheometer. The gel point of the present invention is measured under dynamic oscillation of 0,095 Hz.

[0098] For example, the organogel is placed in a concentric cylinder cup with a cone inside, and heated from 4°C to 110°C at 0,5 °C/min under a dynamic oscillation of 0,095 Hz and under a strain of 1%. As a function of temperature, rheological parameters such as the storage modulus (G’, in Pa, reflecting the solid-like nature of the gel), loss modulus (G", in Pa, reflecting the liquid-like nature of the gel) and the complex viscosity η^* (in Pa.s) can be recorded. The gel point is then defined as the temperature at which the storage modulus G’ is equal to the loss modulus G".

[0099] The impregnating temperature of the cable is preferably higher than the gel point of the applied organogel in the insulating layer, whereas the operating temperature of the cable is preferably lower than or not much higher than this gel point.

[0100] In particular, the gel point of the organogel can be chosen from 45°C to 90°C. This specific gel point range allows for an organogel that gives the impregnated electrically insulating layer of the invention all the advantageous properties.

[0101] A gel point higher than 90°C is preferably not desired as this implicates that too high impregnating temperatures have to be used.

[0102] A gel point less than 45°C induces a risk of creating cavities in the electrically insulating layer due to polarity reversal of the cable at operating temperatures. Polarity reversal induces a temperature change in the cable, and said temperature change can modify the dielectric fluid structure, possibly resulting in cavity formation (i.e. small gas bubble formation). Such cavities can severely increase the chance on a breakdown (failure) of the cable.

[0103] Typically, the rheological behaviour of the dielectric fluid of the invention can be characterized by a "solid" (elastic) behaviour from 0°C to approximately 60°C, and a more viscous behaviour from 60°C to 100°C. The complex viscosity at 0°C can be about 100 to 5000 Pa.s. At the gel point, the viscosity can be about 50 to 2000 Pa.s, and at 110°C, the viscosity can be about 0,01 to 10 Pa.s.

[0104] The well-know method to characterize the organogel complex viscosity in Pa.s is to use a dynamical rheometer in oscillatory mode, as mentioned and described above, by use of e.g. a Brookfield rheometer.

[0105] Accordingly, the dielectric fluid of the invention displays a sharp complex viscosity drop somewhere in the temperature window between 45 °C and 110 °C. The complex viscosity drop is preferably more than 2 decades (e.g. from 200 Pa.s to 2 Pa.s) within 40 °C, more preferably more than 3 decades within 35 °C, and even more preferably more than 3 decades within 30 °C. Said complex viscosity drop is preferably larger than 100 Pa.s, more preferably larger than 250 Pa.s, most preferably larger than 500 Pa.s.

[0106] In particular, the organogel can include to the maximum 20% by weight of organo-gelator, more preferably include to the maximum 10% by weight of organo-gelator. The dielectric fluid can include at least 2% by weight of organo-gelator. Preferably, the organogel can include from 3% to 7% by weight of the organo-gelator. The organogel preferably only contains the oil and the organo-gelator according to the invention.

[0107] However, the dielectric fluid, including said organogel, can further comprise additional components, such as for example rheology modifiers, anti-oxidants, metal deactivators or hydrogen scavengers. The dielectric fluid preferably comprises more than 97% by weight of organogel.

[0108] Examples of rheology modifiers are elastomers to make the gel more elastic, said elastomer being not more than 2% by weight in the dielectric fluid. The addition of more than 2% by weight of said elastomer may induce a rheological problem due to the compatibility between said elastomer and the organo-gelator, as well as a risk of bleeding. For example, the elastomer can be polyisobutene (PIB), more preferably a low molecular weight polyisobutene (LMWPIB) such as a molecular weight inferior to 10000 g/mol, and more preferably inferior to 2000 g/mol.

[0109] Example of anti-oxidants are phenol derived anti-oxidants, such as 2,6-di-tert-butyl-4-methylphenol (BHT), or Irganox type of anti-oxidants as commercialized by Ciba (these are sometimes also phenol derivatives).

The electrically insulating layer and the electrical cable

[0110] According to the invention, the electrically insulating layer can typically be a porous, fibrous and/or laminated structure, such as tape, based preferably on cellulose or paper fibers.

[0111] One understands by "laminated structure" a structure including at least three layers, in which the intermediate layer is based on cellulose or paper fibers and the two other layers are different layers such as atactic polypropylene layers (i.e. polypropylene layers stretched in random direction).

[0112] The electrically insulating layer of the invention is impregnated with the dielectric fluid, such that essentially all voids of said electrically insulating layer are filled with the dielectric impregnating fluid.

[0113] In a specific embodiment, when using porous and/or fibrous structure (e.g. kraft paper), or in other terms non-laminated structures, the gel point of the organogel of the invention can be from 45 to 80°C, and more preferably from 50 to 75°C, most preferably from 55 °C to 65°C.

[0114] When using laminated structures, the gel point of the organogel of the invention can be from 80 to 90°C.

[0115] In a specific embodiment, the electric cable according to the invention can be an electric direct current transmission cable comprising a first semi-conducting layer surrounding said conductor, the insulating layer surrounding said first layer; a second semi-conducting layer surrounding said insulating layer, and a protective sheath surrounding said second layer. Optionally, a metallic screen can be positioned between the second semi-conductive layer and the protective sheath along the electric cable.

[0116] The present invention will become more fully understood from the detailed description given herein below and from the accompanying drawings which are given by way of illustration only, and thus, which are not limits of the present invention, and wherein:

> Figure 1 represents a schematic view of an embodiment of a DC cable according to the invention, favorable for use as a cable for transmission of electric power. For reasons of clarity, only the elements that are essential for understanding the invention are shown in diagrammatic manner, and scale is not complied with.
> Figure 2 represents the storage modulus G' and the loss modulus G" curves as well as the complex viscosity η^* curve, respectively, in function of the temperature for an organogel according to the invention.
> Figure 1 illustrates a DC cable comprising from the center and outwards:

- a stranded multi-wire conductor 10;
- a first semi-conducting shield 11 disposed around the conductor 10;
- a wound and impregnated electrically insulating layer 12 comprising a dielectric fluid according to the invention;
- a second semi-conducting shield 13 disposed outside the electrically insulating layer 12;
- a metallic screen 14 around the second semi-conducting shield 13; and
- a protective sheath 15 arranged outside the metallic screen 14.

[0117] The DC cable can be a single conductor DC cable having a multi-wire core as shown in Figure 1 or a DC cable with two or more conductors. A DC cable comprising two or more conductors can be of any known type with the conductors placed side-by-side in a flat cable arrangement, or in a two-conductor arrangement with one first central conductor surrounded by a concentrically arranged second outer conductor, i.e. a coaxial two-conductor cable.

Examples

[0118] In order to show the advantage of the electric cable of the invention, the visual aspect of different organogels according to the prior art and to the invention is studied.

[0119] The different properties of the oil used to prepare an organogel are described in the following table 1.

Table 1

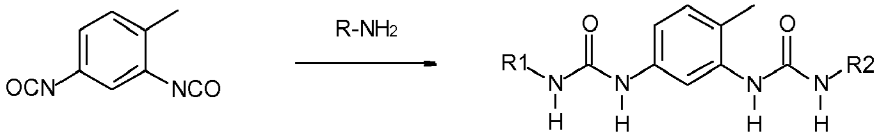
Oil and its properties	Nyflex 200 (Nynas S8,5)	Nyflex 222B (Nynas S100B)	Nyflex 800 (Nynas NS8)	Nytex 801 (Nynas T9)	Nytex 820 (Nynas T110)	Hepta-methyl nonane
Type of oil	Hydrotreated naphthenic	Hydrotreated naphthenic	Hydrotreated naphthenic	Hydrotreated naphthenic	Hydrotreated naphthenic	Isoparaffinic
Viscosity at 40 °C (cSt) according to ASTM D 445	8.6	102	7.7	9.1	114	3.0
Flash point (°C) according to ASTM D 93A standard	144	218	144	146	212	95
C_A (%) ASTM D 2140 standard	3	< 1	5	9	12	Not determined with ASTM-test.

[0120] The oils referenced in table 1 are commercialized by Nynas, except for heptamethylnonane (CAS 4390-04-9), a non-aromatic oil that can be bought from sources such as Aldrich.

[0121] The preparation of the different organo-gelators and organogels are explained as below. Isolated materials were molecularly characterized by NMR and MALDI-TOF-MS spectrometry and the analytical data were in line with the assigned structures.

Preparation of bis-urea substituted toluenes

[0122] Bis-urea substituted toluenes can be prepared according to the following scheme:



2,4-toluene-diisocyanate (2,4-TDI)

Bis-urea substituted toluene

[0123] The 2,4-toluene di-isocyanate, or tolylene-2,4-diisocyanate, (TDI) that is used in the experiments that are described below in detail is of 95% purity. According to the specifications of the supplier (Aldrich T39853; CAS 584-84-9) it contains about 4% of the 2,6-toluene di-isocyanate isomer. As a result, the described bis-urea (or diurea) products derived from TDI also contain a small percentage of 2,6-diureido isomers, typically about 4%.

[0124] Alternatively, it is possible to use tolylene-2,4-diisocyanate (TDI) of technical grade as starting material (Aldrich 216836, 80% purity according to the specifications of the supplier; the remaining 20% is the tolylene-2,6-diisocyanate isomer), or to mix this 80% grade of TDI with the 95% grade of TDI in a certain ratio to acquire the reactant of choice. In this way, the percentage of 2,6-isomer in the bis-urea product can be controlled.

Organo-gelator 1 (OG1):

[0125] The synthesis of 2,4-bis(2-ethylhexylureido)toluene (EHUT), with R = R1 = R2 = (R/S)-2-ethyl-hexyl, can be done from 2,4-toluene-diisocyanate and racemic 2-ethyl-hexylamine according to the document Langmuir, 2002, 18, 7218-7222.

[0126] Accordingly, as the R-groups can be different, this organo-gelator OG1 contains 4 different 2,4-bis-(2-ethylhexylureido)-toluene isomer compounds (the R,R-, S,S-, R,S- and S,R-isomers), as well as small amounts of 3 different 2,6-bis-(2-ethylhexylureido)-toluene isomer compounds (the R,R-, the S,S- and the R,S-isomers). Therefore, OG1 is composed of in total 7 compounds, where the 2,4-isomers are examples of structures (III), while the 2,6-isomers are examples of the structures (II). Both the 2,4- and 2,6-isomers are di-ureas with the two urea groups attached in metha-positions onto the benzene ring.

Organo-gelator 2 (OG2):

[0127] The synthesis of 2,4-bis(1,5-dimethylhexylureido)toluene (DMHUT), with R = R1 = R2 = (R/S)-1,5-dimethylhexyl can be done from 2,4-toluene-diisocyanate and racemic 1,5-dimethyl-hexylamine according to the document JACS, 2003, 125, 13148-13154. Similarly as for OG1, OG2 is composed of a mixture of organo-gelator compounds.

Organo-gelator 3 (OG3):

[0128] The synthesis of 2,4-bis(3,7-dimethyloctylureido)toluene (DMOUT), with R = R1 = R2 = (R/S)-3,7-dimethyloctyl, can be done from 2,4-toluene-diisocyanate and racemic 3,7-dimethyl-octylamine, in a similar way such as mentioned above for OG1 and OG2. The product is a white solid. Racemic 3,7-dimethyl-octylamine is not routinely commercially available, and was prepared in two steps from racemic citronellol according to literature procedures (Tetrahedron, 61, 2005, 687-691). Similarly as for OG1, OG3 is composed of a mixture of organo-gelator compounds.

Organo-gelator 4 (OG4):

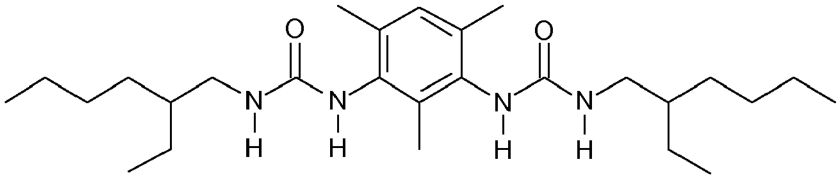
[0129] Organo-gelators EHUT (OG1) and DMHUT (OG2) have been mixed in a weight ratio of 4-to-1. The mixture was homogenized by dissolution in a mixture of chloroform and methanol, after which these solvents were removed again by vacuum evaporation. The product is a white solid.

Organo-gelator 5 (OG5):

[0130] In a similar way as described for the preparation of OG4 (cf. homogenization step), EHUT (OG1) and DMOUT (OG3) have been mixed in a weight ratio of 1-to-1.

Organo-gelators 6, 7 and 8 (OG6, OG7 and OG8):

[0131] The metha bis-urea benzene EHUM, i.e. 2,4-bis(2-ethyl hexylureido)-mesitylene, as drawn below, was prepared by activation of racemic 2-ethyl hexylamine with carbonyldiimidazole (CDI) and reaction of an excess of the resulting product with 1,3,5-trimethyl-2,4-diaminobenzene. Alternatively, the bis-urea EHUM can be prepared according to the document J.Phys.Chem.B, 2009, 113, 3360-3364.



EHUM

[0132] Due to the racemic nature of the starting material 2-ethyl hexylamine, EHUM is composed of a mixture of stereoisomers.

[0133] In a similar way as described for the preparation of OG4 (cf. homogenization step), the organogelators OG6, OG7 and OG8 were prepared by mixing EHUT (OG1) with EHUM in weight ratios of 60-to-40 (OG6), 70-to-30 (OG7) and 80-to-20 (OG8), respectively.

Preparation of organogels from OG1 to OG8

[0134] Organogel formation from OG1 to OG8 in oils as detailed in Table 1 was tested by stirring the oil and the organo-gelator at elevated temperatures (about 80 to 120 °C, typically 100 °C), overnight or during a few hours, and inspecting the solution after cooling down to room temperature.

Results

Successful organogel preparations.

[0135] OG1 was used to prepare clear, macroscopically homogeneous and stable 5 w/w% and 10 w/w% organogels in heptamethylnonane, Nynas S8,5 and Nyflex 800. Furthermore, 2.5 w/w% and 15 w/w% organogels were prepared in heptamethylnonane.

[0136] The vials containing these OG1-organogels can be kept up-side down and no flowing of the gel-solution is observed. In the time scale of hours, flow can be recorded, so the organogels are visco-elastic. The 5 w/w% organogel has elastic properties, while the 10 w/w% organogel is also elastic, but is harder in nature.

[0137] The 5 w/w% organogels from OG1 in heptamethylnonane and Nynas S8,5 have been monitored during at least 2 and a half years and remain stable, as inverting the vials does not result in flowing, the organogels remain clear, no precipitation or bleeding is observed, and stirring with a pipet in the organogel does not induce bleeding or precipitation.

[0138] Additionally, OG2, OG3, OG4 and OG5 were used to prepare clear, stable and homogeneous 5 w/w% organogels in heptamethylnonane, Nynas S8,5 and Nyflex 800, while OG3 was used to prepare a 5 w/w% organogel in Nynas T9 oil. Finally, OG6, OG7 and OG8 were used to prepare 5 w/w% organogels in Nynas S8,5.

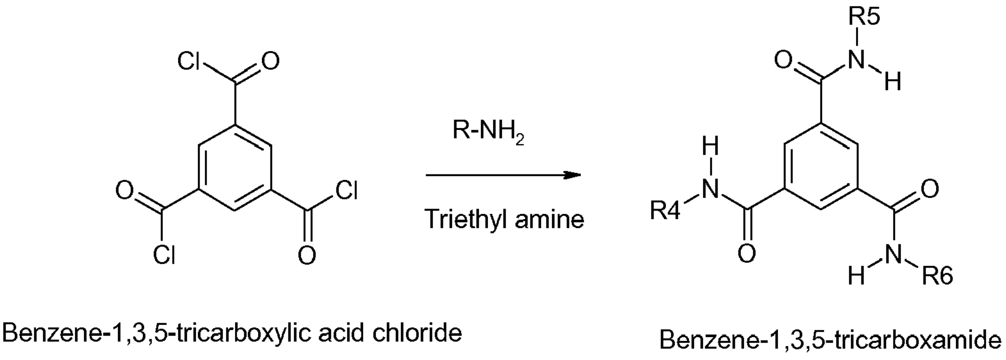
[0139] Typically, the stirred mixtures of the organo-gelators and the used oils already become swollen at room temperature, but stirring at elevated temperatures is required to quickly and conveniently obtain homogeneous gels.

Unsuccessful organogel preparations

[0140] The organo-gelators OG1 and OG3 could not be properly dissolved at elevated temperatures in the Nynas S100B or the Nynas T110 oil, not even at further heating to about 120 °C, and on cooling further precipitation occured, leaving inhomogeneous mixtures at room temperature.

Preparation of benzene-1,3,5-tricarboxamides (BTAs)

[0141] Benzene-1,3,5-tricarboxamides can be prepared according to the following scheme:



Organo-gelator 9 (OG9):

[0142] The synthesis of N,N',N"-tri-(3,7-dimethyloctyl)-benzene-1,3,5-tricarboxamide (DMO-BTA), with R = R4 = R5 = R6 = (R/S)-3,7-dimethyloctyl, can be done from benzene-1,3,5-tri-carboxylic acid chloride, racemic 3,7-dimethyloctyl amine and triethyl amine. See for a similar synthesis Chem.Lett., 2000, 292-293.

[0143] This organo-gelator is therefore composed of 4 different BTA-compounds: the S,S,S-, the S,S,R-, the S,R,R- and the R,R,R-isomer. These BTAs are examples of structures VII.

Organo-gelator 10 (OG10):

[0144] The synthesis of N,N',N"-tri-(3,7-dimethyloctyl)-benzene-1,3,5-tricarboxamide (SSS-DMO-BTA), with R = R4 = R5 = R6 = (S)-3,7-dimethyloctyl, can be done from benzene-1,3,5-tri-carboxylic acid chloride, (S)-3,7-dimethyloctyl amine and triethyl amine. See Chem.Lett., 2000, 292-293.

[0145] This organo-gelator is therefore composed of only 1 BTA-compound: the S,S,S-isomer.

Organo-gelator 11 (OG11):

[0146] Separately, six different benzene-1,3,5-tricarboxamides (BTAs) have been prepared with R4 = R5 = R6 = either n-butyl (C4-BTA), n-hexyl (C6-BTA), n-octyl (C8-BTA), n-decyl (C10-BTA), n-dodecyl (C12-BTA) or n-tetradecyl (C14-BTA). See for example Bull.Chem.Soc.Jpn., 61, 207-210, 1988.

[0147] Organo-gelator OG11 was then prepared by mixing C4-BTA, C6-BTA, C8-BTA, C10-BTA, C12-BTA and C14-BTA in an even molar ratio.

Organo-gelator 12 (OG12):

[0148] The organo-gelator OG12 was prepared by reacting benzene-1,3,5-tricarboxylic acid chloride with a mixture of primary amines R-NH_2 in the presence of triethylamine base.

[0149] Using this approach, a more or less statistical mixture of benzene-1,3,5-tricarboxamides (BTAs) can be obtained, with R4, R5 and R6 groups that may or may not be different from one another. In varying the molar ratio of the different primary amine R-NH_2 reactants, the population of the various BTA-molecular structures in the BTA-product mixture can be controlled.

[0150] For OG12, the five primary amine reactants n-hexyl amine, n-octyl amine, n-decyl amine, n-dodecyl amine and cyclohexyl amine were applied in a 1:1:1:1:4 molar ratio. After aqueous extraction into chloroform and purification by silica column chromatography, the isolated organo-gelator material was a white solid.

Organo-gelator 13 (OG13):

[0151] The organo-gelator was prepared in a similar way as OG12. Here, the five primary amine reactants n-hexyl amine, n-octyl amine, n-decyl amine, n-dodecyl amine and racemic 2-ethyl-hexyl amine were applied in a 1:1:1:1:4 molar ratio. The isolated organo-gelator was a white solid material.

Preparation of organogels from OG9 to OG13

[0152] In a similar way as for OG1 to OG8, organogel formation of OG9 to OG13 in oils as detailed in Table 1 was tested by stirring the oil and the organo-gelator at elevated temperatures (about 80 to 100 °C), overnight or during a few hours, and inspecting the solution after cooling down to room temperature.

Results

Successful organogel preparations

[0153] Stable, clear and homogeneous 5 w/w% organogels were prepared from organo-gelator OG9 in the heptamethylnonane, Nynas S8,5, Nyflex 800 and Nynas T9 oils.

[0154] Solutions of 5 w/w% OG11 in Nynas S8,5 and Nyflex 800 were clear and very highly viscous, while 5 w/w% solutions of OG12 and OG13 in Nynas S8.5 and Nyflex 800 gave clear gels.

Unsuccessful organogel preparations

[0155] The organo-gelators OG9 and OG10 could not be properly dissolved at elevated temperatures in the Nynas S100B or the Nynas T110 oil, and on cooling further precipitation occurred, leaving inhomogeneous mixtures at room temperature.

Other organo-gelators

Organo-gelator 14 (OG14): 1-benzyl-3-octyl urea

[0156] n-Octyl isocyanate (1.38g) was added to a solution of benzyl amine (1g) in toluene (50 mL). The reaction mixture was stirred overnight at room temperature under an inert nitrogen atmosphere, and was then diluted with hexane to induce precipitation of the white product. The solid was collected by filtration, was then washed with several portions of hexane, and dried.

Organo-gelator 15 (OG15):

[0157] 3,4-Dimethyldibenzylidene sorbitol (DMDBS, CAS 135861-56-2) can be bought from commercial sources, such as Allichem or APAC Pharmaceutical.

Organo-gelator 16 (OG16):

[0158] Dibenzylidene sorbitol (DBS, CAS 19046-64-1) can be bought from commercial sources, such as Allichem or APAC Pharmaceutical.

Organogel preparations from OG14, OG15 and OG16

[0159] Organo-gelators OG14, OG15 and OG16 could not be dissolved in the Nynas T110 or Nynas S100B oils. Stirring at room temperature showed no swelling or thickening of the mixture, and subsequent heating to about 100 °C, and thereafter over 100 °C (120 °C for OG14, and 180 °C for OG15 and OG16), did also not result in dissolution, leaving a suspension of organo-gelator and oil after cooling to room temperature. OG14 was tested on a 5 w/w% level, while OG15 and OG16 were tested on a 2 w/w% level.

Preparation of dielectric fluid comprising organogels and additional components

[0160] BHT (butyl hydroxytoluene; 2,6-di-tert-butyl-4-methylphenol, CAS 128-37-0), a known anti-oxidant and stabilizer, was stirred in the Nynas S8,5 oil at room temperature to give a 0.2 w/w% BHT solution. This solution and the appropriate amount of EHUT (OG1) was stirred at room temperature (swelling was observed), and then at about 100 °C for several hours. Cooling to room temperature produced a clear 5 w/w% dielectric fluid containing the BHT antioxidant. In the same way, a 5 w/w% organogel of OG1 in Nyflex 800 with 0.2 w/w% BHT was prepared. A clear dielectric fluid was as well obtained.

[0161] PIB (poly isobutylene/butene co-polymer; Indopol H-100 from BP, CAS 9003-29-6, viscosity 196-233 cSt at 99 °C, Mn = about 920) was stirred in Nyflex 800 at room temperature to produce a 0.25 w/w% PIB solution. This solution and the appropriate amount of EHUT (OG1) was stirred overnight at about 80 °C, and was then cooled to room temperature to produce a clear 5 w/w% dielectric fluid containing PIB and OG1-organogel.

Measurement of the gel point of a 5 w/w% organogel of EHUT (OG1) in Nyflex 800

[0162] The gel point is determined thanks to a Brookfield rheometer. The viscosity measurements are done from 4°C to 110°C at 0,5 °C/min under oscillation of 0,095 Hz and under a strain of 1%.

[0163] Figure 2 represents the storage modulus G' and the loss modulus G" curves as well as the complex viscosity respectively in function of the temperature of the 5 w/w% organogel of EHUT (OG1) in Nyflex 800.

[0164] The gel point of said organogel is the intersection of the G' curve and the G" curve, which is at 55-60°C.

[0165] Accordingly to the complex viscosity (η*) curve, the complex viscosity drop between 45 °C and 90°C is from about 800 Pa.s to less than 0,2 Pa.s, and a complex viscosity drop of more than three decades and more than 500 Pa.s is observed within 30 °C.

Measurement of the gel points of 5 w/w% organogels of OG6, OG7 and OG8 in the Nynas S8,5 oil

[0166] In a similar way as for the 5 w/w% gel of OG1 in Nyflex 800, the gel points of the 5 w/w% organogels of OG6, OG7 and OG8 in Nynas S8,5 oil were determined, giving the following results.

[0167] The OG6 (EHUT-to-EHUM = 60-to-40 by weight) gel displays a gel point at 86°C, while OG7 (EHUT-to-EHUM = 70-to-30 by weight) gives a gel point at 78°C and OG8 (EHUT-to-EHUM = 80-to-20 by weight) has a gel point of 71°C.

[0168] These results show that the gel point of a gel can be adjusted by mixing various alike organogelators.

[0169] The complex viscosity (η*) plateau, i.e. the complex viscosity at lower temperatures than the gel point, was observed at about 1000 to 2000 Pa.s for the three gels (OG6, OG7 and OG8), while a complex viscosity of 0.1 Pa.s was recorded at about 110 °C for said three gels. Furthermore, it was observed that the complex viscosity drop in the 3 prepared gels was more than 3 decades within 30 °C, and it was larger than 500 Pa.s.

Preparation of an impregnated electrically insulating layer from the 5 w/w% organogel of EHUT (OG1) in Nyflex 800

[0170] The impregnation step, well-known in the art, consists on impregnating the insulating paper tape after this latter is applied around the conductor.

[0171] More particularly, the insulating paper tape is wound around the conductor to form an electric cable and this latter is introduced into a vessel in presence of the organogel. The impregnation step into the vessel is done at a temperature superior to the gel point of the organogel (superior to 60°C). Said temperature range allows to optimize the impregnation from the organogel to the insulating paper. Then the organogel excess in the vessel is pumped through a heat exchanger and, after the vessel is cooled, an impregnated insulating paper tape is obtained.

[0172] The organo-gelator EHUT (OG1) can stably gelate non-polar Nynas oils, as the impregnated insulating paper tape does not show bleeding (i.e. bleeding is phase separation between an oil phase and a gel phase), even after standing for 6 months.

Measurement of the breakdown voltage of the impregnated electrically insulating layer from the 5 w/w% organogel of EHUT (OG1) in Nyflex 800

[0173] The breakdown voltage of the organogel is measured according to IEC 156 standard. The high breakdown properties of the insulating paper impregnated with organogel is obtained in using two electrodes with three layers of impregnated DC-paper of 70 micron each in between. A Haefely DC generator is used to apply voltage steps of 5 kV (during 1 minute) until a DC breakdown appears in the impregnated insulating paper tape. The DC breakdown is measured at 60 °C, and the DC breakdown occurs at a value superior to 200 kV/mm.

Claims

1. Electric cable comprising at least one conductor (10), and an electrically insulating layer impregnated with a dielectric fluid (12), said insulating layer (12) surrounding said conductor (10), the dielectric fluid comprising an organogel including an oil and an organo-gelator, **characterized in that** the oil is a non-polar oil with a flash point inferior or equal to 200°C.

2. Electric cable according to claim 1, **characterized in that** the flash point of the oil is superior or equal to 95°C.

3. Electric cable according to claim 1 or 2, **characterized in that** the oil has a content of aromatics (CA) inferior to 12% according to ASTM D 2140 standard.

4. Electric cable according to any of the preceding claims, **characterized in that** the oil is selected among a naphthenic oil, a paraffinic oil and an isoparaffinic oil, or mixtures thereof.

5. Electric cable according to any of the preceding claims, **characterized in that** the organo-gelator comprises a mixture of at least two organo-gelators compounds, and more preferably a mixture of at least two alike organo-gelators compounds.

6. Electric cable according to any of the preceding claims, **characterized in that** the organo-gelator is selected among urea-based compounds, a mixture of urea-based compounds, amide-based compounds, and a mixture of amide-based compounds, or mixtures thereof.

7. Electric cable according to claim 6, **characterized in that** the urea-based compound is selected among mono-ureas or a mixture of mono-ureas, bis-ureas or a mixture of bis-ureas, and tris-ureas or a mixture of tris-ureas.

8. Electric cable according to claims 6, **characterized in that** the urea-based compound is a bis-urea substituted toluene.

9. Electric cable according to claims 6, **characterized in that** is the amide-based compound is selected among di-amides or a mixture of di-amides, tri-amides or a mixture of tri-amides, and tetra-amides or a mixture of tetra-amides.

10. Electric cable according to claims 6, **characterized in that** is the amide-based compound is an aromatic tricarboxamide.

11. Electric cable according to claim 10, **characterized in that** the aromatic tricarboxamide is a benzene-1,3,5-tricarboxamide.

12. Electric cable according to any of the claims 6 to 11, **characterized in that** the urea-based compound is an asymmetric urea-based compound when said compound is substituted by at least two different R-groups.

13. Electric cable according to any of the claims 6 to 12, **characterized in that** the amide-based compound is an asymmetric amide-based compound when said compound is substituted by at least two different R-groups.

14. Electric cable according to any of the preceding claims, **characterized in that** the organogel has a gel point from 45 to 90°C.

15. Electric cable according to any of the preceding claims, **characterized in that** the organogel includes to the maximum 20% by weight of organo-gelator.

16. Electric cable according to any of the preceding claims, **characterized in that** it is an electric direct current transmission cable comprising a first semi-conducting layer (11) surrounding said conductor (10), the insulating layer (12) surrounding said first layer (11); a second semi-conducting layer (13) surrounding said insulating layer (12), and a protective sheath (15) surrounding said second layer (13).

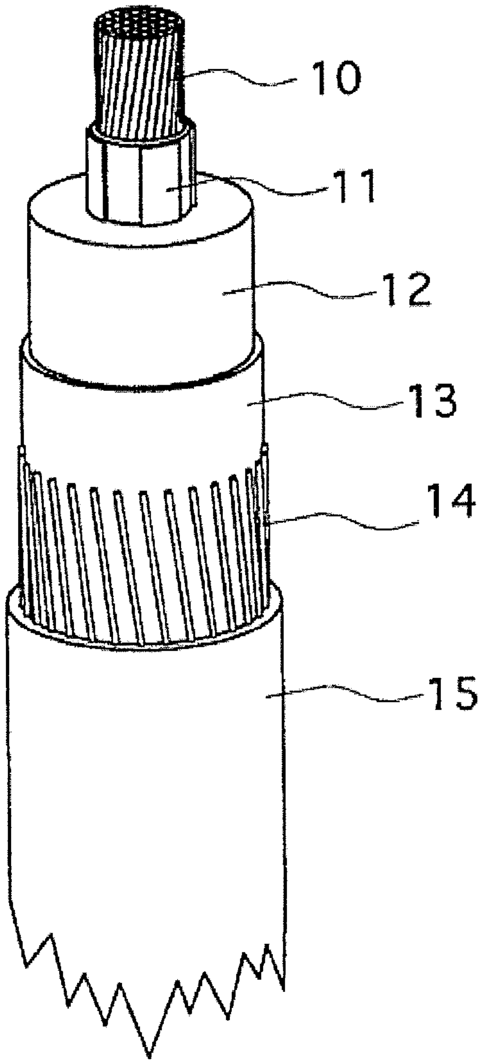


FIG.1

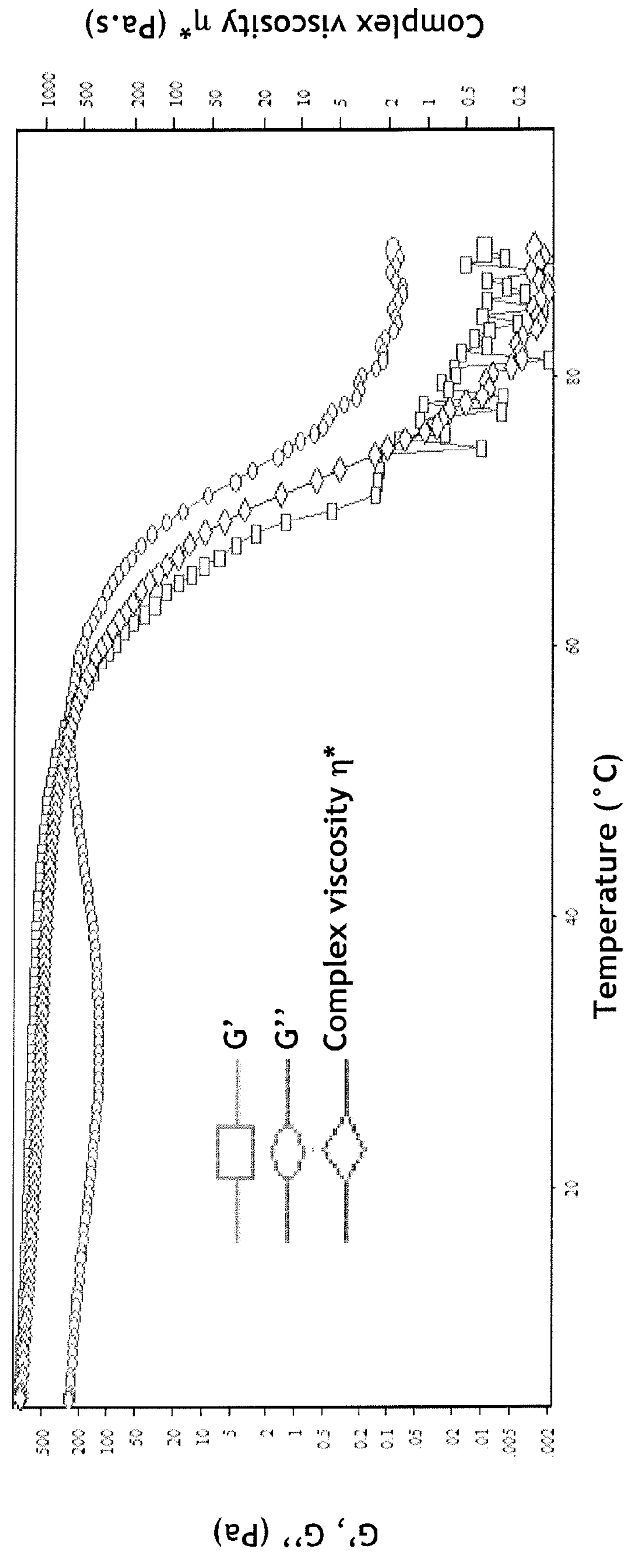

Complex viscosity η* (Pa.s)
1000
500
200
100
50
20
10
5
2
1
0.5
0.2
G'
G''
Complex viscosity η*
20
40
60
80
Temperature (°C)
500
200
100
50
20
10
5
2
1
0.5
0.2
0.1
.05
.02
.01
.005
.002
G', G'' (Pa)

FIG.2

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EUROPEAN SEARCH REPORT

Application Number
EP 10 16 3155

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