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(54) **AN ELECTRICALLY INSULATING COMPOSITION, A METHOD OF PRODUCING SUCH A COMPOSITION AND AN ELECTRIC POWER DEVICE PROVIDED WITH SUCH A COMPOSITION**

(57) An electrically insulating composition comprising a mixture of one or more oils, a thermal conductivity-increasing additive in a concentration of 0.1-10 wt% and consisting of particles of a material having higher thermal conductivity and higher density than the oil and having a size of less than 100 nm in at least one dimension. The composition also comprises a thickener agent bringing said mixture into a gel-state up to a predetermined temperature of at least 25°C at a pressure of 1 atmosphere.

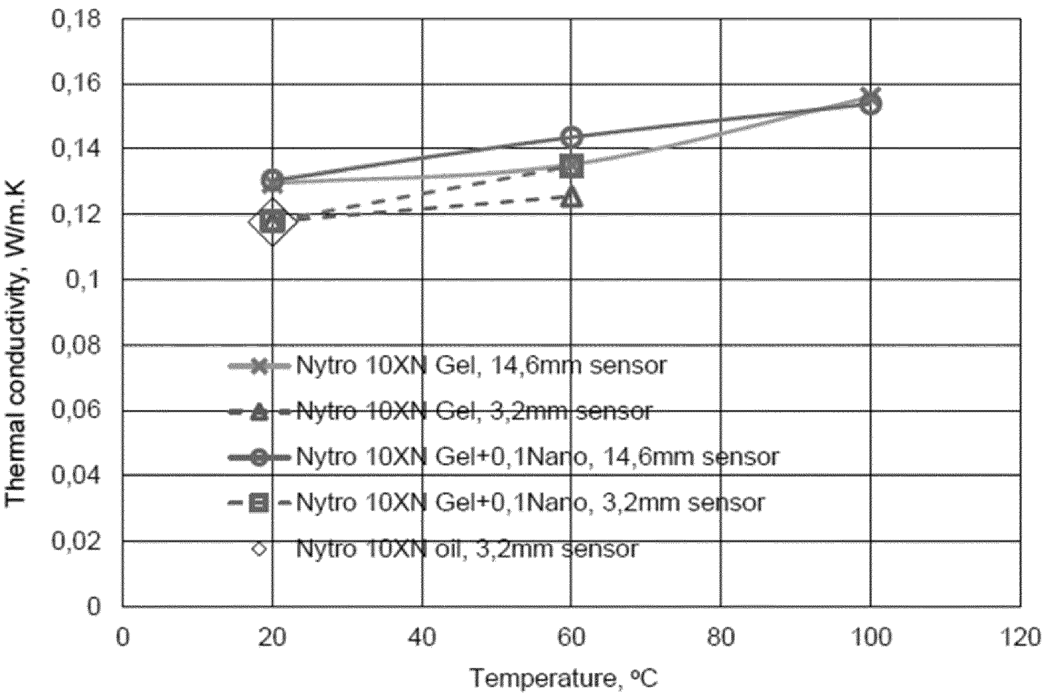

Fig. 1

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Description

TECHNICAL FIELD

[0001] The present invention relates to an electrically insulating composition comprising a mixture of one or more oils, a thermal conductivity-increasing additive in a concentration of 0.1-10 wt% and consisting of particles of a material having higher thermal conductivity and higher density than the oil and having a size of less than 100 nm in at least one dimension.
[0002] The present invention also relates to a method of producing such a composition, and an electric power device provided with an electric insulation comprising such a composition.
[0003] "Composition" may also be referred to as "material" if considered as more convenient.

BACKGROUND ART

[0004] It has been suggested by prior art, as for example by Jaime Taha-Tijerina et al, "Electrically Insulating Thermal Nano-Oils Using 2D Fillers", ACS NANO, Vol. 6, No. 2, pp. 1214-1220, 2012, to include thermal conductivity-increasing additives comprising two dimensional (2D) hexagonal Boron Nitride into mineral oils in order to improve the thermal conductivity thereof without having a too negative impact on the dielectric properties of the oil. It is suggested that such compositions be used as insulating oils in fields such as microelectronics, high voltage power transmission systems, automobiles solar cells, biopharmaceuticals, medical therapy/diagnosis and nuclear cooling.
[0005] However, in many applications, if no specific measure is taken, the additives in question will be subjected to sedimentation caused by gravitational forces, and will thus have a tendency to gather in predetermined regions of the electrical insulation that they form part of, thereby causing a correspond loss of thermal conductivity in other parts of the electrical insulation. This problem is not addressed by the mentioned prior art. One solution to such a problem may be to have any kind of stirrer mounted in the oil or to continually change position of the device in which the electrical insulation is installed in order to prevent such negative effects caused by gravitational forces. However, such solution would in many cases be unrealistic due to the complexity that they would introduce into the technical context they would be used in.
[0006] It an object of the present invention to present an electrically insulating composition that solves the above-mentioned problem in a cost-efficient way and which is a reliable solution.

SUMMARY OF THE INVENTION

[0007] The object of the present invention is achieved by means of the electrically insulating composition defined hereinabove and in the preamble of patent claim 1, which is characterised in that it comprises a thickener agent bringing said mixture into a gel-state up to a predetermined temperature of at least 25°C at a pressure of 1 atmosphere. Accordingly at temperatures up to at least 25°C such a composition will be in a gel-state that will prevent the nano-sized particles of the thermal conductivity-increasing additive from being subjected to sedimentation. The thickener agent preferably has a transition temperature corresponding to said predetermined temperature.
[0008] According to one embodiment, the particles of said thermal conductivity-increasing have a size of less than 10 nm in at least one dimension, and according to yet another embodiment they have a size of less than 1 nm in at least dimension. Accordingly, flake-shaped as well as needle shaped particles that have a size larger than 100 nm, or 10 nm, or 1 nm in at least one other dimension than said dimension are included in the claimed scope of protection of the claimed embodiments. According to one embodiment, the thermal conductivity increasing particles have a size less than 100 μm in any dimension, preferably less than 10 μm. Flake-shaped geometries of the particles may be referred to as two-dimensional (2D) flakes due to the very small thickness of the flakes.
[0009] According to one embodiment, the concentration of the thermal conductivity-increasing additive is above 0.5 wt%. According to one embodiment, the concentration of the thermal conductivity-increasing additive is above 1.0 wt%. According to one embodiment, concentration of the thermal conductivity-increasing additive is below 5 wt%. According to one embodiment the oil consists of mineral oil. According to one embodiment, the oil consists of iso-paraffinic oil. According to one embodiment the oil consists of a mineral oil and iso-paraffinic oil. Thus, mineral oil may be mixed with iso-paraffinic oil to obtain a suitable transition temperature of the composition with any given thickener. The composition, or the gel, may be referred to as a thermo-reversible gel, since it is able of reversing its state between liquid and gel-state depending on the temperature that it subjected to. The composition may comprise other agents such as an anti-oxidising agent, as long as they do not have a detrimental effect on the thermal conductivity, dielectric properties or other properties essential to the functionality of the composition as an electrical insulation and heat-transferring material in a given application. According to one embodiment, however, the composition consists solely of said oil, said thermal conductivity-increasing additive and said thickener agent as they are defined hereinabove and hereinafter.
[0010] According to one embodiment the thickener agent comprises at least one copolymer in an amount within the range of 0.1-10 wt% of the composition. According to one embodiment, the copolymer is present in an amount of at

least at least 1 wt% of the formed gel, and according to yet another embodiment to at least 2 wt% of the formed gel.

[0011] According to one embodiment, the composition comprises a thickener agent bringing said mixture into a gel-state up to a predetermined temperature of at least 80°C at a pressure of 1 atmosphere. According to one embodiment, the composition comprises a thickener agent bringing said mixture into a gel-state up to a predetermined temperature of at least 120°C at a pressure of 1 atmosphere.

[0012] According to one embodiment, said additive comprises particles of one or more of the following, alone or in combination: Fe3O4, Fe2O3, ZnO, Al2O3, SiO2, CeO2, TiO2, Kaolin, carbon black, SiC, BaTiO3, SrTiO3, MgO, graphene, and BN.

[0013] According to one embodiment, at least a major part of said thermal conductivity-increasing additive consists of Boron Nitride, BN. According to one embodiment, the thermal conductivity-increasing additive consists solely of Boron Nitride, BN. Boron Nitride has proven to be a very effective in increasing the thermal conductivity of oils, and while at the same time have little or no negative effect on the dielectric properties of the oil.

[0014] According to one embodiment, said Boron Nitride additive consists of hexagonal Boron Nitride, h-BN.

[0015] According to one embodiment, said particles of said additive consist of flakes that have a medium diameter in the range of 1-100 μm in one plane and a thickness in the range of 1-20 times the thickness of an atomic layer of the additive in question.

[0016] According to one embodiment, said particles of said additive consist of flakes having a medium diameter in the range of 1-3 μm in one plane and a thickness in the range of 1-10 times the thickness of an atomic layer of the additive in question.

[0017] According to one embodiment, the thickener comprises a styrene-based copolymer. According to one embodiment, the styrene-based copolymer has an average molecular weight of at least 200 kg/mole. According to one embodiment, the styrene-based copolymer has an average molecular weight of at least 300 kg/mol. According to one embodiment, the styrene-based copolymer has an average molecular weight of 400 kg/mol or 500 kg/mol.

[0018] According to one embodiment, said thickener agent comprises a tri-block copolymer. According to one embodiment, the tri-block polymer is present in an amount of at least 0.1 wt% of the formed gel, according to one embodiment to at least 1 wt% of the formed gel, and according to yet another embodiment to at least 2 wt% of the formed gel.

[0019] According to one embodiment, said tri-block copolymer consists of any of polystyrene-block-poly(ethylene-ethylene/propylene)-block-polystyrene (SEEPS), polystyrene-block-poly(ethylene/butylene)-block-polystyrene (SEBS), polystyrene-block-poly(ethylene/propylene)-block-polystyrene (SEPS), enhanced rubber segments (ERS) polymers, S-EB/S-S, alone or combination.

[0020] According to one embodiment, the molecular weight of the tri-block copolymer are from 10 kDa to about 1000 kDa.

[0021] According to one embodiment, said thickener agent comprises a di-block copolymer. According to one embodiment, the di-block polymer is present in an amount of at least 0.1 wt% of the formed gel, according to one embodiment to at least 1 wt% of the formed gel, and according to yet another embodiment to at least 2 wt% of the formed gel.

[0022] According to one embodiment, the di-block copolymer is polystyrene-block-poly(ethylene/propylene).

[0023] According to one embodiment, the thickener consists of said tri-block copolymer and said di-block copolymer.

[0024] According to one embodiment, the electrically insulating composition in the gel-state has a viscosity value of at least 1 Pa·s up to said predetermined temperature at a pressure of 1 atmosphere. According to one embodiment, the viscosity of the electrically insulating composition in the gel-state is at least 5 Pa·s. According to one embodiment the viscosity is at least 10 Pa·s. According to one embodiment, the viscosity is at least 100 Pa·s.

[0025] The object of the invention is also achieved by mean of a process of producing an electrically insulating composition according to the invention, comprising the steps of mixing the oil with the thickener agent at a temperature above a transition temperature of the thickener agent, thereafter cooling the mixture to a temperature below the transition temperature of the thickener agent such that a gel is formed, and thereafter adding the thermal conductivity-increasing additive and dispersing it into the gel. Sedimentation is thereby prevented also during the production of the composition, since the thermal conductivity-increasing additive is added when the mixture of the oil and the thickener agent is forming or has formed said gel.

[0026] The invention also relates to an electric power device provided with an electric insulation and characterised in that it the electric insulation comprises an electrically insulating composition according to the present invention.

[0027] According to one embodiment, the electric power device is any of a transformer, a transformer cable box, a transformer cable termination, a bushing, a tap changer, a switchgear and a robot.

BRIEF DESCRIPTION OF THE DRAWINGS

[0028] Fig. 1 is a diagram showing thermal conductivity against temperature for performed tests.

EXAMPLES

[0029] A tri-block copolymer consisting of polystyrene-b-poly(ethylene-ethylene/propylene)-b-polystyrene under the commercial name of Septon SEEPS 4099 was added in an amount of 1 wt% to a mineral transformer oil available under the commercial name of Nytro 10XN, commercialized by Nynäs Petroleum AB. The resulting mixture formed a gel that, at room temperature and a pressure of 1 atmosphere, had a viscosity of 100 Pa·s.

[0030] To one part of the resulting gel, flake-shaped particles of hexagonal Boron Nitride having a medium diameter size of 2 μm in their main extension plane and a thickness of 1-10 times the thickness of the Boron Nitride atomic layer were added in a concentration of 0.1 wt%. The Boron Nitride particles were evenly dispersed in the formed gel.

[0031] Samples of said gel containing said Boron Nitride additive and samples of said gel free from such additive were prepared, and were compared to each other with respect to their thermal conductivity at different temperatures. A previous measurement of the thermal conductivity of the oil itself was also included in the test as a reference point.

[0032] The thermal conductivity measurements of the samples were performed with hotdisk instrument. The measurement of the thermal conductivity was based on the transient plane source method.

[0033] Kapton (trade mark) sensors with a radius of 3.2 mm and 14.6 mm respectively were prepared from the above-mentioned gel samples. The measurements were carried out at temperatures of 20°C, 60°C and 80°C respectively. Five successive measurements were performed for each experiment. The standard model has been used for the measurement of the thermal conductivity of the samples. The results are presented in table 1 below, and are also illustrated by the enclosed drawing.

Table 1 Summary of results

Sample ID	Radius of sensor used in measurement	Temperature	Power, time	Cv	Thermal Conductivity, W/(mK),		Probing. Depth
		°C	mW, s	MJ/m3.K	average of 5 measurements	stdev of 5 measurements	mm
Nytro 10XN oil 1)	3,2 mm	20	N/A	1,66	0,118	N/A	N/A
Nytro 10XN Gel RT	14,6 mm	20	80,2	1,71	0,1295	0,0038	0,11
	3,2 mm			1.71	0,1178	0,0009	0,503
Nytro 10XN Gel 60°C	14,6 mm	60		1.75	0,1351	0,0046	0,717
	3,2 mm			1.75	0,1255	0,002	0,501
Nylro 10XN Gel 100°C	14,6 mm	100		1,8	0,1558	0,0013	0,707
Nytro 10XN Gel + 0,1Nano RT	14,6 mm	20		1,71	0,1304	0,0061	0.696
	3,2 mm			1.71	0,1179	0,0021	0,508
Nytro 10XN Gel + 0,1 Nano 60°C	14,6 mm	60		1.75	0,1435	0,0014	0,72
	3,2 mm			1.75	0,1348	0,0034	0,509
Nytro 10XN Gel + 0,1 Nano 100°C	14,6 mm	100		1,8	0,1538	0,0032	0.716

[0034] The accuracy of the sense roused in the measurements was examined by measuring samples with known conductivity (calibration), i.e. stainless cylinder sample and rubber sample powersil32. The comparison of measured values and the thermal conductivity is shown in table 2 below.

Table 2

Sample ID	Temperature	Diameter thickness	Power, time	Thermal Conductivity, W/(mK),		
	°C	mm	mw, s	Calibration value	Measured value	Error. %
Stainless steel	22	15/30	300,2	13.46	13,51+/- 0,01	0,4
Powersil32	22	7115	10,5	0,58	0,6141+/-0,0031	7

[0035] It could be concluded that the samples of the present invention, comprising the added Boron Nitride, showed an improved thermal conductivity at 60°C, while there was not any significant improvement at 20°C and at 100°C. It is concluded that a slightly higher amount of Boron Nitride would have resulted in improvement over a larger range of temperatures.

[0036] In the samples according to the invention no tendency of sedimentation of the added Boron Nitride particles has been observed.

Claims

1. An electrically insulating composition comprising a mixture of:

   - one or more oils,
   - a thermal conductivity-increasing additive in a concentration of 0.1-10 wt% and consisting of particles of a material having higher thermal conductivity and higher density than the oil and having a size of less than 100 nm in at least one dimension,

   and **characterised in that** it comprises a thickener agent bringing said mixture into a gel-state up to a predetermined temperature of at least 25°C at a pressure of 1 atmosphere.

2. An electrically insulating composition according to claim 1, **characterised in that** it comprises a thickener agent bringing said mixture into a gel-state up to a predetermined temperature of at least 80°C at a pressure of 1 atmosphere.

3. An electrically insulating composition according to claim 1 or 2, **characterised in that** said additive comprises particles of one or more of the following, alone or in combination: Fe_3O_4, Fe_2O_3, ZnO, Al_2O_3, SiO_2, CeO_2, TiO_2, Kaolin, carbon black, SiC, $BaTiO_3$, $SrTiO_3$, MgO, graphene, and BN.

4. An electrically insulating composition according to any one of claims 1-3 **characterised in that** at least a major part of said thermal conductivity-increasing additive consists of Boron Nitride, BN.

5. An electrically insulating composition according to any one of claims 1-4, **characterised in that** said thickener agent comprises a styrene-based copolymer.

6. An electrically insulating composition according to any one of claims 1-5, **characterised in that** said thickener agent comprises a tri-block copolymer.

7. An electrically insulating composition according to 6, **characterised in that** said tri-block copolymer consists of any of polystyrene-block-poly(ethylene-ethylene/propylene)-block-polystyrene (SEEPS), polystyrene-block-poly(ethylene/butylene)-block-polystyrene (SEBS), polystyrene-block-poly(ethylene/propylene)-block-polystyrene (SEPS), enhanced rubber segments (ERS) polymers, S-EB/S-S, alone or combination.

8. An electrically insulating composition according to claim 6 or 7, **characterised in that** the molecular weight of the tri-block copolymer are from 10 kDa to about 1000 kDa.

9. An electrically insulating composition according to any one of claims 1-8, **characterised in that** said thickener agent

comprises a di-block copolymer.

10. An electrically insulating composition according to claim 9, **characterised in that** the di-block copolymer is polystyrene-block-poly(ethylene/propylene).

11. An electrically insulating composition according to any one of claims 6-8 and any one of claims 9-10, **characterised in that** the thickener consists of said tri-block copolymer and said di-block copolymer.

12. An electrically insulating composition according to any one of claims 1-11, **characterised in that** the electrically insulating composition in the gel-state has a viscosity value of at least 1 Pa·s up to said predetermined temperature at a pressure of 1 atmosphere.

13. A process of producing an electrically insulating composition according to any one of claims 1-12, comprising the steps of mixing the oil with the thickener agent at a temperature above a transition temperature of the thickener agent, thereafter cooling the mixture to a temperature below the transition temperature of the thickener agent such that a gel is formed, and thereafter adding the thermal conductivity-increasing additive and dispersing it into the gel.

14. An electric power device provided with an electric insulation and **characterised in that** it the electric insulation comprises an electrically insulating composition according to any one of claims 1-12.

15. An electric power device according to claim 14, **characterised in that** it is any of a transformer, a transformer cable box, a transformer cable termination, a bushing, a tap changer, a switchgears and a robot.

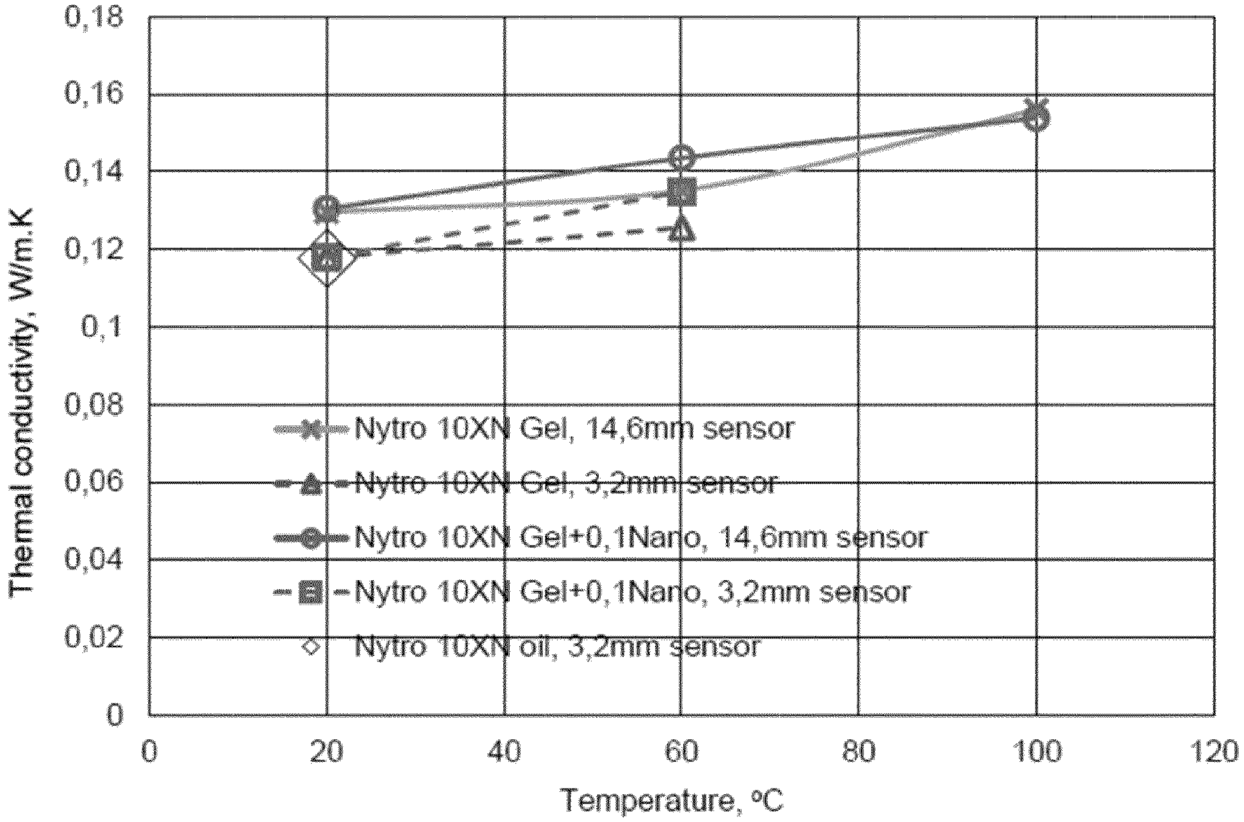
0,18
0,16
0,14
0,12
0,1
0,08
0,06
0,04
0,02
0
Thermal conductivity, W/m.K
0
20
40
60
80
100
120
Temperature, ºC
Nytro 10XN Gel, 14,6mm sensor
Nytro 10XN Gel, 3,2mm sensor
Nytro 10XN Gel+0,1Nano, 14,6mm sensor
Nytro 10XN Gel+0,1Nano, 3,2mm sensor
Nytro 10XN oil, 3,2mm sensor

Fig. 1

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EUROPEAN SEARCH REPORT

Application Number
EP 18 16 2537

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	WO 99/33067 A1 (ASEA BROWN BOVERI [SE]; KORNFELDT ANNA [SE]; FELIX JOHAN [SE]; BERGKVI) 1 July 1999 (1999-07-01) * page 1 - page 17; claims 1-50; examples 1, 7 * -----	1-15	INV. H01B3/22 ADD. H01B3/20
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TECHNICAL FIELDS SEARCHED (IPC)

H01B
C08K
C08L

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	23 August 2018	Marsitzky, Dirk

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 18 16 2537

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23-08-2018

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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