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

(11) EP 2 333 043 A1

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
15.06.2011 Bulletin 2011/24

(21) Application number: **09178180.7**

(22) Date of filing: **07.12.2009**

(51) Int Cl.:
C11D 11/00 (2006.01)
C11D 3/20 (2006.01)
C11D 3/30 (2006.01)
C11D 3/36 (2006.01)
C11D 3/43 (2006.01)
C11D 3/28 (2006.01)
C11D 3/33 (2006.01)

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

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Remarks:
A request for correction of the drawings has been filed pursuant to Rule 139 EPC. A decision on the request will be taken during the proceedings before the Examining Division (Guidelines for Examination in the EPO, A-V, 3.).

(54) Method for removing copper sulphide (cu2s) deposited onto cellulose-based material in transformer

(57) A method for removing copper sulphide (Cu_2S) deposited onto electrically insulating materials of components in an electrical apparatus, such as a transformer or a bushing, wherein normally present electrically insulating oil has been substantially removed, and on other surfaces of such apparatus, comprising the following steps: providing a chemical treatment solution comprising a polar aprotic solvent, and preferably a chelating agent being able of forming complexes with copper from the surface of Cu_2S deposited onto the insulating material, said chelating agent containing free electrons capable of forming a complexation with Cu, being at least a bidentate, but preferably a multidentate, i.e. being able of forming complexes with Cu from more than one point in the chelating agent, and having a solubility in the polar aprotic solvent of at least $5 \cdot 10^{-4}$ mol/L to allow extraction of copper by solvation of the formed copper-chelating complex; and optionally additional components, said chemical treatment solution being non-aqueous; subjecting the insulating material to the solution, preferably at a temperature of 30-130 °C, more preferably 50-90°C, for a predetermined time period, preferably 2 to 10 days, more preferably 3 to 7 days; and removing the chemical treatment solution from the insulating material.

Printed by Jouve, 75001 PARIS (FR)

Description

[0001] The present invention relates to a method of removing copper sulphide deposits present in electrically insulating layers in an electrical apparatus, such as transformers, bushings or the like, wherein a substantial amount of an electrically insulating oil, normally present in the electrical apparatus has been removed.

Background

[0002] Insulating oils are widely used in a number of apparatus in the field of electrical power transmission and electrical power generation, for example; power transformers, distribution transformers, tap changers, switchgear and reactors. Such electrically insulating oils often contain traces of reactive sulphur compounds, which may react with copper, forming copper sulphide (Cu_2S). Copper sulphide is insoluble in oil and may form deposits on surfaces and materials in contact with the electrically insulating oils inside the electrical apparatus. Copper sulphide is a conductor and the formation of a semi-conducting deposit on surfaces and materials in the electrical apparatus may degrade or disrupt the operation of the apparatus.

[0003] If the semi-conducting copper sulphide is deposited on the isolation material (usually cellulose material e.g. paper) used to cover the copper conductors in the electrical apparatus, this might lead to a degrading of the insulation properties of the isolation material which could lead to leak currents or short circuits. Semi-conducting copper sulphide deposits on surfaces of solid isolation materials, such as cellulose-based material, ceramic, polymer and composite inside the electrical apparatus may also create similar problems. Copper sulphide deposits can also occur on other surfaces in an electrical apparatus, such as pressboards, spacers and magnetic cores.

[0004] Attempts have been made to overcome the problem of formation of Cu_2S deposits by method for removing sulphur-containing compounds from the insulating oil, see e.g. WO2005115082. Further, attempts have been made to treat Cu_2S deposits already formed. WO2008024060 discloses a method of treating Cu_2S deposits with an oxidizing gas. However, these attempts have some undesirable side effects, e.g. in that oxidizing treatments are aggressive and may cause corrosion and degradation of the electrically insulating material.

[0005] There is a need for a method of removing Cu_2S deposits from insulating cellulose-based materials, such as winding paper, without significantly damaging the properties of the insulating material and causing corrosion of the metal parts contained in the transformer.

Summary of the invention

[0006] The present invention relates to a method for removing copper sulphide (Cu_2S) deposited onto electrically insulating materials of components in an electrical apparatus, such as a transformer or a bushing, wherein normally present electrically insulating oil has been substantially removed, and on other surfaces of such apparatus, comprising the following steps:

- providing a chemical treatment solution comprising a polar aprotic solvent, and preferably a chelating agent being able of forming complexes with copper from the surface of Cu_2S deposited onto the insulating material, said chelating agent containing free electrons capable of forming a complexation with Cu, being at least a bidentate, but preferably a multidentate, i.e. being able of forming complexes with Cu from more than one point in the chelating agent, and having a solubility in the polar aprotic solvent of at least $5 \cdot 10^{-4}$ mol/L to allow extraction of copper by solvation of the formed copper-chelating complex; and optionally additional components,
  said chemical treatment solution being non-aqueous, i.e. comprising an amount of water corresponding to the environmental humidity dissolved in the solvent;
- subjecting the insulating material to the solution, preferably at a temperature of 30-130 °C, more preferably 50-90°C, for a predetermined time period, preferably 2 to 10 days, more preferably 3 to 7 days; and
- removing the chemical treatment solution from the insulating material. By means of this method Cu_2S deposits can be removed from insulating cellulose-based materials, without significantly damaging the properties of the insulating material and causing corrosion of the metal parts contained in the transformer

[0007] The method may further comprise the steps of rinsing the insulating material with a polar aprotic solvent, and drying with a non polar solvent at a temperature of at least 15°C, at a pressure below atmospheric pressure. A chemical treatment solution comprising a chelating agent in an amount of 0,01-10 % by mol of the polar aprotic solvent, preferably 0,1 to 5 % by mol, most preferably 0,1 to 1 % by mol is suitable. The chemical treatment solution preferably comprises a chelating agent in an amount of at least 0,01 % by mol based upon the entire treatment solution.

[0008] Chelating agents, which have a solubility of at least $5 \cdot 10^{-4}$ mol/L in the polar aprotic solvent, preferably at least $5 \cdot 10^{-3}$ mol/L, most preferably at least $3 \cdot 10^{-2}$ mol/L as suitable for use in the present method.

[0009] The chelating agent preferably comprises at least one group which contains free electrons capable of bonding toward Cu, said group being amine, hydroxy, carboxylate, phosphorous containing, nitril or thio groups, and may be chosen among: amine based carboxylic acids with at least two carboxylic acid groups, e.g. ethylene diamine tetra acetic acid, ethylene diamine-N,N'-disuccinic acid, imino disuccinate, or nitrilo triacetic acid; salicylidene compounds, e.g. N, N'-Bis(salicylidene)ethylenediamine, or pyridylazo naphthol; amine-based compounds such as triaza molecule, e.g.Triazabicyclo dec-5-ene; multidentate carboxylic acids, e.g. oxalic acid or succinic acid; carbazones and thiocarbazones, e.g. diphenyl thiocarbazone (dithizone); phosphinic acid derivatives, e.g. diisooctylphosphinic acid; porphyrin, tetrabenzoporphyrin, tetraazaporphyrine and phthalocyanine-type molecules. A preferred chelating agent is N,N'-Bis(salicylidene)ethylenediamine.

[0010] The polar aprotic solvent suitably has a flash point above 50 ˚C, preferably above 80 ˚C, and is advantageously dimethyl sulfoxide, isobutyl sulfoxide, N-methyl pyrrolidone, N-ethyl pyrrolidone, or propylene carbonate, hexyl glycol diacetate, isoamyl propionate, benzonitrile, dimethyl formamide.

[0011] In the method the chemical treatment solution may be fed to a space in which the insulation material to be treated is located, and wherein the chemical treatment solution is sprayed through spray nozzles over the surface to be treated, such that it flows over the surface having the Cu_2S deposit, and is collected at the bottom of the space, and is recirculated to the spray nozzles. The chemical treatment solution may alternatively be fed to a space in which the insulation material to be treated is located, such that said insulation material is substantially immersed in chemical treatment solution, and that the chemical treatment solution is circulated through said space, by taking out treatment solution through an outlet opening arranged in the space, leading it through a circulation conduit, and returning it through an inlet opening arranged in the space, while keeping the amount of chemical treatment solution inside the space at a level ensuring that the insulation material is substantially immersed in the solution.

Detailed description

[0012] Conducting copper sulphide deposited on the isolation material (usually cellulose material e.g. paper) used to cover the copper conductors in an electrical apparatus, might lead to degradation of the insulation properties of the insulating material, which could lead to leak currents or short circuits. Therefore, such copper sulphide deposits on surfaces and materials in the electrical apparatus may degrade or disrupt the operation of the apparatus.

[0013] The present invention relates to a method for removing copper sulphide (Cu_2S) deposited onto electrically insulating materials of components in an electrical apparatus, such as a transformer or a bushing, wherein normally present electrically insulating oil has been substantially removed, and on other surfaces of such apparatus. The method comprises the steps of providing a chemical treatment solution, subjecting the insulating materials having the Cu_2S deposits to the solution at a predetermined temperature and time, and removing the chemical treatment solution.

[0014] The electrically insulating material may be a cellulose material, e.g. winding paper, or solid isolation materials, such as cellulose-based material, ceramic, polymer and composite. It is important to ensure that the electrically insulating material of the electrical apparatus is not damaged by the treatment, and that metal parts are not affected by corrosion. Some of the electrical apparatus, like transformers, cables, or bushings contain oil impregnated paper. For insulating cellulose-based materials, such as e.g. paper it is important to maintain the degree of polymerisation of the component contained in the insulating paper, as well as mechanical, electrical and dielectric properties.

[0015] It has been found within the present invention that a non-aqueous chemical treatment solution comprising a polar aprotic solvent is effective for removing Cu_2S deposits from electrically insulating materials. By non-aqueous solution in this context is meant a solution having a water content corresponding only to the environmental air humidity partially solved in the solvent, and therefore being dry enough not to cause swelling of the cellulose based material. The maximum water content will depend upon the choice of solvent and may be approximately 10 000 - 30 000 ppm (by weight) in the liquid solution, or approximately 1 % by weight, and up to approximately 3 % by weight. By using a non-aqueous treatment solution for the treatment of the Cu_2S deposits the mechanical and electrical properties of the cellulose-based insulating material (paper) can be maintained since swelling of the paper is avoided, and thus the hydrogen bonds between the fibers in the paper are maintained. By avoiding swelling of the paper, it can also be ensured that the geometry of the paper will not change from its original state, and thus there is no risk of deformation of the electrical structure. Acidic or basic aqueous solutions may be harmful also to ceramic insulating materials, due to dissolution of certain elements in the ceramic, making it more porous, more fragile and with inferior electrical properties.

[0016] A polar aprotic solvent is capable of solubilizing chelating agents due to its polarity, and does not cause swelling of cellulose-based materials and hydrolysis due to being aprotic. It has been found that the polar aprotic solvent can be used for removing Cu_2S deposits without addition of chelating agent. The treatment with polar aprotic solvent without addition of chelating agent may need a higher temperature or a longer treatment time in order to successfully remove the Cu_2S deposits. Treatment with polar aprotic solvents (e.g. N-methyl pyrrolidone) at temperatures of 75 ˚C or higher, preferably 90 ˚C or higher, has proven to be quite effective for removal of Cu_2S deposits. The polar group of the polar aprotic solvent will have some chemical interaction with the copper. Preferably, the polar aprotic solvent has a flash point above 50 ˚C, preferably above 80 ˚C. A high flash point allows for enough efficiently kinetics. The reaction temperature should preferably be kept below its flash point of the solvent so as to decrease the risk of explosion of a flammable solvent in contact with air. Preferred polar aprotic solvents selected from the group consisting of dimethyl sulfoxide, isobutyl sulfoxide, N-methyl pyrrolidone, N-ethyl pyrrolidone, or propylene carbonate, hexyl glycol diacetate, isoamyl propionate, benzonitrile, and dimethyl formamid.

[0017] The chemical treatment solution used within the method of the present invention preferably comprises a chelating agent, which is able of forming complexes with copper from the surface of Cu_2S deposited onto the isolation material. The chelating agent should contain free electrons capable of forming a complexation with Cu and should be at least a bidentate, but preferably a multidentate, i.e. being able of forming complexes with Cu from more than one point in the chelating agent. Further the chelating agent should have a solubility in the polar aprotic solvent of at least $5 \cdot 10^{-4}$ mol/L to allow extraction of copper by solvation of the formed copper-chelating complex. If desired additional components may optionally be included. The chemical treatment solution should preferably not comprise oxidizing agents, since that may cause undesired corrosion on metal parts of the electrical apparatus and partial degradation of paper and other cellulose-based materials. Strong oxidants could also damage some polymers and composites.

[0018] Chelating agents used for the treatment are soluble enough in the solvent to not stick on the surface of the paper. The copper in the Cu_2S deposit is very mobile, which means that when there is a depletion of copper from the top layer of the deposit, a concentration gradient of copper throughout the thickness of the deposit is created, which will be a driving force for the migration of copper from inner layers of the deposit to an outer layer where the copper is scavenged by the chelating agent and the solvent.

[0019] The chemical treatment solution preferably comprises a chelating agent in an amount of 0,01-10 % by mol of the polar aprotic solvent, in order to increase the removal efficiency as compared to the solvent without addition of chelating agent. A content of chelating agent above 0,01 % by mol, decreases the time needed for the reaction. A content of chelating agent above 10 % by mol does not add so much to the kinetics of the reaction and is therefore less economic. The chemical treatment solution more preferably comprises 0,1 to 5 % by mol, most preferably 0,1 to 1 % by mol, in order to obtain an efficient treatment at reasonable temperatures and time periods. The concentration may vary with the type of chelating agent, the number of wrapped paper layers to be treated in the electrical apparatus, and the temperature.

[0020] The chemical treatment solution advantageously comprises a chelating agent in an amount of at least 0,01 % by mol based upon the entire treatment solution, in order to increase the removal efficiency as compared to the solvent without addition of chelating agent.

[0021] The chelating agent preferably has a solubility of at least $5 \cdot 10^{-4}$ mol/L in the polar aprotic solvent, preferably at least $5 \cdot 10^{-3}$ mol/L, most preferably at least $3 \cdot 10^{-2}$ mol/L, in order to be able to effectively extract the copper by salvation of the formed copper-chelating agent complex.

[0022] As indicated above, the chelating agent comprises at least one group containing free electrons capable of bonding toward Cu, suitably amine, hydroxy, carboxylate, phosphorous containing, nitril or thio groups.

[0023] It has been found within the present invention that the chelating agents listed below are particularly suitable for use the chemical treatment solution:

- amine based carboxylic acids with at least two carboxylic acid groups, e.g. ethylene diamine tetra acetic acid, ethylene diamine-N,N'-disuccinic acid, imino disuccinate, or nitrilo triacetic acid;
- salicylidene compounds, e.g. N,N'-Bis(salicylidene)ethylenediamine, or pyridylazo naphthol;
- amine-based compounds such as triaza molecule, e.g.Triazabicyclo dec-5-ene;
- multidentate carboxylic acids, e.g. oxalic acid or succinic acid;
- carbazones and thiocarbazones, e.g. diphenyl thiocarbazone = dithizone;
- phosphinic acid derivatives, e.g. diisooctylphosphinic acid;
- porphyrin, tetrabenzoporphyrin, tetraazaporphyrine and phthalocyanine-type molecules.

[0024] Among these N,N'-Bis(salicylidene)ethylenediamine (Salen) is particularly preferred as excellent results have been obtained using this chelating agent. N,N'-Bis(salicylidene)ethylenediamine is a relatively mild chelating agent, which is also easy to remove from the treated equipment.

[0025] Before initiating the treatment for removing Cu_2S deposits from the insulating material, any insulating oil contained in the electrical apparatus is substantially drained. Cleaning of the surfaces is typically not necessary.

[0026] The insulating materials to be treated are subjected to the chemical treatment solution described above at a predetermined temperature, suitably 30-130 ˚C. At temperatures below 30˚C, the reaction is too slow. While above 130˚C the insulating material may be damaged. Above 130˚C the degradation rate of paper may become significant, with the treatment times that are needed. If the temperature is too low (below 30˚C) the kinetic of extraction would be too slow. The treatment temperature is more preferably 50-90˚C. The treatment is performed for a predetermined time period, preferably 2 to 10 days, more preferably 3 to 7 days. The time period depends mostly on the efficiency of the chelating agent, the temperature, the number of wrapped paper layer to treat, and the chelating agent concentration. A short treatment time is advantageous from an economical point of view. Cellulose-based insulating materials such as winding paper should not be subjected to too high temperatures for a too long time. Treatment at temperatures of 130 ˚C or lower for up to ten days will not harm the insulating material.

[0027] After the treatment, the chemical treatment solution is removed from the insulating material. The method may include steps of rinsing the insulating material with a polar aprotic solvent, and drying with a non polar solvent at a temperature of at least 15˚C, at a pressure below atmospheric pressure. Drying can also be performed with non polar solvent in vapour phase. By rinsing or cleaning with a polar aprotic solvent residual chelating agent can be effectively removed. The chelating agent which is partly polar may crystallize in the insulation material. By effectively removing the chelating agent, the risk of electrical failure after refilling with oil, caused by local electric stress due to different dielectric constants between such crystals and the oil in the equipment is reduced. Drying with a nonpolar solvent allows removal of the polar solvent, and leads to creation of an azeotrope with any water present in the electrical apparatus, so that any water can be removed at a temperature below 100˚C, thus preventing ageing of the insulating material.

[0028] The insulating material is suitably located inside a space enclosing the insulating material during the treatment. Typically, the treatment is performed by feeding chemical treatment solution directly to the electrical apparatus, after having substantially removed any normally present electrically insulating oil. Thus, the space in which the insulting material is located during treatment is the electrical apparatus. Cleaning of the insulating material surface is not necessary before subjecting it to the treatment solution.

[0029] The chemical treatment solution may be fed to the space in which the insulation material to be treated is located, e.g. the electrical apparatus, such that said insulation material is substantially immersed in chemical treatment solution. By immersing the insulating material in the treatment solution it can be ensured that all parts of the insulating material surface area is in contact with the treatment solution, such that effective removal of Cu_2S deposits can be achieved. The chemical treatment solution is preferably circulated through the space, in order to enhance the rate of Cu_2S deposit removal, by taking out treatment solution through an outlet opening arranged in the space, leading it through a circulation conduit, and returning it through an inlet opening arranged in the space, while keeping the amount of chemical treatment solution inside the space at a level ensuring that the insulation material is immersed in the solution. Conveniently, the outlet opening is arranged at or near the bottom of the space, and the inlet opening is arranged at or near the top of the space, so that the treatment solution is taken out in the lower part of the space, and is pumped through the circulation conduit to the upper part of the space. However, other locations for the inlet and outlet openings may be desired, depending e.g. on how the insulating material is oriented inside the space.

[0030] Alternatively, the chemical treatment solution can be sprayed through spray nozzles over the surface to be treated, such that it flows over the surface having the Cu_2S deposit, and is collected at the bottom of the space, and is recirculated to the spray nozzles. By spraying, a smaller amount of treatment solution is required for performing the method, thus decreasing the expenses for chemical treatment solution. In order to obtain effective treatment, several spray nozzles may be arranged such that all parts of the surface to be treated will come into contact with the treatment solution.

Examples

[0031] The following abbreviations will be used in the description of the experiments:

NMP: N-methyl pyrrolidone
Salen: N,N'-Bis(salicylidene)ethylenediamine
DBDS: dibenzyl disulfide
Cu_2S: copper sulfide

1. Sample preparation

1.1 Process to deposit copper sulphide (Cu_2S) on kraft paper

[0032] A corrosive oil was prepared by mixing 1 liter of Nytro10 XN and 1L of Nytro 10GBN oil (both from Terna, Italy) with 2.7 g of 2,6-ditert-butyl-4-methphenol (antioxidant) and adding 440 mg of dibenzyldisulfide, such that the total content of DBDS in the oil mixture was approximately 350 ppm (the initial content in Nytro 10GBN is approximately 200 ppm, Nytro 10XN does not contain DBDS).

[0033] Three windings made of two layers of kraft paper wrapped around neat copper pieces having a length of about 15 cm were immersed in the corrosive oil mixture in test tubes. The test tubes were degassed under vacuum over night, and then placed in a heating block at 120 ˚C. A gas flow of 2% of oxygen in nitrogen at a rate of approximately 17 mL/min was continuously injected through the oil over a period of about 500 h. The collected copper sulphide (Cu_2S) deposited papers were washed in cyclohexane to remove oil and were allowed to dry in air. The amount of copper and sulphur deposited on the paper was measured by ICP-OES, as described below in the characterization section: the amount of copper measured was 65 to 67 μg/cm^2 and the amount of sulphur measured was 13 to 15 μg/cm^2 .

[0034] In some experiments described below the Cu_2S deposited paper was treated with chemical solutions as it is, while in other experiments the Cu_2S deposited paper was wrapped around a piece of copper as described below to evaluate the efficiency of the chemical treatment to diffuse through paper layers.

1.2 Wrapping Cu_2S deposited paper around neat copper

[0035] A strip of Cu_2S deposited paper (180 mm long and 20 mm broad) was tightly wrapped around a piece of neat copper (from an electrical winding, surface: 10x9 mm^2 and 1 mm thick) to form 4 to 8 layers of paper, in such a way that the Cu_2S deposit was facing toward the copper wire on every turn. The lateral paper edges were sewn together with cotton thread to avoid free contact of the copper with the treatment solution.

1.3 Impregnation in oil

[0036] Some of the paper samples were impregnated in oil (Nytro 10XN) under vacuum over night to minimize residual air bubbles. The paper was then removed from the oil, and excess oil was removed into an absorbing paper.

2. Characterizations

[0037] 2.1 Concentrations of copper and sulphur deposited on the paper were measured by ICP-OES (Inductively Coupled Plasma with Optical Emission Spectrometers) Varian "Vista-Pro CCD simultaneous" with radial plasma. The copper reference standard was Accu Trace 1000 mg/mL of Cu in water and 2 % HNO^3 (according to standard NIST SRM# 928). The sulphur reference standard was purchased from Alfa Aesar (Specpure®) : 1000 mg/mL of sulphur in water and 1002 mg/L of $(NH_4)_2SO_4$ (according to standard NIST SRM 3154). The ICP equipment was calibrated with 4 pieces of reference paper (no Cu_2S deposit) of 8 cm^2 surface area each, which were cut into pieces and placed in 4 Teflon tubes. In each tube, both copper and sulphur reference standards were added at the following concentrations 0; 2; 6; and 20 mg/mL. In each tube 8 mL of concentrated nitric acid (HNO_3) was added.

[0038] To check the calibration curve a fifth Teflon tube was prepared with 8 cm^2 of reference paper cut into pieces, 10 mg/mL of both Cu and S standard references and 8 mL of concentrated nitric acid.

[0039] The paper samples to be analyzed (with Cu_2S) were of 25 to 33 cm^2 surface area, cut in pieces, and placed into Teflon tubes with 8 mL of concentrated nitric acid.

[0040] All the tubes were then placed in a microwave oven of 600 W power with the following temperature steps: heating from 23 °C to 130 °C in 60 min, holding at 130 °C for 15 min and cooling down back to 23 °C in about 50 min. The resulting solutions became completely transparent. All the tubes were then diluted up to 25 mL with demineralised water and ready to be analyzed by ICP-OES.

[0041] 2.2 Concentrations of copper, sulphur and iron dissolved in the solutions, after treatment of Cu_2S deposited paper, were measured by ICP-OES (Inductively Coupled Plasma with Optical Emission Spectrometers) Varian "Vista-Pro CCD simultaneous" with radial plasma. The copper reference standard was Accu Trace 1000 mg/mL of Cu in water and 2 % HNO_3 (according to standard NIST SRM# 928). The sulphur reference standard was purchased from Alfa Aesar (Specpure®) : 1000 mg/mL of sulfur in water and 1002 mg/L of $(NH_4)_2SO_4$ (according to standard NIST SRM 3154). The iron reference standard was purchased from Alfa Aesar (Specpure®): 1000 mg/mL of Fe in water and 2-5 % HNO_3 (according to standard NIST SRM# 3126a).

[0042] The ICP equipment was calibrated with 5 reference samples prepared in 10 mL graduated flasks such that each flask contained 2 mL of NMP and each of the three copper, sulphur and iron reference standards at the following concentrations: 0; 3; 10; 30 and 100 mg/mL. In each flask, 0,5 mL of concentrated nitric acid was added and the solutions were diluted up to a volume of 10 mL with demineralised water.

[0043] To confirm the calibration curve a sixth graduated flask was prepared with 2 mL of a solution that had been used for treatment of Cu_2S deposit (already containing a measured amount of copper, sulphur and iron), into which all three standards (Cu, S and Fe) were added at a concentration of 10 mg/mL. 8 mL of concentrated nitric acid was added and the solution was diluted up to 10 mL with demineralised water. After analysis by ICP it was checked that the values of Cu, S and Fe did increased by 10 mg/mL.

[0044] The treatment solutions having unknown amounts of dissolved copper, sulphur and iron were prepared as follows: 2 mL of the solution to be analyzed was added in a 10 mL graduated flask with 0,5 mL of concentrated nitric acid and the solution was diluted up to a volume of 10 mL. Each prepared sample was then ready to be analyzed by ICP-OES.

2.3 Measurement of degree of polymerization in paper

[0045] This measurement was performed according to the IEC 60450 standard, i.e. measurement of the average viscometric degree of polymerization of new and aged cellulosic electrically insulating materials.

2.4 Surface resistance

[0046] Surface resistance was measured using a concentric ring probe geometry consisting of a center measuring electrode (outer diameter = 2 mm) and an outer voltage ring electrode (inner diameter of the electrode = 4 mm), which leads to a measuring distance of 1 mm. A Keithley 617 electrometer was used for voltage supply and resistance measurement. The relationship between surface resistivity and the surface resistance for cylindrical electrodes geometry is given by the following equation:

$$\rho = R\frac{2\pi}{\ln\frac{r_1}{r_2}}$$

With

ρ= surface resistivity (Ohm)
R= surface resistance (Ohm)
r_1= inner radius of the outer ring electrode
r_2= outer radius of the center electrode

3. Examples of Removal of Cu_2S

[0047] For each reaction of the examples described below, the solvent was degassed under nitrogen for 30 min prior to being added into the reaction flask.

3.1 Removal of Cu_2S with polar aprotic solvent (NMP)

Example 1 - NMP at 90 ˚C, unwrapped paper

[0048] A piece of Cu_2S deposited paper of 16.6 cm^2, prepared as described above, was immersed in a solution containing 10 mL of NMP such as all the paper was immersed in the solvent. The flask was capped and heated to 90 ˚C for 7 days. The solution was then removed from the flask and the paper was washed three times with NMP followed by 3 times with cyclohexane. After drying the paper at 90 ˚C for 2h, the surface resistance of the paper was measured at five measurement points and the surface resistivity was calculated to in average $12\cdot10^{10}$ Ohm. As a comparison, the Cu_2S deposited paper before treatment was $15\cdot10^3$ Ohm. Kraft paper free from Cu_2S contamination presented a surface resistivity over $2\cdot10^{12}$ Ohm.

Example 2- NMP at 70 ˚C, unwrapped paper

[0049] The same treatment as above in Example 1 was repeated, but with a treatment performed at 70 ˚C for 7 days. This treatment did not lead to an increase of the surface resistivity of the Cu_2S-deposited paper as compared to the reference untreated sample.

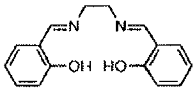
3.2 Removal of Cu_2S with polar aprotic solvent (NMP) and chelating agent

Example 3 - Salen as chelating agent at 70 ˚C on wrapped paper

[0050] A Cu_2S deposited paper wrapped around a copper piece to form 8 layers (total Cu_2S deposited surface 30.06 cm^2, and a total copper weight of approximately 2.34 mg), as described in the sample preparation above, was immersed in a solution of 4.942 mL of NMP containing 0.1061g of salen. The flask was heated to 70 ˚C for 7 days. The solution was then removed from the flask, and the wrapped sample was washed 3 times with hot NMP (70 ˚C) and then 5 times with hot cyclohexane (70 ˚C). The wrapped sample was dried at 70 ˚C over night and unwrapped to measure surface resistance of each layer (see **table 1**). The amount of the copper and sulphur dissolved in the solution after treatment is 280 and 30 wt% respectively of the initial copper and sulphur amount measured in the initial Cu_2S deposited paper (ICP measurements). The excess of dissolved copper originates from the dissolution of copper from the neat copper wire placed in the middle of the sample. The remaining sulphur amount in the treated paper is 70 wt% of the initial sulphur contained in the Cu_2S deposited paper.

[0051] Figure 1a illustrates the copper having paper wrapped around it (cross-section), and Figures 1b and 1c illustrate the Cu_2S deposit on the paper, before (Fig 1b) and after (Fig 1c) treatment, where the copper piece is shown in one end of the wrapping paper and the outermost paper layer is located at the other end of the paper.

Table 1: Surface resistivity calculated from the surface resistance measurements performed on the wrapped paper treated with Salen as chelating agent at 70 ˚C.

Sample	Layer #	Surface Resistivity before treatment (Ohm)	Surface Resistivity after treatment (Ohm)
Cu_2S deposited paper wrapped around copper wire treated wiith salen : 	1	$18\cdot10^{3}$	$5\cdot10^{11}$
	2	$9\cdot10^{3}$	$5\cdot10^{11}$
	3	$14\cdot10^{3}$	$4\cdot10^{11}$
	4	$20\cdot10^{3}$	$5\cdot10^{11}$
	5	$15\cdot10^{3}$	$4\cdot10^{11}$
	6	$18\cdot10^{3}$	$5\cdot10^{11}$
	7	$12\cdot10^{3}$	$2\cdot10^{11}$
	8	$17\cdot10^{3}$	$17\cdot10^{3}$ (in contact with Cu wire)
Reference Kraft paper (no Cu_2S contamination) wrapped around copper wire	1	$> 2\cdot10^{12}$	$> 2\cdot10^{12}$
	2	$> 2\cdot10^{12}$	$> 2\cdot10^{12}$
	3	$> 2\cdot10^{12}$	$> 2\cdot10^{12}$
	4	$> 2\cdot10^{12}$	$> 2\cdot10^{12}$
	5	$> 2\cdot10^{12}$	$> 2\cdot10^{12}$
	6	$> 2\cdot10^{12}$	$> 2\cdot10^{12}$
	7	$> 2\cdot10^{12}$	$> 2\cdot10^{12}$
	8	$> 2\cdot10^{12}$	$> 2\cdot10^{12}$

[0052] As can be seen from Table 1 the treatment is very efficient, since the surface resistivity is substantially increased.

Example 4 - Salen as chelating agent at 90 ˚C on wrapped paper:

[0053] A Cu_2S deposited paper wrapped around a copper piece to form 8 layers (total Cu_2S deposited surface : 29,75 cm^2, and a total copper weight of approximately 1,98 mg), as described in the sample preparation above, was immersed in a solution of 7,050 mL of NMP containing 0.1007g of salen. The flask was heated to 90 ˚C for 7 days. The solution was then removed from the flask, and the wrapped sample was washed 3 times with hot NMP (90 ˚C) and then 5 times with hot cyclohexane (90 ˚C). The wrapped sample was dried at 90 ˚C over night and unwrapped to measure surface resistance on each layer:

Table 2: Surface resistivity calculated from the surface resistance measurements performed on the wrapped paper treated with Salen as chelating agent at 90 ˚C.

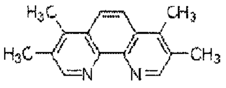
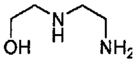
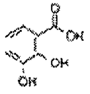
Sample	**Layer#**	**Surface Resistivity before treatment (Ohm)**	**Surface Resistivity after treatment (Ohm)**
Cu_2S contaminated Kraft paper wrapped around copper wire	1	$11 \cdot 10^3$	$> 2 \cdot 10^{12}$
	2	$13 \cdot 10^3$	$> 2 \cdot 10^{12}$
	3	$17 \cdot 10^3$	$> 2 \cdot 10^{12}$
	4	$22 \cdot 10^3$	$> 2 \cdot 10^{12}$
	5	$21 \cdot 10^3$	$> 2 \cdot 10^{12}$
	6	$16 \cdot 10^3$	$> 2 \cdot 10^{12}$
	7	$15 \cdot 10^3$	$30 \cdot 10^6$
	8	$20 \cdot 10^3$	$20 \cdot 10^3$ (in contact with Cu wire)

[0054] This Example shows that the use of Salen can restore the surface resistivity to a level corresponding to wrapping paper without Cu_2S deposits.

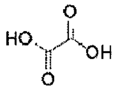
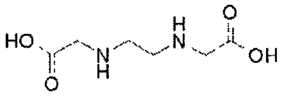
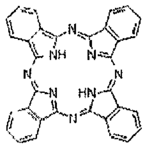
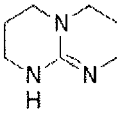
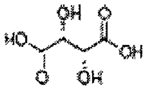
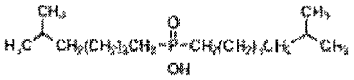
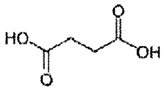
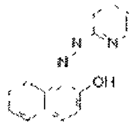
Example 5 - Removal of Cu_2S with other chelating agents at 70 ˚C on unwrapped paper:

[0055] Cu_2S deposited papers of 4 cm length and 2 cm width were immersed in solution containing the following components listed in **Table 3.** The flasks were heated to 70 ˚C for 28h. The solution was then removed from the flask, and the paper was washed 3 times with NMP followed by 3 times with cyclohexane. The paper samples were dried at 70 ˚C over night and the obtained surface resistivity values are given in **Table 3.** At these given condition parameters, salen, nitrilotriacetic acid and diphenylthiocarbazone give the best results.

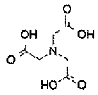
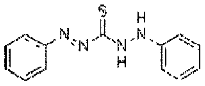
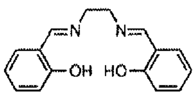
Table 3: Experimental parameters and surface resistivity calculated from the surface resistance measurements performed on the unwrapped paper treated with various chelating agents at 70 ˚C.

Chelatant	**Weight of chelatant (g)**	**Volume of solvent (mL)**	**Surface resistivity (Ohm) after treatment.**
Tetramethyl-phenanthroline 	0.0631	4.048	$30 \cdot 10^6$
Aminoethylamino-ethanol or N-(2-Hydroxyethyl)-ethylendiamine 	0.0278	4.048	$3 \cdot 10^9$
2,3-Dihydroxybenzoic acid 	0.0412	4.048	$4 \cdot 10^9$

(continued)

Chelatant	Weight of chelatant (g)	Volume of solvent (mL)	Surface resistivity (Ohm) after treatment.
Oxalic acid 	0.0240	4.048	$90 \cdot 10^9$
Ethylenediamine-N,N'-diacetic acid 	0.0475	4.048	$100 \cdot 10^9$
Phthalocyanine 	0.1387	4.048	$100 \cdot 10^9$
Triazabicyclo dec-5-ene 	0.0375	4.048	$300 \cdot 10^9$
Tartaric acid 	0.0401	4.048	$400 \cdot 10^9$
Diisooctylphosphinic acid 	0.0845	4.048	$600 \cdot 10^9$
Succinic acid 	0.0315	4.048	$1 \cdot 10^{12}$
Pyridylazo naphthol 	0.0672	4.048	$1 \cdot 10^{12}$

(continued)

Chelatant	Weight of chelatant (g)	Volume of solvent (mL)	Surface resistivity (Ohm) after treatment.
Nitrilotriacetic acid (IDRANAL I) 	0.0510	4.048	> $2 \cdot 10^{12}$
Diphenylthiocarbazone (Dithizone) 	0.0684	4.048	> $2 \cdot 10^{12}$
Salen 	0.0684	4.048	> $2 \cdot 10^{12}$

4. Impact of the treatment solution onto metal plates

[0056] An iron metal plate of 2 cm^2 surface and 0,35 mm thick coated with enamel on its upper and lower surface but not in the edges was immersed in a solution of 5.641 mL of NMP containing 0.0482 g of salen. The flask was heated to 90 ˚C for 7 days. The solution was then removed from the flask, and the metal plate was washed 3 times with hot NMP (90 ˚C) and then 5 times with hot cyclohexane (90 ˚C). The plate was dried at 90 ˚C over night, the surface resistance of the metal plate was measured to $5 \cdot 10^{11}$ Ohm. The reference untreated metal plate shows a surface resistance of the same value: $5 \cdot 10^{11}$ Ohm. The dissolved iron in the solution after treatment was measured to 0.00081 g/mL. No corrosion was observed on the neat edge by optical microscope.

5. Impact of the treatment solution on the degree of polymerization (DP) of the paper

[0057] The degree of polymerization of papers treated according to the above procedures were measured by viscosimetry:

- Reference kraft paper before any treatment: DP= 1175 ±25
- Kraft paper aged according to the Cu_2S deposition procedure (see sample prepartion above), but where no neat copper was in contact with the paper, so that the paper does not contain Cu_2S deposit: DP = 910 ±25.
- Cu_2S deposit paper which was treated according to Example 3 (4.942 mL of NMP containing 0.1061g of salen, at 70 ˚C for 7 days): DP= 890 ±25.

[0058] Comparing the paper before and after the Cu_2S removal treatment shows that not significant decrease of the DP was observed.

Claims

1. A method for removing copper sulphide (Cu_2S) deposited onto electrically insulating materials of components in an electrical apparatus, such as a transformer or a bushing, wherein normally present electrically insulating oil has been substantially removed, and on other surfaces of such apparatus, comprising the following steps:

- providing a chemical treatment solution comprising a polar aprotic solvent, and preferably a chelating agent being able of forming complexes with copper from the surface of Cu_2S deposited onto the insulating material, said chelating agent containing free electrons capable of forming a complexation with Cu, being at least a

bidentate, but preferably a multidentate, i.e. being able of forming complexes with Cu from more than one point in the chelating agent, and having a solubility in the polar aprotic solvent of at least $5 \cdot 10^{-4}$ mol/L to allow extraction of copper by solvation of the formed copper-chelating complex; and optionally additional components;
said chemical treatment solution being non-aqueous, i.e. comprising an amount of water corresponding to the environmental humidity dissolved in the solvent;
- subjecting the insulating material to the solution, preferably at a temperature of 30-130 ˚C, more preferably 50-90˚C, for a predetermined time period, preferably 2 to 10 days, more preferably 3 to 7 days;
- removing the chemical treatment solution from the insulating material.

2. The method of claim 1, further comprising the steps of rinsing the insulating material with a polar aprotic solvent, and drying with a non polar solvent at a temperature of at least 15˚C, at a pressure below atmospheric pressure.

3. The method of claim 1 or 2, wherein the chemical treatment solution comprises a chelating agent in an amount of 0,01-10 % by mol of the polar aprotic solvent, preferably 0,1 to 5 % by mol, most preferably 0,1 to 1 % by mol.

4. The method of claim 3, wherein the chemical treatment solution comprises a chelating agent in an amount of at least 0,01 % by mol based upon the entire treatment solution.

5. The method of claim 3 or 4, wherein chelating agent has a solubility of at least $5 \cdot 10^{-4}$ mol/L in the polar aprotic solvent, preferably at least $5 \cdot 10^{-3}$ mol/L, most preferably at least $3 \cdot 10^{-2}$ mol/L.

6. The method of any one of claims 3-, wherein chelating agent comprises at least one group which contains free electrons capable of bonding toward Cu, said group being amine, hydroxy, carboxylate, phosphorous containing, nitril or thio groups.

7. The method of any one of claims 3-6, wherein chelating agent is chosen among:

- amine based carboxylic acids with at least two carboxylic acid groups, e.g. ethylene diamine tetra acetic acid, ethylene diamine-N,N'-disuccinic acid, imino disuccinate, or nitrilo triacetic acid;
- salicylidene compounds, e.g. N,N'-Bis(salicylidene)ethylenediamine, or pyridylazo naphthol;
- amine-based compounds such as triaza molecule, e.g.Triazabicyclo dec-5-ene;
- multidentate carboxylic acids, e.g. oxalic acid or succinic acid;
- carbazones and thiocarbazones, e.g. diphenyl thiocarbazone = dithizone;
- phosphinic acid derivatives, e.g. diisooctylphosphinic acid;
- porphyrin, tetrabenzoporphyrin, tetraazaporphyrine and phthalocyanine-type molecules.

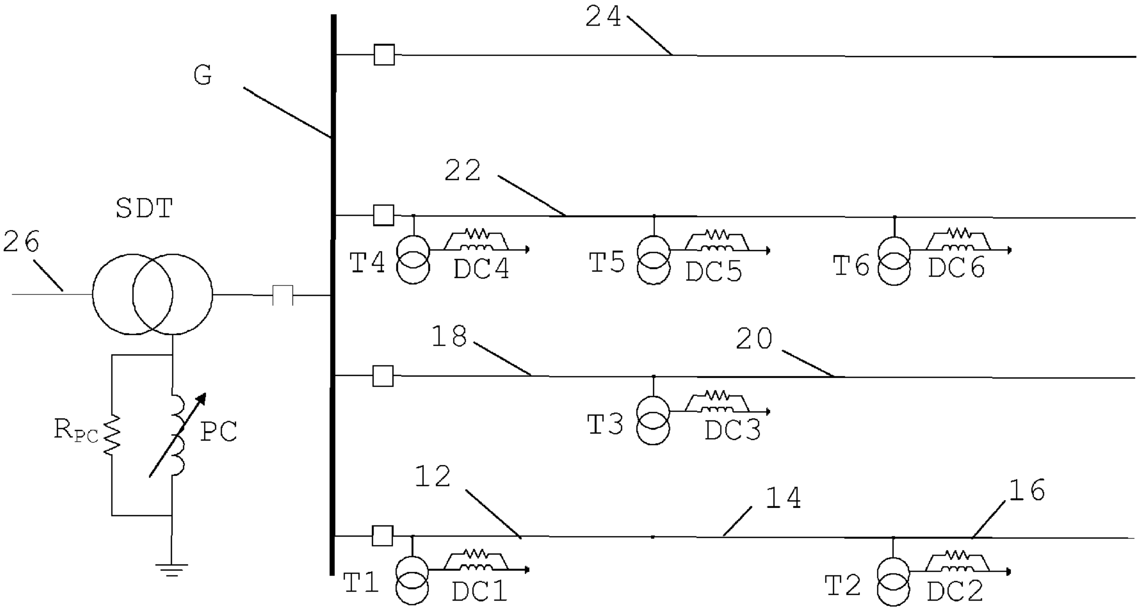
8. The method of any one of claims 3-7, wherein chelating agent is N,N'-Bis(salicylidene)ethylenediamine.

9. The method of any one of claims 1-8, wherein the polar aprotic solvent has a flash point above 50 ˚C, preferably above 80 ˚C.

10. The method of any one of claims 1-9, wherein the polar aprotic solvent is selected from the group consisting of dimethyl sulfoxide, isobutyl sulfoxide, N-methyl pyrrolidone, N-ethyl pyrrolidone, or propylene carbonate, hexyl glycol diacetate, isoamyl propionate, benzonitrile, dimethyl formamide.

11. The method of any one of claims 1-10, wherein the chemical treatment solution is fed to a space in which the insulation material to be treated is located, and wherein the chemical treatment solution is sprayed through spray nozzles over the surface to be treated, such that it flows over the surface having the Cu_2S deposit, and is collected at the bottom of the space, and is recirculated to the spray nozzles.

12. The method of any one of claims 1-10, wherein the chemical treatment solution is fed to a space in which the insulation material to be treated is located, such that said insulation material is substantially immersed in chemical treatment solution, and that the chemical treatment solution is circulated through said space, by taking out treatment solution through an outlet opening arranged in the space, leading it through a circulation conduit, and returning it through an inlet opening arranged in the space, while keeping the amount of chemical treatment solution inside the space at a level ensuring that the insulation material is substantially immersed in the solution.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DC5
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16
T1
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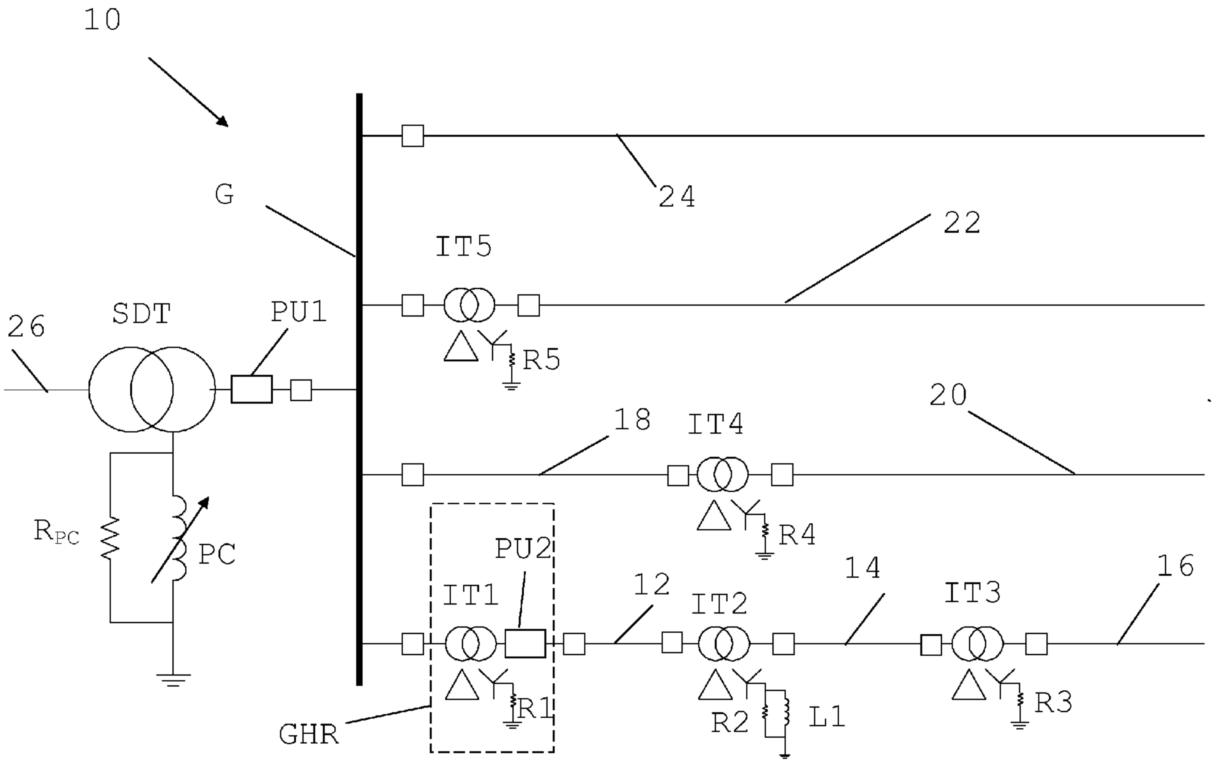
DC2

FIG. 1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IT4
R4
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R3

FIG. 2

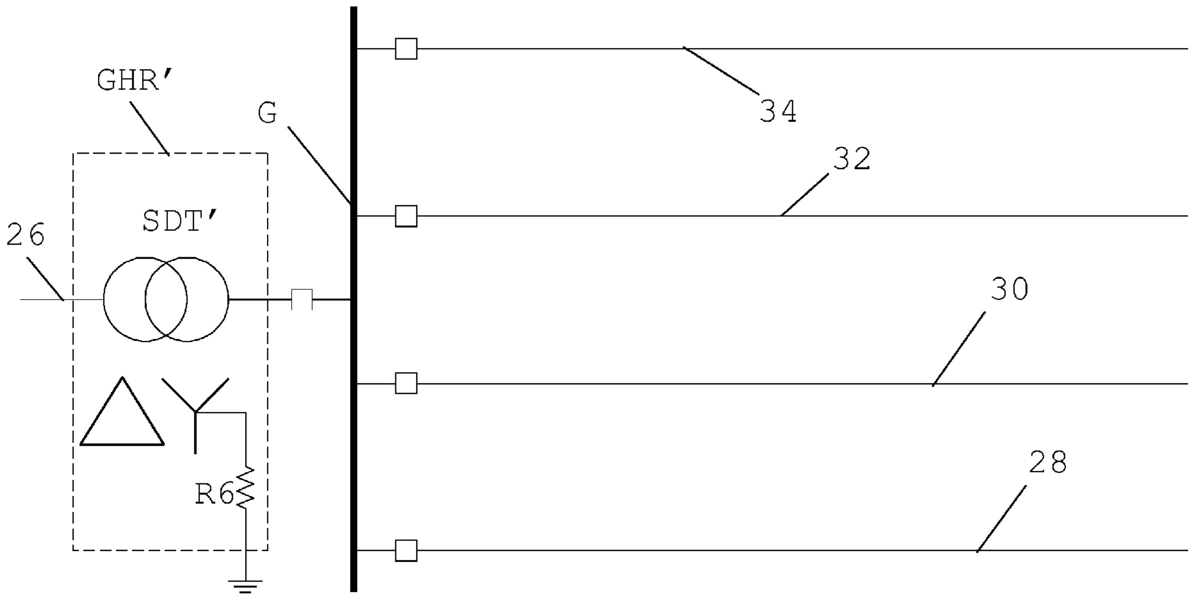

FIG. 3

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EUROPEAN SEARCH REPORT

Application Number
EP 09 17 8180

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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A	WO 2008/024061 A1 (ABB RESEARCH LTD [CH]; GUSTAFSSON KARIN [SE]; LEANDERSSON ROBERT [SE]) 28 February 2008 (2008-02-28) * claims 1-20 * -----	1-12	
A	CLAES BENGTSSON ABB POWER TECHNOLOGIES AB LUDVIKA: "Oil corrosion and cu2s deposition in power transformers" CIGRE MOSCOW SYMPOSIUM, 1 January 2005 (2005-01-01), pages 1-5, XP003018682 * the whole document * -----	1-12	TECHNICAL FIELDS SEARCHED (IPC) C11D

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	7 May 2010	Richards, Michael

CATEGORY OF CITED DOCUMENTS

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07-05-2010

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