A method for removing sulfur from insulating oil. The oil is exposed to at least one sulfur scavenging material and at least one polar sorbent.
METHOD FOR REMOVAL OF REACTIVE SULFUR FROM INSULATING OIL

FIELD OF THE INVENTION

[0001] The present invention relates to methods and devices for treatment of oil containing reactive sulfur-containing compounds.

BACKGROUND OF THE INVENTION

[0002] Insulating oils are used in power transformers, distribution transformers and reactors. These oils often contain traces of reactive sulfur compounds, especially thiols (a.k.a. mercaptans). The reactive sulfur compounds may react with copper, forming copper mercaptides. The copper mercaptides can decompose further, leading to the formation of copper(I) sulfide, Cu$_2$S. The net reactions could be as shown below:

\[ \text{Cu}_2\text{O}+2\text{RSH}\rightarrow 2\text{CuSR}+\text{H}_2\text{O} \]
\[ 2\text{CuSR}\rightarrow \text{Cu}_2\text{S}+2\text{R} \]

where —SH is a thiol group (or mercaptan), —R is an alkyl group.

[0003] Other sulfur organics, especially sulfides, can also be active, either by direct reaction with copper or via conversion to thiols.

[0004] Cu$_2$S is insoluble in oil and may form deposits, especially on surfaces of cellulose material. Once deposition of Cu$_2$S has started the process is believed to be self-catalytic. The surface selectively adsorbs the reactants and intermediates, and also catalyzes the decomposition of intermediates to Cu$_2$S.

SUMMARY OF THE INVENTION

[0005] A method for removing sulfur-containing compounds from insulating oil is provided. The method includes exposing the oil to at least one sulfur scavenging material and exposing the oil to at least one polar solvent.

[0006] A system for removing sulfur-containing compounds from insulating oil is also provided. The system includes a pump to pump the oil through the system, at least one sulfur scavenger containing device, and at least one sulfur solvent containing device.

[0007] Further objectives and advantages, as well as the structure and function of exemplary embodiments will become apparent from a consideration of the description, drawings, and examples.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] The foregoing and other features and advantages of the invention will be apparent from the following, more particular description of an exemplary embodiment of the invention, as illustrated in the accompanying drawings wherein like reference numbers generally indicate identical, functionally similar, and/or structurally similar elements.

[0009] FIG. 1 illustrates an embodiment of a winding with spacers separating turns;

[0010] FIG. 2 represents a graph that illustrates a typical voltage transient generated by line or commutation fault;

[0011] FIG. 3a represents a schematic diagram illustrating one embodiment of a system according to the present invention;

[0012] FIG. 3b represents a schematic diagram illustrating another embodiment of a system according to the present invention;

[0013] FIG. 4 represents a schematic diagram illustrating a further embodiment of a system according to the present invention; and

[0014] FIG. 5 represents a schematic diagram illustrating another embodiment of a system according to the present invention.

DETAILED DESCRIPTION OF EMBODIMENTS OF THE INVENTION

[0015] Embodiments of the invention are discussed in detail below. In describing embodiments, specific terminology is employed for the sake of clarity. However, the invention is not intended to be limited to the specific terminology so selected. While specific exemplary embodiments are discussed, it should be understood that this is done for illustration purposes only. A person skilled in the relevant art will recognize that other components and configurations can be used without parting from the spirit and scope of the invention.

[0016] Power transformers, distribution transformers and reactors usually include an insulation system consisting of oil and cellulose. These two components have been used for a long time due to their relatively low price and good performance. The dielectric strength of such an insulation system is strongly dependent on its insulating properties.

[0017] During operation of such devices, copper(II)sulfide may be deposited on the cellulose of the insulation. This can lower the initiation level for partial discharges (PD). With deposition in areas of the windings, with high electrical stresses and under certain operating conditions, especially the abundance of transients, PD activity may lead to degradation of the solid insulation and ultimately to dielectric breakdown.

[0018] An example of an area where the electrical stress is high is between turns in the windings. This turn-to-turn insulation is typically built up by conductor insulation, which may include paper wrapping, for example, and sometimes also spacers separating the conductors from each other. FIG. 1 illustrates one example of a winding with spacers separating the turns. The conductors are insulated with paper wrapping. Both the conductor insulation and the spacers will then be very sensitive for copper(I)sulfide deposits.

[0019] From time to time, transformers are subjected to voltage transients coming from lightning, so-called lightning impulse. Other sources of voltage transients are, for example, commutation faults or line faults in high voltage direct current (HVDC) systems. FIG. 2 is a graph that illustrates a relationship between voltage and time, showing a typical voltage transient generated by line or commutation fault. These faults are especially dangerous due to that the repetitive nature of these faults. In some installations, hundreds of commutation faults and line faults can occur within a typical 24 hour period.

[0020] Reactions leading to Cu$_2$S formation can be prevented or suppressed by removing or reducing active copper and sulfur containing components. However, conventional insulating oil processing techniques, such as reconditioning and reclaiming have little or no effect. Reclaiming, which is typically carried out by treating the oil with a sorbent for polar contaminants, such as Fullers earth or alumina, has as its primary purpose to remove oxidation products from aged oil, and restore it to a condition similar to that of new oil. Copper mercaptides and other copper-organic compounds can be
removed with this process. However, the effect on mercaptan content is limited, and that on content of sulfides and disulfides even less.

[0021] The present invention provides both methods for removal of reactive sulfur from oil as well as apparatus for carrying out removal processes. These potentially harmful reactive sulfur compounds, which can include sulfur organics can be removed and/or converted to more easily removed compounds by treating the oil with material with a high reactivity towards sulfur. Such materials with a high reactivity toward sulfur may be referred to as sulfur scavengers. Reaction with sulfur scavengers can convert the sulfur containing compounds into more easily removed compounds. For example, the reactive sulfur containing compounds may be converted to insoluble metal sulfides, or oil-soluble metal mercaptides. These mercaptides could then be captured by polar sorbent materials, e.g. of the types used in normal oil reclaiming. Accordingly, the oil may also or alternatively be treated with at least one polar sorbent material.

[0022] The oil may be exposed to the sulfur scavenger(s) and/or polar solvent(s) in any order. Also, the oil may be exposed to the sulfur scavenger(s) and/or polar solvent(s) more than one time. The exposure may take place in any order. For example, the oil may be exposed to the scavenger(s) twice and then to the solvent(s). A combination of one or more sulfur scavenger materials and one or more polar sorbent materials can be used. The best results may be obtained if the last exposure of the oil to scavenger(s) is followed by exposure to polar sorbent(s). This can remove any oil soluble products produced by the exposure to the scavenger. However, good results may be obtained with any of the treatment schemes herein.

[0023] Exposure to scavengers and sorbents may be carried out in a number of different ways. For example, the scavenger(s) and/or sorbent(s) may be exposed to the oil. According to another example, the scavenger(s) and/or sorbent(s) may be contained in a vessel, such as a column. The oil may be exposed to the scavenger(s) and/or sorbent(s) in other ways as well.

[0024] One way to realize this combined treatment is to first let the oil flow through a device with a large area of such materials that act as sulfur scavengers. For example, the oil may be directed through a column filled with one or more sulfur scavengers described below. Then, the oil may flow through a vessel filled with a polar sorbent material. Unsoluble reaction products, such as copper sulfide, may be retained on the scavenger material. On the other hand, soluble reaction products, such as copper mercaptides, may be transported with the oil to the sorbent material, where they are adsorbed.

[0025] If the exposure in done by suspending the sulfur scavengers and sorbent materials in oil the exposure time is from a few minutes to several hours. For example, the exposure time may be about 1 minute to about 10 hours. Typically, the exposure time is about 5 minutes to about 60 minutes. This time may include exposure to all sorbents and scavengers. Alternatively, the oil may be exposed to scavenger(s) for such a period of time and then sorbent(s) for such a period of time. In fact, if the oil is exposed to scavengers and/or sorbents a number of times, each exposure period may be for a length of time as described above. The exact time period may depend upon the level of reactive sulfur-containing compounds in the untreated oil and/or the reduction in the level of such compounds that is desired to achieve.

[0026] If the exposure is carried out in a flow system with the reagents contained in columns typical flow rates would be from about 500 to about 5000 liters/hours, with typical contact times from a fraction of a minute to several minutes. For example, the contact time may be about 20 seconds to about 10 minutes.

[0027] In order to more efficiently remove sulfur-containing compounds that the scavenger(s) are less efficient at removing, the oil may be exposed to one or more scavengers. The exposure to scavenger(s) may take place prior to exposing the oil to the sorbent(s). Also, one or more scavengers may be combined with one or more sorbents in one vessel. In fact, the each scavenger and/or sorbent could be in a separate container. One or more scavengers may be in one container and one or more sorbents may be in one container. The arrangement of the scavengers and sorbents may depend upon their nature. For example, since elemental copper and copper oxide have different selectivity their combined effect is sometimes greater than that of only one of them. In cases where the sorbent material is reactivated instead of discarded after use, at least some of the sulfur scavenger materials may have to be kept in separate containers, since they may be affected by the reactivation. Such a situation is illustrated with the embodiment shown in FIG. 3a, which is discussed below in greater detail. To permit the scavenger(s) to more efficiently remove sulfur-containing compounds, the scavenger(s) may be provided in a manner that provides a large surface area including the scavenger(s).

[0028] The large surface area may be accomplished in a variety of different ways. For example, the scavenger(s) may be provided on a substrate having a high surface area. Additionally or alternatively, the scavenger(s) may be provided in a form that has a high surface area.

[0029] One or more scavengers may be utilized according to the present invention. The scavenger may include any material that can remove or convert the desired sulfur-containing compounds from the oil into more polar compounds. Examples of sulfur scavengers can include elemental copper and other metals that easily form sulfides, such as ferrous metals, for example Fe, Ni, and Cr. The metals can also be in an oxidized state, such as a salt. Metal oxides may be particularly useful. One metal salt that may be utilized is copper(II) oxide Cu₂O. Those skilled in the art may be aware of other scavengers that may be utilized. The above list is meant to be exemplary and not exhaustive.

[0030] The form of the scavenger(s) may vary, depending upon the composition of the scavenger. For example, metals and metal salts can be in the shape of pieces of wire, wool, cuttings, granulate, sponge, or any other preparation with a large surface area. Other scavengers may have different forms and/or may be provided on a substrate.

[0031] The oil may be exposed to the sulfur scavengers in any suitable structure. For example, the scavenger(s) may be contained within a treatment column. The column may be filled with one or more scavengers in forms described above or one or more substrates in and/or on which one or more scavengers may be arranged.

[0032] Different scavengers and/or sorbent materials may be utilized to remove different sulfur-containing compounds. For example, soluble reaction products can be removed or reduced by treating the oil with one or more sorbents for polar contaminants. Examples of soluble sulfur-containing compounds includes thiols and copper mercaptides. Examples of sorbents for polar contaminants can include phosphates, sili-
icates and/or metal oxides. Examples of silicates can include Fullers earth and zeolites. Examples of metal oxides can include copper(II) oxide (Cu₂O), titanium oxide (TiO₂), or aluminas (Al₂O₃). Examples of phosphates can include hydroxyapatite. Those skilled in the art may be aware of other sorbents that may be utilized. The above list is meant to be exemplary and not exhaustive.

[0033] The sorbent(s) may be used and reactivated. In fact, the sorbent may be used and reactivated several times. In this case such large amounts of copper and other metals may accumulate on the sorbent that it may also act as a sulfur scavenger.

[0034] Although sorbents for polar contaminants may be highly efficient for removing dissolved copper and some thiols, other components such as sulfides, disulfides, less polar mercaptans and insoluble reaction products may be less efficiently removed by a sorbent treatment. Examples of compounds that are less efficiently removed by sorbent treatment can include sulfides, disulfides, and some thiols.

[0035] Treatment of the oil may be preferably carried out at a temperature higher than normal bulk oil temperature. In other words, the oil may be treated at a temperature higher than the normal operating temperature of the oil. For example, the treatment may be carried out at a temperature of about 60°C or greater. The temperature range may also be about 70°C or greater and even about 80°C or greater. In fact, temperatures of up to about 100°C or more may be utilized. The treatment may also be successful at lower temperatures and even at ambient temperature.

[0036] The efficiency of sulfur scavengers, as well as the sorption process, are typically greater at higher temperature. However, at too high temperatures decomposition of the oil may take place and/or other unwanted side effects may occur. The optimal temperature for carrying out the process typically depends upon the condition and composition of the oil. The oxygen content of the oil may affect the temperatures that may be utilized. For example, low oxygen content may permit higher temperatures to be utilized in the sulfur removal process while not destroying the oil.

[0037] Exposure to temperatures above the normal operating temperature of the oils maybe carried out at any point during the treatment. Typically, the temperature of the oil is raised prior to exposure to the sorbent(s) and/or the scavenger(s).

[0038] Treatment methods may also include filtering the oil. Filtration may occur prior to exposing the oil to scavenger(s) and/or sorbent(s). Along these lines, the oil may be filtered prior to any treatment with scavenger(s) and/or sorbent(s). Alternatively and/or additionally, the oil may be filtered after all treatment with scavenger(s) and/or sorbent(s). Furthermore, the oil may also or alternatively be filtered after any treatment of the oil with scavenger(s) and/or sorbent(s).

[0039] Treatment methods may be implemented in a variety of ways. For example, a commercially available mobile oil reclaiming plant may be utilized. In such a case, a top layer of sorbent in one or more columns typically included in such plants may be replaced with one or more sulfur scavenging materials. Each column may be altered in this manner.

[0040] The treatment may be carried out in a continuous mode, tank-to-tank, or on-line on equipment. However, it is also possible to carry out treatment methods by contacting the scavenger and sorbent materials in bulk, in two consecutive steps, with filtration after each step.

[0041] The present invention also includes a system for treating oil. A system includes at least one structure including at least one sulfur scavenger. The oil is contacted with the sulfur scavenger in the structure. The system also includes at least one structure including at least one polar sorbent. The oil is contacted with the sorbent in the structure. The structures can include a treatment column or other structure. In some embodiments, a single structure may contain both scavenger(s) and sorbent(s). The single structure may include one or more separating structures for separating the scavenger(s) and sorbent(s) from each other and/or from other scavenger(s) and sorbent(s) in the structure. A system may include multiple structures that contain scavenger(s) and/or sorbent(s). The structures may be arranged in parallel and/or in series.

[0042] The system may include a pump operative to pump the oil through the system. A heater may be included to heat the oil to temperatures above the typical operating temperature of the oil. The heater may be arranged at any location within the system to provide the heated oil where desired. One or more filters may be arranged with in the system to filter the oil as desired. For example, filters could be arranged prior to and/or subsequent to any treatment with scavenger(s) and/or sorbent(s). One or more filters could also be arranged prior to or after individual treatment with scavenger(s) and/or sorbent(s). Along these lines, the oil could be filtered after treatment with scavenger(s) and before treatment with sorbent(s). The oil may be transferred to a conservator or expansion vessel after treatment and before being returned to a transformer or other tank. The oil may also be returned by a valve in a transformer tank or oil cooling system. The system may be connected directly to a transformer tank. Alternatively, the system could receive the oil to be treated after the oil is removed from a transformer tank.

[0043] FIG. 3c illustrates an embodiment of a system for on-line treatment of oil according to the present invention. The system is arranged to treat oil in a transformer. The system 10 is connected to a transformer tank 12. A pump 14 pumps oil from the tank to be treated. The oil is pumped from the tank to a heater 16 for heating the oil. The oil then moves to a single column 18 containing a first sulfur scavenger 1 and a second sulfur scavenger 2. A sorbent 3 is also arranged in the column. A filter 20 filters the oil after treatment by the scavengers and the sorbent. After filtration, the oil passes to a conservator 22. The oil is then returned to the tank. The tank, pump, heater, column, filter and conservator are connected by pipes. In this embodiment, the first sulfur scavenger 1 can be copper shavings, the second sulfur scavenger 2 can be copper (II) oxide wire, and the sorbent can be activated Fullers earth or alumina.

[0044] FIG. 3d illustrates another embodiment of a system according to the present invention. The system shown in FIG. 3d also for on-line treatment of oil in a transformer, using a combination of two sulfur scavenger materials and one sorbent material. However, this embodiment may be utilized in applications where one scavenger material would be affected by the reactivation process used for the sorbent material. One example of such an application would be when sulfur scavenger 1 is elemental copper, sulfur scavenger 2 is a mix of copper oxides, and the sorbent is reactivated by in-situ incineration. The reactivation in this embodiment takes place in reactivation zone 24.

[0045] FIG. 4 illustrates an embodiment that may be utilized for tank-to-tank processing. Along these lines, the
embodiment includes a first tank 26 containing oil to be treated. The oil is transferred from the first tank 26 to a column 28 containing a mixture of one or more scavengers and one or more sorbents. After exposure to the scavenger(s) and sorbent(s) in the column, the oil is transferred to a second tank 30, which holds the treated oil.

[0046] FIG. 5 illustrates an embodiment of the present invention that includes a column train that may be utilized when oil to be treated contains a metal passivator that could prevent reaction with the scavenger materials and that can be removed by a sorbent as a first step. Along these lines, the embodiment shown in FIG. 5 includes a first column 32 containing Fullers earth. The second column 34 includes copper shavings. The third column 36 contains copper oxide and the fourth column 38 Fullers earth. The oil flows from column to column as indicated by the arrows. For such case a mixed bed could also be used.

[0047] Typically, methods according to the present invention are carried out on oil filled in transformers, without de-energizing them. A continuous process, such as may be carried out with the embodiment shown in FIG. 3, may be the best option for carry out the treatment. In this case, the oil may be pumped and heated, keeping scavengers and sorbents in columns, and using a sorbent that can be in-situ reactivated. Such a continuous treatment may be carried out with a modified commercially available mobile reclaiming plants, such as are

1. A method for removing sulfur from insulating oil, the method comprising:
   a. exposing the oil to at least one sulfur scavenging material; and
   b. exposing the oil to at least one polar sorbent.
2. The method according to claim 1, further comprising: filtering the oil.
3. The method according to claim 1, further comprising: heating the oil prior to exposing the oil to the sulfur scavenging material and exposing the oil to the polar sorbent.
4. The method according to claim 1, wherein the at least one sulfur scavenging material is provided on a high surface area substrate.
5. The method according to claim 4, wherein the at least one sulfur scavenging material is provided in a column.
6. The method according to claim 1, wherein the at least one sulfur scavenging material comprises at least one of elemental copper or other sulfide forming metal or metal salts.
7. The method according to claim 6, wherein metal salt comprises copper oxide.
8. The method according to claim 6, wherein the at least one sulfur scavenging material is provided in a shape include at least one of wire, wool, cuttings, granules, foil and sponge.
9. The method according to claim 1, wherein the at least one sulfur scavenging material retains insoluble reaction products.

10. The method according to claim 1, wherein at least one polar sorbent absorbs soluble reaction products.
11. The method according to claim 10, wherein the soluble reaction products comprise copper mercaptides.
12. The method according to claim 1, wherein at least one polar sorbent comprises at least one of Fullers earth and alumina.
13. The method according to claim 1, further comprising: reactivating the at least one polar sorbent.
14. The method according to claim 13, wherein the at least one polar sorbent is reactivated a plurality of times.
15. The method according to claim 1, wherein the method is carried out at a temperature higher than an operating temperature of the oil.
16. The method according to claim 1, wherein the method is carried out at a temperature of at least 70° C.
17. The method according to claim 1, wherein the method is carried out in a continuous mode.
18. The method according to claim 1, wherein the method is carried out on-line.
19. The method according to claim 1, wherein the oil is exposed to the at least one sulfur scavenging material a plurality of times, the method further comprising:
   a. filtering the oil after each time that the oil is exposed to the at least one sulfur scavenging material.
20. A system for removing sulfur from insulating oil, the system comprising:
   a. a pump operative to pump the oil through the system;
   b. at least one sulfur scavenger containing structure; and
   c. at least one polar sorbent containing structure.
21. The system according to claim 20, further comprising:
   a. at least one filter operative to filter the oil after treatment with the at least one sulfur scavenger containing structure or the at least one sulfur sorbent containing structure.
22. The system according to claim 20, further comprising:
   a. a heater operative to heat the oil prior to treatment with the at least one sulfur scavenger containing structure or the at least one sulfur sorbent containing structure.
23. The system according to claim 20, wherein the pump is interconnected with a transformer tank.
24. The system according to claim 20, comprising a plurality of sulfur scavenger containing structures.
25. The system according to claim 20, wherein the oil passes through the at least one sulfur scavenger containing structure prior to passing through the at least one sulfur sorbent containing structure.
26. The system according to claim 20, wherein the at least one sulfur scavenger containing structure and the at least one sulfur sorbent containing structure are parts of a single container.