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(54) METHOD FOR REMOVING CORROSIVE SULFUR COMPOUNDS FROM A TRANSFORMER OIL

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(57) **ABSTRACT**

A method removes corrosive sulfur compounds from transformer oil. By adding a mixture of rare earths containing aluminum oxide and aluminum silicate to the transformer oil, and enriching the same with an aqueous solution of soluble metal salts, the corrosive sulfur compounds in the transformer oil are neutralized with defined heating and cooling phases. Advantageously, no additional chemical components, such as passivators, are added to the transformer oil. When using a tank for receiving the mixture of the rare earths containing aluminum oxide and aluminum silicate, the reaction can run in the tank. Any aging products that may be present, and the bonded corrosive sulfur compounds are effectively retained within the tank by a filter system, and can be disposed of with the tank.

METHOD FOR REMOVING CORROSIVE SULFUR COMPOUNDS FROM A TRANSFORMER OIL

[0001] The invention relates to a method for removing corrosive sulfur compounds from a transformer oil.

[0002] Transformers frequently use as insulation and cooling media transformer oils which, due to their long-term chemical characteristics, have for many years been used for operating transformers. One problem associated with using transformer oils is, however, the presence of natural or added sulfur compounds which contribute to the oxidation stability of the oil itself, in particular in the case of uninhibited transformer oils. Conductive copper sulfide compounds are consequently formed which are preferentially deposited in the paper insulation and impair its insulating properties. This phenomenon is promoted in particular at elevated operating and ambient temperatures.

[0003] When unlacquered, paper-insulated copper conductors are used within a transformer and under conditions of limited oxygen content, for example when a transformer is operated with exclusion of air, transformer oils comprising corrosive sulfur-containing constituents form layers of copper sulfate on the paper insulation. Starting from the copper conductor, copper sulfide layers form within the paper layers surrounding the copper conductor. As a result, the insulation properties of the paper insulation are sometimes durably impaired, such that partial discharges and voltage flashovers may occur between the live copper conductors due to the reduced insulation properties of the paper insulation.

[0004] These corrosive sulfur compounds, in particular mercaptans and disulfides, form above all in transformers, chokes or passages under specific operating and temperature conditions and reduce the insulation properties of the paper insulation to a considerable extent; sometimes down to just 20 percent of the original electric strength of the paper insulation.

[0005] The attempt has accordingly been made in the prior art to suppress the reaction of the corrosive sulfur compounds within the transformer oils with the copper conductor and simultaneously to improve oxidation resistance by "passivating" the transformer oils, in particular by means of metal passivators comprising benzotriazole-based compounds. A problem in this case is in particular that the metal passivator may be consumed during the ongoing operation of the transformer and the quantity of passivator available must thus be permanently monitored. Moreover, the extent to which long-term passivation modifies the properties of the transformer oils is as yet unknown.

[0006] WO 2005/117031 A2, for example, accordingly describes a method and a device for adding a passivator to a conductor. The above-stated patent application proposes winding the passivator directly around the conductor and then sheathing it with a further layer of an electrical insulator and so providing overall electrical insulation for the conductor with the passivator layer.

[0007] WO 2007/096709 A2 moreover describes a method for permanently removing corrosive components from a transformer oil. The above-stated patent application proposes removing the transformer oil from a transformer tank and, after heating and addition of an acid-containing liquid, bringing it into contact by means of a sulfide free-radical scavenger and then filtering it. After filtration, the transformer oil purified in this manner is reintroduced into the transformer tank.

[0008] The same applies to WO 2007/144696 A2 as a method for deactivating corrosive sulfur in transformer oils. According to the invention, the above-stated patent application proposes adding a sulfide-forming chemical component to the transformer oil comprising corrosive sulfur compounds, such that said chemical component reacts with the sulfur compound and the corrosive sulfur compounds are thus removed from the transformer oil.

[0009] DE 10 2005 006 271 A1 moreover describes a method for purifying transformer oil, the transformer oil initially being subjected to a pretreatment by filtration, before it is passed through a packing of an inert inorganic support coated with a reactive metal. The transformer oil is then filtered through a bleaching earth bed and then returned to the transformer.

[0010] The object of the present invention is accordingly to avoid the disadvantages in the prior art and to provide a method for removing corrosive sulfur compounds from a transformer oil which easy to handle and ensures virtually complete removal of corrosive sulfur compounds from the transformer oil.

[0011] Said object is achieved by the features of the method as claimed in claim **1**. According to the invention, a method is proposed for removing corrosive sulfur compounds from a transformer oil, in which, with addition of a mixture of rare earths containing aluminum oxide/aluminum silicate to the transformer oil, said transformer oil enriched in this manner is heated to up to 300 degrees Celsius and then, with enrichment with an aqueous solution of soluble metal salts, is cooled.

[0012] The transformer oil enriched with the rare earth mixture containing aluminum oxide/aluminum silicate is then once more heated to up to 200 degrees Celsius for at least two hours and then cooled to room temperature.

[0013] Heating of the mixture of rare earths containing aluminum oxide/aluminum silicate activates the adsorption centers of the matrix by removing water fractions. The heavy metal salts present in the mixture of the rare earths containing aluminum oxide/aluminum silicate are thereafter dispersed in a little water and the mixture is slowly heated. This gives rise to heavy metal oxides which are insoluble and firmly bound to the fuller's earth matrix of the mixture of rare earths containing aluminum oxide/aluminum silicate.

[0014] In this manner, the adsorbent is prepared. The solution presented here is based on removing the reactive corrosive sulfur compounds present in the transformer oil by using a mixture of inorganic adsorbents with a wide range of applications. It mainly comprises a mixture of rare earths containing aluminum oxide/aluminum silicate and are optionally enriched with silver, copper, zinc and/or iron in metallic or oxide form. In particular, the metal oxides formed by means of the rare earth mixture containing aluminum oxide/aluminum silicate bind the corrosive sulfur compounds and may be collected at a suitable point and removed from the transformer oil, optionally together with simultaneous removal of oil ageing products.

[0015] The advantage of this method is that no additional foreign substances, such as for example passivators, are added to the transformer oil. Ageing products and corrosive sulfur compounds are simultaneously eliminated from the transformer oil. Oxidation capacity is consequently increased and the fraction of corrosive sulfur compounds within the transformer oil is greatly reduced, so durably increasing the service life of the transformer.

[0016] It is considered advantageous according to the present method for the ratio between the fraction comprising aluminum oxide and the fraction of aluminum silicate in the rare earth mixture containing aluminum oxide/aluminum silicate to be in a ratio of 20:80 to 80:20, preferably of 50:50. The catalytic action of the rare earth mixture containing aluminum oxide/aluminum silicate is best ensured within the preferred ratio range of the fractions.

[0017] A bulk density of 50 to 80 g/l is advantageously used in order to provide the greatest possible surface area of the rare earth mixture containing aluminum oxide/aluminum silicate. In this bulk density range, an in particular granular rare earth mixture containing aluminum oxide/aluminum silicate has an effective surface area for binding the corrosive sulfur compounds present in the transformer oil. The aqueous solution advantageously has a solution fraction of up to 40% of in particular soluble metal salts. Adding copper and silver salts in particular leads to improved binding of the corrosive sulfur compounds onto the metal salts present in the aqueous solution. This precisely prevents the corrosive sulfur compounds present in the transformer oil from reacting chemically with the copper conductor. The pH value of the rare earth mixture containing aluminum oxide/aluminum silicate is advantageously 6.5 to 9.0. The metal oxides formed react with the corrosive sulfur compounds at the highest possible rate of reaction in the above-stated pH range.

[0018] An advantageous development of the method provides that the ratio of the rare earth mixture containing aluminum oxide/aluminum silicate to transformer oil, relative to their respective weights, is in a ratio of 0.01:100 to 40:100, preferably of 10:100. The highest possible rate of reaction is ensured in particular at the preferred weight ratio of 10:100 of rare earth mixture containing aluminum oxide/aluminum silicate to transformer oil due to their respective concentrations. Advantageously, the rare earth metals of group 3 of the periodic table of elements including the lanthanoids are a constituent of the rare earth mixture containing aluminum oxide/aluminum silicate. In an advantageous development of the method, silver, copper, zinc and/or iron are admixed with the rare earth mixture containing aluminum oxide/aluminum silicate. Moreover, silver nitrate to form silver oxides and/or copper salts to form copper oxides and/or iron oxides is/are admixed with the rare earth mixture containing aluminum oxide/aluminum silicate. The metal oxides present in this manner within the rare earth mixture containing aluminum oxide/aluminum silicate are highly reactive and combine with the corrosive sulfur compounds within the transformer oils and neutralize the corrosive sulfur compounds.

[0019] An advantageous development of the method provides that the rare earth mixture containing aluminum oxide/aluminum silicate is arranged in a container, in which the container may be fitted on a transformer housing and the transformer oil is passed into the container and purified, and the sulfides bound in the rare earth mixture containing aluminum oxide/aluminum silicate as reaction products of the corrosive sulfur compounds remain in the container. Thanks to the reaction of the corrosive sulfur compounds of the transformer oils within the container and the accumulation of the bound sulfides in the container, these waste products may be disposed of on removal of the container. At the same time, any further contamination of the transformer oils with the bound sulfides in the container is ruled out, such that corrosive sulfur compounds may virtually completely be removed from the transformer oil by the above-stated method.

[0020] In the event of complete consumption of the rare earth mixture containing aluminum oxide/aluminum silicate, the container is advantageously removed from the transformer housing. In an advantageous development of the method, the container comprises an indication of the reactive rare earth mixture containing aluminum oxide/aluminum silicate which is present. In the context of servicing, this indication may be used to establish whether sufficient reactive rare earth mixture fractions containing aluminum oxide/aluminum silicate are present and proper performance of the method is ensured.

[0021] A filter system is advantageously introduced within the container, the filter system comprising the rare earth mixture containing aluminum oxide/aluminum silicate, and the transformer oil is introduced into the filter system. By means of the filter system, the bound sulfides and the transformer oil end-of-life products may in particular more readily be retained within the filter system and so collected within the container.

[0022] An advantageous development of the method provides that the container may be connected with a purifying device, in which the purifying device may be connected with the transformer housing and the transformer oil may be transferred out of the transformer housing for purification in the purifying device and thus the corrosive sulfur compounds are removed in the container outside the transformer housing.

[0023] Further advantageous developments are revealed by the subclaims.

EXAMPLE

[0024] A rare earth mixture containing aluminum oxide/aluminum silicate has a bulk density of 600 g/l with a ratio of aluminum oxide to aluminum silicate of 50:50. The pH value is 7.0. One kilogram of the rare earth mixture containing aluminum oxide/aluminum silicate is activated at 150° C. and, after cooling, treated in portions with 400 ml of a 20% aqueous solution of soluble salts of silver, copper, zinc or iron. The mixture is homogenized and heated stepwise to 120° C. within five hours. This temperature is maintained for 15 to 20 hours. After cooling, the mixture is kept in a closed vessel. The ratio relating to the weights of the active rare earth mixture containing aluminum oxide/aluminum silicate to treated transformer oil is 0.5:100 to 10:100, depending on the state of ageing and corrosiveness of the transformer oil.

1-15. (canceled)

16. A method for removing corrosive sulfur compounds from transformer oil, which comprises the steps of:

adding a mixture of rare earths containing aluminum oxide/aluminum silicate to the transformer oil;

heating the transformer oil enriched with the rare earth mixture containing the aluminum oxide/aluminum silicate to up to 300 degrees Celsius;

cooling the transformer oil enriched with the rare earth mixture containing the aluminum oxide/aluminum silicate;

enriching the transformer oil with an aqueous solution of soluble metal salts; and

heating the transformer oil to up to 200 degrees Celsius for at least two hours and subsequent cooling to room temperature.

17. The method according to claim **16**, which further comprises setting a ratio between a fraction containing the aluminum oxide and a fraction of the aluminum silicate in the rare earth mixture containing the aluminum oxide/aluminum silicate to be in a range of 20:80 to 80:20.

18. The method according to claim **16**, which further comprises setting a bulk density of the mixture of rare earths containing the aluminum oxide/aluminum silicate to be 50 to 800 g/l.

19. The method according to claim **16**, wherein the aqueous solution has a solution fraction of up to 40% of the soluble metal salts.

20. The method according to claim **16**, which further comprises setting a pH value of the mixture of rare earths containing the aluminum oxide/aluminum silicate to be 6.5 to 9.0.

21. The method according to claim **16**, which further comprises setting a ratio of the mixture of rare earths containing the aluminum oxide/aluminum silicate to the transformer oil, relative to their respective weights, to be in a range of 0.01:100 to 40:100.

22. The method according to claim **16**, which further comprises using rare earth metals of group 3 of the periodic table of elements and lanthanoids.

23. The method according to claim **16**, which further comprises admixing at least one of silver, copper, zinc or iron with the mixture of rare earths containing the aluminum oxide/aluminum silicate.

24. The method according to claim **16**, which further comprises admixing at least one of silver nitrate to form silver oxides, copper salts to form copper oxides, zinc oxides or iron oxides with the mixture of rare earths containing the aluminum oxide/aluminum silicate.

25. The method according to claim **16**, which further comprises disposing the mixture of rare earths containing the aluminum oxide/aluminum silicate in a container, and the container is connected with a transformer housing and the transformer oil is passed into the container and purified, and sulfides bound in the mixture of rare earths containing the aluminum oxide/aluminum silicate remain in the container.

26. The method according to claim **25**, which further comprises in an event of a complete consumption of the mixture of rare earths containing the aluminum oxide/aluminum silicate, removing the container from the transformer housing.

27. The method according to claim **25**, wherein the container contains an indication of the reactive mixture of rare earths containing the aluminum oxide/aluminum silicate which is still present.

28. The method according to claim **25**, wherein the container has a heating unit for heating the transformer oil enriched with the mixture of rare earths containing the aluminum oxide/aluminum silicate.

29. The method according to claim **25**, wherein a filter system within the container contains the mixture of rare earths containing the aluminum oxide/aluminum silicate and the transformer oil is introduced into the filter system.

30. The method according to claim **25**, which further comprises connecting the container with a purifying device, the purifying device being connected with the transformer housing and the transformer oil may be transferred out of the transformer housing for purification in the purifying device and thus the corrosive sulfur compounds are removed in the container outside the transformer housing.

31. The method according to claim **16**, which further comprises setting a ratio between a fraction containing the aluminum oxide and a fraction of the aluminum silicate in the mixture of rare earths containing the aluminum oxide/aluminum silicate to be 50:50.

32. The method according to claim **16**, which further comprises setting a ratio of the mixture of rare earth containing the aluminum oxide/aluminum silicate to transformer oil, relative to their respective weights, to be 10:100.

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