

Investigation of Copper corrosion in transformer oil

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Abstract

Power transformers are the important equipments in power generation, transmission and distribution and the oil used in the transformer acts as liquid insulant and heat transfer medium which plays an important role in safe and efficient functioning of the transformer. Mineral oil is a mixture of paraffinics, naphthenics, aromatics, few nitrogen and sulphur compounds. Recently number of failures of generator and *HVDC* transformers are reported due to formation of copper sulphide. The reaction between copper conductor and the reactive sulphur compounds occur at stringent operating conditions i.e. at high temperatures, overloads, local overheating and etc. Though the transformer oil passes the standard corrosive sulphur test, the sulphur compounds which are non reactive at normal operating conditions become reactive at extreme conditions in the transformer. The copper corrosion tests were conducted as per ASTM D1275 and DIN 51353 for fresh oils and also for aged oils with 100 ppm of passivator. The formation of copper sulphide is analysed by the Electron spectroscopy for Chemical Analysis (ESCA). The ESCA report after adding the passivator reveals that 100 ppm concentration of the passivator Irgamet 39 (N,N-bis-(2ethylhexyl)-4-methyl-1H-benzotriazole-1-methanamine) is effective in protecting the copper conductors effectively.

Key words: ASTM; Copper conductor; Corrosive sulphur; Dibenzylsulphide (DBDS); ESCA; Transformer oil.

1. Introduction:

Mineral based insulating oils are used in transformers as an insulant and a coolant due to their abundant availability and low cost. Its insulation capacity depends upon the electrical properties of the oil and its physical properties are related to heat transferability. Sulphur exists in many forms like mercaptans and dibenzylsulphide (DBDS) etc in the oil and also in copper, insulation paper and rubber gaskets used in the transformer. Total removal of sulphur compounds in transformer oil is expensive and also removes the compounds which are natural inhibitors. Some trace quantities of reactive sulphur compounds may remain in the oil which may not be detected during the corrosive sulphur [1,2,3,4] test as done according to the ASTM D 1275 test procedure. Though the transformer oil passes the standard corrosive sulphur test, the sulphur compounds which are non reactive at normal operating conditions become reactive at extreme conditions in

the transformer and form copper sulphide. The copper sulphide formed at the copper surface can also migrate to the paper insulation. The conductive copper sulphide causes a reduction in dielectric strength of the paper insulation. The result is arcing between two or more turns or disks which lead to catastrophic failure of the transformer. Recent failures are reported due to presence of dibenzyl disulphide (DBDS). The mechanism of conversion of DBDS in the presence of copper and heat into copper sulphide is shown in Figure (1).

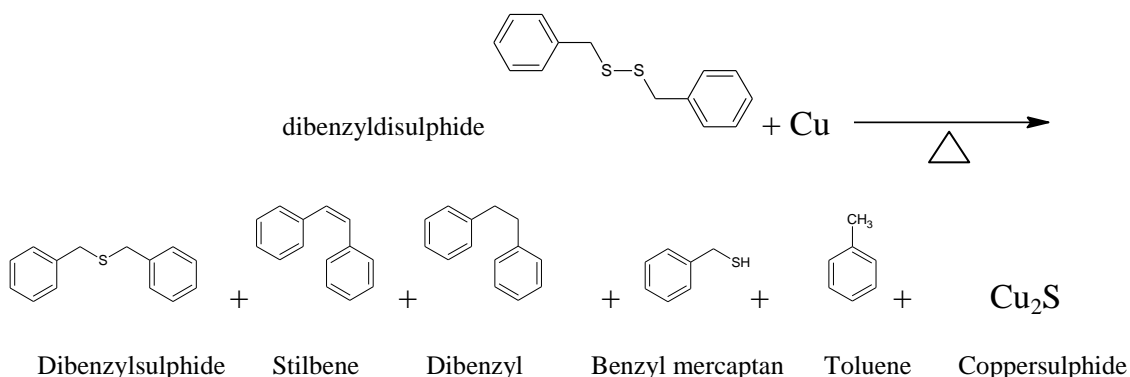


Figure 1. Mechanism of breakdown of DBDS

1.1.Passivator: Passivators are metal deactivators that bind with certain reactive metal surfaces to retard attack by corrosive sulphur. Passivators act by blocking the sites for corrosive sulphur compounds and are used as a remediation technique to protect the copper against corrosive sulfur attack and form copper sulphide. The passivator used for the study is Irgamet 39 (N,N-bis-(2ethylhexyl)-4-methyl-1H-benzotriazole-1-methanamine[5,6,7,9]). Though this passivator has been extensively studied for naphthenic oils its performance had not yet been reported in literature for Indian paraffinic oils.

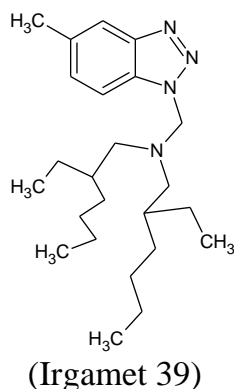


Figure 2. The structure of Irgamet 39 passivator

2. Experimental:

2.1. Testing of oil and copper conductor

Fresh oil characteristics as per IEC 60296 passed all tests including copper strip colour code. Testing of fresh transformer oil for copper corrosion was done as per ASTM D 1275 by Method –A and Method –B. The oil was subjected to DIN 51353 by ageing with silver strip. The oil impregnated paper covered copper conductors were immersed in fresh transformer oil and aged in an oven at 140° C for 1500 hrs without passivator. The paper covered copper conductors were tested for electrical parameters such as tan delta, capacitance and surface resistivity before and after ageing. The paper insulation after the ageing was tested by ESCA. Though the transformer oil passes the standard corrosive sulphur test, the sulphur compounds which are non reactive at normal operating conditions become reactive at extreme conditions in the transformer. Hence, the fresh transformer oil was mixed with passivator Irgamet 39, at an optimum concentration of 100 ppm and aged with paper covered copper conductor for 1500 hrs at 140° C .The paper insulation after the ageing with passivator was tested by ESCA and the insulated copper conductor for electrical properties.

2.2. Procedure for copper corrosion test as per ASTM D 1275 and DIN 51353

The ASTM D 1275 test method describes the detection of corrosive sulphur compounds (both inorganic and organic) in electrical insulating oils of petroleum origin. It detects the presence of or the propensity to form, free (elemental) sulphur and corrosive sulphur compounds by subjecting copper to contact with oil under prescribed conditions.

A strip of copper was cut and blemishes from surfaces were removed with the 240-grit silicon carbide paper and cleaned with Demineralised water and acetone. It is dried in an oven for 3 to 5 min at 80-100°C and immediately the copper strip was immersed in oil.

Method A: The prepared copper strip was placed in a 250ml flask and 220 ml of the oil was added. Nitrogen gas was bubbled for 1 min and stoppered tightly and placed in an oven at 140° C for 19 hrs. The copper strip was carefully taken out and washed with acetone to remove all the oil and observed with the ASTM copper strip corrosion colour standard as referenced in test method ASTM D 130 [8].

Method B: The cleaned copper strip was placed in a 250ml flask to which was added 220 ml of the oil to be tested. Nitrogen gas was bubbled through the oil for 5 min at a rate of 0.5 L/min. The flask was stoppered and placed in the oven at 150° C for 48 hrs. The copper strip was carefully taken out and washed with acetone to remove all the oil and observed with the ASTM copper strip corrosion colour standard as referenced in test method ASTM D 130.

Similarly, the silver strip corrosion test was done as per DIN 51353 by ageing with silver strip at 100° C for 18 hrs and observed with ASTM colour code.

3. Results and Discussion

Fresh oil characteristics as per IEC 60296 passed all tests including copper strip colour code.

3.1. The silver strip after testing for silver corrosion in fresh transformer oil and colour comparison with ASTM colour code is shown in figure 3. The copper strip after testing for copper corrosion in fresh transformer oil and color comparison with ASTM copper strip corrosion standard as referenced in ASTM method D 130 indicated 1a grade is shown in Figure 4. Both of them indicated non-corrosiveness of oil.



Figure 3. Silver strip corrosion test for fresh transformer oil as per DIN compared with ASTM colour code. Figure 4. Copper strip corrosion test for fresh transformer oil compared with ASTM colour code.

3.2. The oil is meant for use in a converter transformer for a critical application. Though the transformer oil passes the standard corrosive sulphur test, the sulphur compounds which are non reactive at normal operating conditions become reactive at extreme conditions in the transformer. So, accelerated ageing of oil with paper covered conductors were conducted at 140°C for 1500 hrs. Then, the insulated copper conductors were tested for electrical properties and these values were compared with nonaged oil impregnated fresh paper covered conductors. The results indicate deterioration in the values and tarnishing of copper conductors.

The electrical properties of the insulated copper conductor before and after ageing in transformer oil in an oven at 140° C for 1500 hrs with and without passivators are tabulated in table 1.

Table 1 Electrical properties of insulated copper conductor

Electrical Property	Before ageing	After ageing without passivator	After ageing with passivator
Tandelta	0.004	0.019	0.006
Capacitance in pF	34.05	27.54	29.22
Insulation Resistance	1.5×10^{13}	1.8×10^{12}	2.4×10^{12}

3.3. To find out the deterioration in the value and to investigate the tarnishing, ESCA of insulation paper was conducted which indicated formation of copper sulphide due to the decomposition of DBDS and conversion of nonreactive sulphur to reactive sulphur. The ESCA scan of paper sample of aged paper covered copper conductor in transformer oil at 140° C for 1500 hrs shows the presence of copper and sulphur and indicates characteristic energy peak levels at 934 eV, 954 eV for copper and 162 eV, 168 eV for sulphur indicating the formation of copper sulphide on copper conductor as shown in Figure 5.

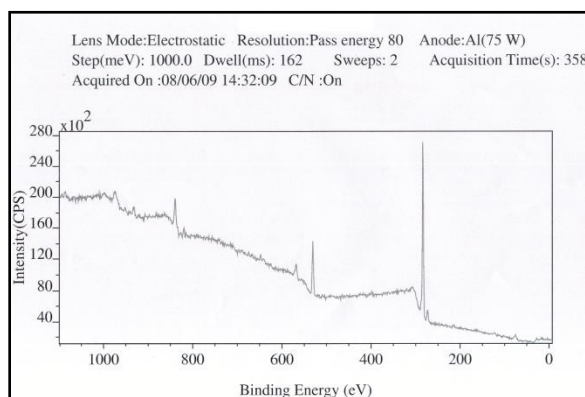


Figure 5. ESCA scan of paper sample of paper covered copper conductor immersed in Transformer oil and aged without passivator at 140°C for 1500 hrs.

To mitigate this deterioration Irgamet 39 passivator was selected as it is a liquid and is easily miscible with oil and experimented the ageing at 140°C for 1500hrs with passivator. The electrical properties of paper covered conductor have improved (table 1). For further confirmation, the paper sample of copper conductor was tested for ESCA which has not indicated any copper sulphide formation. The copper corrosion colour code tests of oil sample also passed ASTM and DIN tests. Irgamet 39 in 100 ppm concentration is found to be successfully passivating the copper surfaces with out any deterioration.

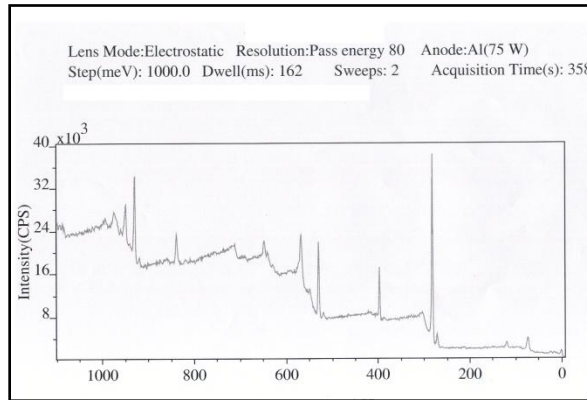


Figure 6. ESCA scan of paper sample of paper covered copper conductor immersed in Transformer oil and aged with passivator at 140°C for 1500 hrs.

3.4. The silver strip after testing for corrosion in aged transformer oil mixed with Irgamet 39 and color comparison with ASTM colour code is shown in Figure 7. The copper strip after testing for copper corrosion in aged transformer oil mixed with 100 ppm of Irgamet 39 and color comparison with ASTM copper strip corrosion standard is shown in figure 8. Both the tests indicated non-corrosiveness.

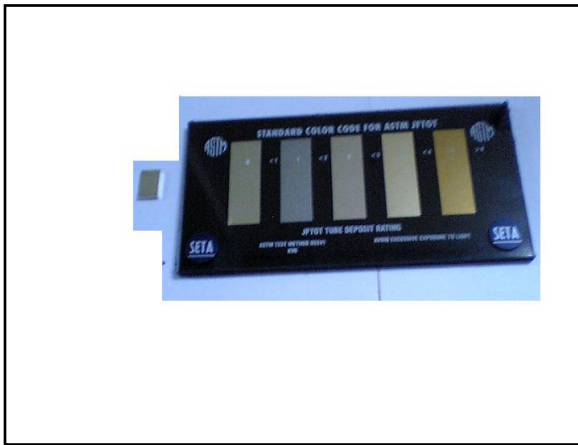


Figure7. Silver strip corrosion test for transformer oil as per DIN with 100 ppm Irgamet 39 compared with ASTM colour code.



Figure 8. Copper strip corrosion test for transformer oil with 100 ppm Irgamet 39 compared with ASTM colour code.

As per ASTM 1275 the oil is classified as corrosive or noncorrosive in accordance with the following:

Noncorrosive: Orange, red, Lavender, multicoloured with lavender blue or silver, or both, overlaid on claret red, silvery, brassy or gold, magenta overcast on brassy strip, multicoloured with red and green showing (peacock) but no gray.

Corrosive: Transparent black, dark gray or dark brown, graphite or lusterless black, glossy or jet black, any degree of flaking

4. Conclusion:

The following conclusions are drawn based on the above conducted tests:

- a) Transformer oils contain some sulphur compounds undetected by the ASTM colour code test but become reactive during high operating temperatures which react with copper to form copper sulphide.
- b) The formation of copper sulphide on paper sample of aged paper covered copper conductor in oil is detected by the ESCA analysis.
- c) The ESCA scans of aged paper sample indicates that the sulphur peak intensity is drastically reduced after adding the passivator which indicates that the passivator is preventing the formation of copper sulphide.
- d) The copper corrosion tests by copper and silver strips for aged oils with 100 ppm passivator showed non corrosiveness.
- e) A 100 ppm of the passivator is sufficient for effectively passivating the copper.

5. ACKNOWLEDGEMENT

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REFERENCES

- [1] Lewand Lance R (2002), The Role of Corrosive Sulfur in Transformers and Transformer Oil, Proceedings of the Sixty-Ninth Annual International Conference of Doble Clients, Boston, MA, Insulating Materials Session.
- [2] Wilson, A.C.M (1980), Insulating Liquids: Their Uses, Manufacture and Properties, IEEE, (New York and UK).
- [3] Vander Tumiatti, Michela Tumiatti, Riccardo Maina, Carlo Roggero, Integrated methods for the determinations of corrosivity, aging, finger printing as well as the diagnosis, decontamination, depolarization and detoxification of mineral insulating oils & transformers, Sea Marconi Technologies Sas, Italy.

- [4] Vander Tumiatti, R. Maina, F. Scatiggio, M. Pompili and R. Bartnikas (2006), Corrosive Sulfur in mineral oils: its detection and correlated power transformer failures”, Proc. IEEE Int. Symposium on Electrical Insulation, Toronto, June 12-14.
- [5] Amimoto,T, Nagao,E.: Tanimura, J.; Toyama,S.; Yamada,N. Duration and mechanism for suppressive effect of triazole-based passivators on copper-sulfide deposition on insulating paper Mitsubishi Electr. Corp., Ako Dielectrics and Electrical Insulation, IEEE transactions on Volume: 16, Issue: 1, Page(s)-257-264.
- [6] Prof. Bruce Pahlavanpour and Mr. Kjell Sundkvist, Mineral Insulating Oil Passivation Effectiveness of Passivation to stop Copper Deposition Nynas Naphthenics Ltd, Wallis House, 76 North street, Guildford Surrey, GUI 4AW, UK.
- [7] Katritzky, A.R.; Lan, X.; Yang, J. Z.; Denisko, O.V, (1998), Properties and Synthetic Utility of N-Substituted Benzotriazoles. Chem. Rev., 409-548.
- [8] Standard Test Method for Corrosiveness to Copper from Petroleum Products by Copper Strip Test ASTM D 130.
- [9] SCHAUT Annelore, EECKHOUDT Steve Laborelec Belgium (2012) “Effects of Triazole additives in Transformer oils” CIGRE, Paris D1 102.