Studies on effect of Copper corrosion passivators on the Paper insulated copper conductor by XRD, SEM and EDX analysis

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ABSTRACT

The paper focuses on corrosion phenomena involving copper, corrosive sulphur and solid insulation of oil-immersed transformers. A study of the available mitigation technique such as passivation to reduce the effects of corrosion phenomena is carried out with the commercially available passivator, Irgamet 39 (Toluiltriazole dialkylamine) (ciba), with concentration of 100 ppm. The paper insulated copper conductors with transformer oil are aged for 1400 hrs at 140° C with and without passivators and tested both paper insulation and copper samples with the X-ray Diffraction (XRD), Scanning Electron Microscope(SEM) and Energy dispersive X-ray Spectroscopy (EDX). The SEM scan after ageing with passivator shows the formation of thin film of passivator on the copper surface. The SEM, XRD and EDX scans after ageing without passivator show the formation of copper sulphide on the copper surface as well as on the paper insulation.

Key words: **Copper corrosion, Dibenzyl Disulphide, EDX, Mercaptans, Passivators, SEM, XRD.**

1. INTRODUCTION

A Power transformer is composed of several materials i.e. copper, iron, cellulose, wood, rubber, glues, polymers, and mineral oil which undergo chemical reactions during operation at high temperatures, overloading etc leading to corrosion. Corrosion may cause the formation of contaminants, both dissolved in the oil and forming deposits on the paper or insoluble compounds that precipitate as sludge. Sulphur compounds cause corrosion, accelerate the asphalts production and worsen the dielectric properties of oil. The major corrosion process which leads to catastrophic failure of the transformers is the formation of copper sulphide that grows on the conductor surface and on solid insulation.

Different organo-sulphur compounds which are very corrosive are present in new transformer oils, depending on the crude oil origin and degree and type of refining. Some sulphur compounds have an affinity to metals and they act as copper passivators. Elemental sulfur is the most corrosive against copper, followed by hydrogen sulfide, mercaptans, sulfides and disulfides. Sulfur organic compounds, where the sulfur atom is trapped in an aromatic structure (e.g. thiophenes and related compounds), are usually considered as non reactive. Dibenzyldisulphide (DBDS), identified as a major sulfur compound in several insulating mineral oils, seems to play a predominant role in the problem of corrosion phenomena. At high temperatures, DBDS reacts with copper conductor to form copper sulphides and impacts its conductivity. Detachment of the copper sulfide layer formed on the naked copper surfaces causes the formation of suspended conductive particles, which can act as nuclei for electrical discharge between leads and the grounded tank.

The copper sulfide growth on wrapped conductors is accompanied by its migration within the layers of insulating paper [1,2,3]. Formation of conductive spots in the paper may cause the adjacent cellulose incapable to dissipate the heat generated locally by the increase of conductivity of the insulation. This heat can result in a puncture destroying the paper structure and allowing the discharge between vicinal turns.

1.1 Copper sulphide formation [4]

Dibenzyl sulphide (DBS) and bisbenzyl (BiBZ) will be formed in insulating oil as by-products of copper sulfide formation between copper and DBDS. The rate of sulphide formation reactions seems to approximately double for every 10 º C increase of temperature. Temperature is not the only factor for copper sulphide formation. On-load tap changers (OLTC) switching operations involving high stresses (arcing) through the oil lead to extensive copper sulfide formation.

The mechanism of conversion of DBDS in the presence of copper and heat into copper sulphide is shown in Fig.(1).

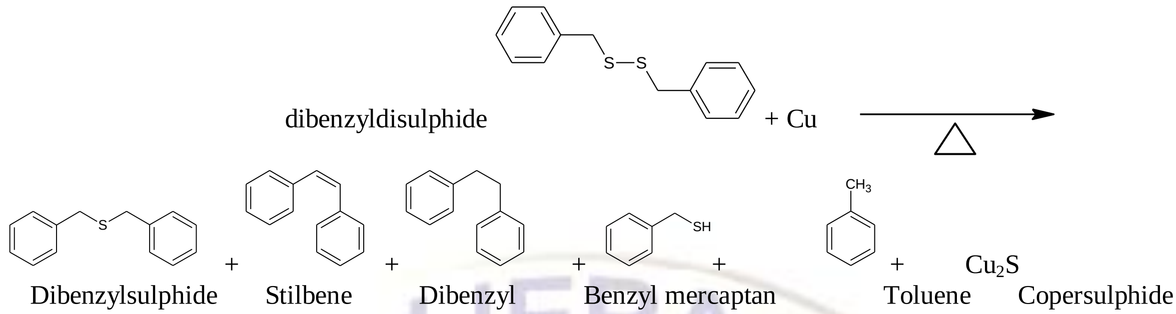

Figure 1. Mechanism of breakdown of DBDS

1.2 Copper passivator [5,6,7]

Addition of copper passivator is one of the mitigation techniques that has been used to the largest extent. An optimum concentration of 100 ppm of passivator is added to inhibit the reaction of copper with corrosive sulfur. The passivators mostly used are BTA and derivatives such as toluiltriazole-dialkyl-amine commercially available as Ciba Irgamet39. The triazolic part of the molecule is likely oriented towards the conductor's surface, shielding it against the chemical attack of corrosive sulfur compounds and acting only as a potentially protective agent. Irgamet 39, a triazole derivative is a liquid with density 0.95g/cm3 at 20° C, flash point is greater than 150° C and offers low volatility, easy to handle, has excellent solubility in mineral oil and does not affect the dielectric properties of transformer oils. It is a better passivator than BTA due to its good miscibility with oil. BTA is a granular solid at room temperature and requires heating and mixing to dissolve in the oil. Passivator structures are shown in Fig.(2)

Benzo Triazole(BTA) Toluiltriazole-dialkylamine (Irgamet 39)

Figure 2 The structure of BTA and Irgamet 39 passivators

I. EXPERIMENTAL

The copper conductors of 8 inches length covered with a number of layers of cellulose paper were dried at 105°C for 24 hours. The dried samples were impregnated with fresh dried filtered transformer oil with vacuum more than 1 torr at 100° C and then immersed in fresh transformer oil. The oil was found to contain trace amounts of DBDS and Mercaptan Sulphur. The paper insulated copper conductors with and without passivators were aged in transformer oil for 1400hrs at 140° C in an oven. The metal passivator used in this experiment is Irgamet39 as it is a liquid and easily miscible with oil. After ageing, the copper and the paper samples were tested by XRD, SEM and EDX analysers.

2.1. X-ray Difractometer(XRD)

The XRD equipment used for this study is of Philips make. It investigates crystalline material structure, including atomic arrangement, crystallite size and imperfections. It reveals information about the crystal structure, chemical composition and physical properties of materials and thin films.

2.1.1 Principle

It is based on observing the scattered intensity of an X-ray beam hitting a material as a function of incident and scattered angle, polarization and wavelength or energy.

2.2. Scanning Electron Microscope(SEM)

The SEM used for this study is of Carl Zeiss Germany make. It is used for high magnification imaging of materials in determination of fibre structure in wood and paper, metal fracture surfaces, production defects. The surface coatings can be analysed by SEM and it is non-destructive. SEM in combination with EDX (Energy Dispersive

X-ray Spectroscopy determines elemental composition of samples.

2.2.1 Principle

It uses a focused beam of high-energy electrons to generate a variety of signals like secondary electrons, back scattered electrons, diffracted back scattered electrons, photons, visible light and heat at the surface of solid. The signals that derive from electron material interactions reveal information about the external morphology (texture), chemical composition, crystalline structure and orientation of materials.

2.3.Energy dispersive X-ray Spectroscopy

It is used for elemental analysis or chemical characterization of material.

2.3.1 Principle

Incident beam excites an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer higher energy shell then fills the hole, and the difference in energy between the higher energy shell and the lower energy shell may be released in the form of an X-ray measured by EDX. The energy of the X-rays is characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted. This allows the elemental composition of the specimen to be measured. The detector converts X-ray energy into voltage signals, which are sent to pulse processor, which measures signals and passes them onto an analyzer for data display and analysis.

II. RESULTS AND DISCUSSIONS

3.1.The X-ray Diffraction studies

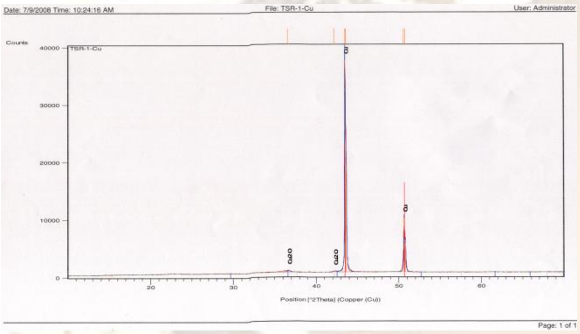

Figure 3.
XRD scan of copper sample of paper insulated copper conductor after ageing in oil without passivator at 140°C for 1400 hr

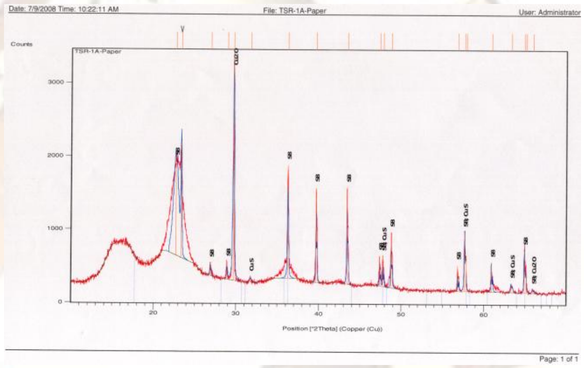

Figure 4.
XRD scan of Paper Sample on copper conductor after ageing in oil without passivator at 140 °C for1400 hr

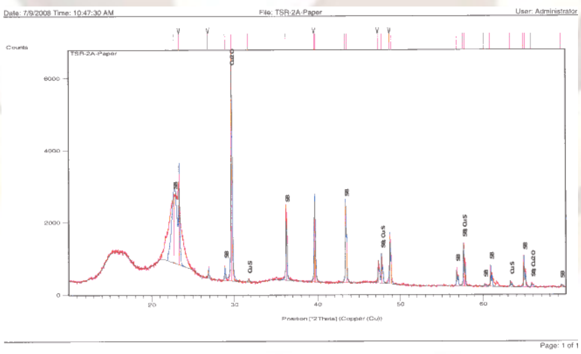

Figure 5. XRD scan of Paper Sample on copper conductor after ageing in oil with passivator at 140 °C for 1400 hr

The presence of copper sulphide on copper conductor could not be established using XRD due to poor resolution and it indicates characteristic bands due to copper only. In addition to copper, the XRD spectrum shows presence of calcium also which could have come from the cellulose paper as shown in Fig. (3). Fig. (4) shows the XRD scan of paper sample on copper conductor aged in transformer oil for 1400 hrs at 140 °C without passivator. The scan indicates Cu_2S peaks at theta (ø) values of 32, 48, 58, 62 on paper insulation aged with transformer oil. Fig. (5) shows XRD scan of Paper Sample on copper conductor after ageing in oil with passivator at 140 °C for 1400 hr.

3.2. Scanning Electron Microscope (SEM) studies

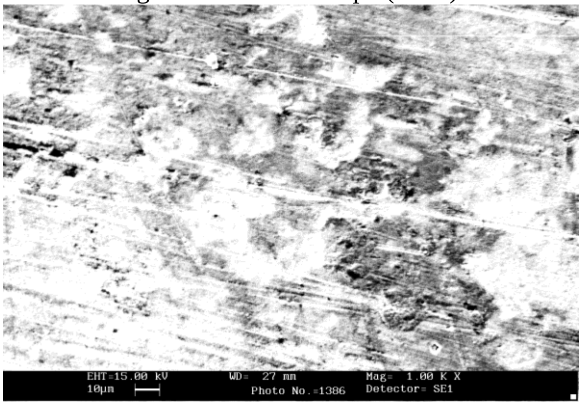

Figure 6
SEM scan of copper sample of paper insulated copper conductor after ageing in oil without passivator at 140 °C for1400 hr

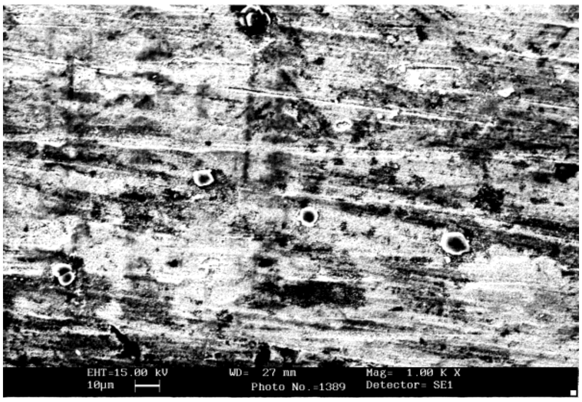

Figure 7
SEM scan of copper sample of paper insulated copper conductor after ageing in oil with passivator at 140 °C for 1400hr

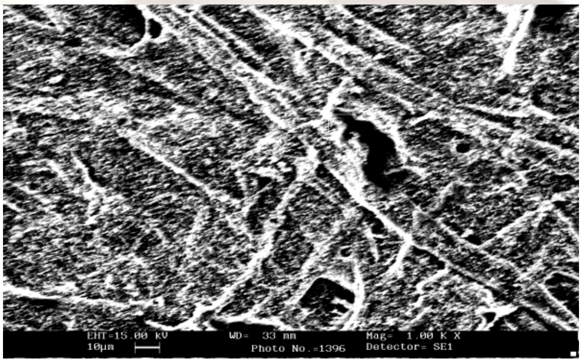

Figure 8 SEM scan of paper sample on copper conductor after ageing in oil with out passivator at 140 °C for 1400 hr

Fig. (6) shows SEM analysis of copper sample of paper insulated copper conductor after ageing with transformer oil without passivator at 140° C for 1400 hr. This indicates globules of copper sulphide on aged copper surface. Fig. (7) shows SEM analysis of copper sample of paper insulated copper conductor after ageing with transformer oil with passivator at 140° C for 1400 hr. This indicates formation of a uniform film of the passivator on the conductor surface. Fig. (8) shows SEM analysis of paper sample after ageing in transformer oil without passivator at 140° C for 1400 hrs. This picture clearly shows contamination on the paper insulation in which all the fiber surfaces and the gaps between the fibers encrusted with the copper sulfides. The copper sulfide formed can be visibly seen on the paper insulation in some cases and ranges considerably in coloration depending upon severity, closeness to the conductor and other factors. The copper sulfide deposit is scattered on the paper insulation.

3.3 Energy dispersive X-ray analysis (EDX) studies

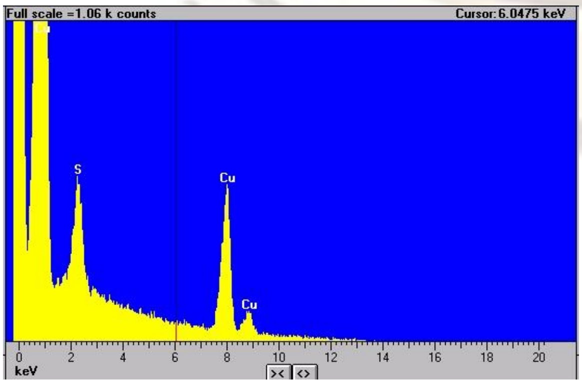

Figure 9
EDX scan of copper sample of paper insulated copper conductor after ageing in oil with out passivator at 140 °C for1400 hr

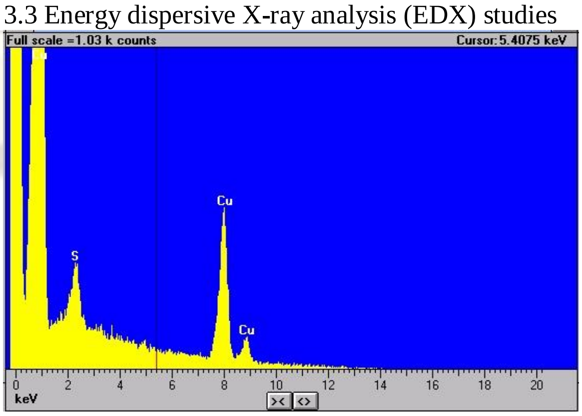

Figure 10
EDX scan of copper sample of paper insulated copper conductor after ageing in oil with passivator at 140°C for 1400 hr

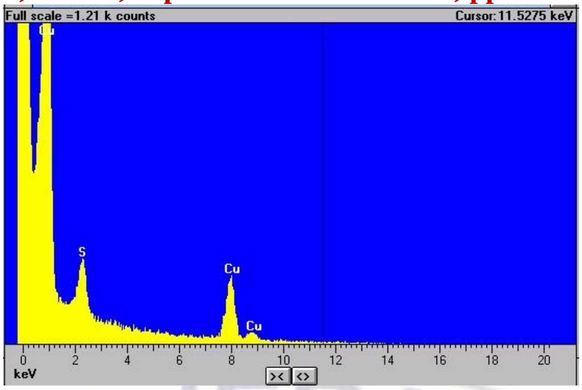

Figure 11 EDX scan of paper sample on copper conductor after ageing in oil with out passivator at 140 °C for1400 hr

Fig. (9) shows EDX scan of copper sample of paper insulated copper conductor after ageing in oil without passivator at 140° C for 1400 hr. This indicates copper and sulphur peaks on aged copper surface. The sulphur peak is seen at 2.1 keV and copper at 7.9 and 8.4 keV. Fig. (10) shows EDX scan of copper sample of paper insulated copper conductor after ageing in transformer oil with passivator at 140° C for 1400 hr. The minute sulphur peak is seen at 2.1 keV and copper peaks at 7.9 and 8.4 keV, but the intensity of the sulphur peaks is drastically reduced due to formation of thin film of passivator on the copper surface. Fig. (11) shows EDX scan of paper sample on copper conductor after ageing with transformer oil without passivator at 140° C for 1400 hr. This also shows the deposition of copper sulphide.

III. CONCLUSION

Copper sulphide formation is one of the possible corrosion mechanisms involving the corrosive sulphur and paper insulated copper conductor.

The SEM scan after ageing the paper insulated copper conductor in transformer oil with passivator at 140° C for 1400 hr shows the formation of thin film of passivator on the copper surface. The SEM, XRD and EDX scans after ageing the paper insulated copper conductor in transformer oil without passivator at 140° C for 1400 hr indicate scattered deposit of copper sulphide showing the formation of copper sulphide on the copper surface as well as on the paper insulation.

IV. ACKNOWLEDGEMENT

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