Assessment of Passivated Mineral Oil in Mitigating the Formation of Copper Sulphide in Transformers

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Abstract—**This study was taken up to understand the variations in concentrations of metal passivators like Irgamet 39 and BTA which are added to mitigate the effects of corrosive sulphur in mineral oil. The study has shown that both BTA and Irgamet 39 are effective in arresting the formation of copper sulphide on conductors. The effect of thermal ageing of oil in presence of reactive species like MBT and DBDS on the concentrations of passivators has been studied and discussed in this paper.**

Keywords— Copper sulphide; Passivators; Irgamet 39; Benzothiazole (BTA); Dibenzyl disulphide (DBDS); Mercaptobenzothiozole (MBT)

I. INTRODUCTION

Corrosive Sulphur compounds in mineral insulating oils are recognized as a serious problem affecting the performance of power and convertor transformers and reactors [1-2]. Hence many mitigation techniques are followed worldwide to arrest the formation of semi-conducting copper sulphide in between paper layers. It is also well known that copper sulphide leads to surface discharges and increase in dissipation factor which finally lead to thermal instability and breakdown of paper insulation and failure of transformers. In order to minimize the effects of corrosive sulphur compounds in mineral insulating oil, oil passivation is generally used by transformer manufacturers. From reported data [3-6] it is observed that metal passivators which are also called metal deactivators tend to decrease the failure rates of transformers when Cu_2S migration is already initiated. However, it is also important to note that metal passivators may not serve the intended purpose when many inner layers of paper are affected. There is always a situation which is determined by local electric stress distribution in clean paper that would make addition of metal passivators ineffective. Such conditions are determined by the number of turns of paper used and the extent of penetration of Cu_2S into paper layers.

Benzotriazole (BTA) or Amino methyl substituted Toluylbenzotriazole (TTA), and in some applications Disalicylidenediamine (DSDA) derivatives, are most commonly used metal passivators. Protection of the copper surface by the use of TTA and BTA derivatives is by chemical bonding of Benzotriazole molecules to copper surfaces [1]. The chemical structure of BTA and Irgamet are shown in Fig.1.

In this paper an attempt is made to explain the degradation of metal passivator due to thermal ageing of insulating oil. The effect of DBDS and Mercaptobenzothiozole (MBT) are also discussed.

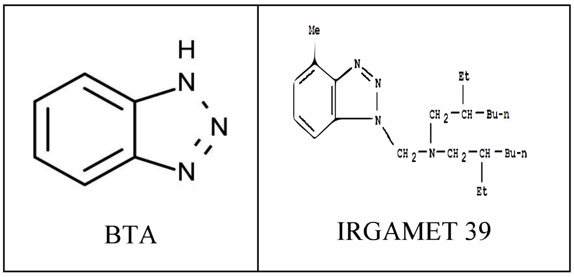

Fig.1. Chemical structure of BTA and Irgamet

II. EXPERIMENTAL PROCEDURE

A. Gas Chromatography–Mass Spectrometry (GC-MS) for the analysis of DBDS

It is an analytical method that combines the features of gas-liquid chromatography and mass spectrometry to identify different substances within a test sample. It is the highly sensitive method for the detection of DBDS in transformer oil sample [4].

The oil sample is diluted approximately 1:20 with a suitable solvent and injected into the split/split less injector of a gas chromatograph with mass spectrometer as detector. Separation of oil constituents is achieved with a suitable column such as a 30-60 m X 0.25 mm (ID) fused silica column with 5 % phenyl and 95 % methyl polysiloxane stationary phase and helium as carrier gas. Separation is facilitated through temperature programming over a suitable temperature range. DBDS is monitored with the detector and quantified with the internal standard.

B. High Performance Liquid Chromatography (HPLC)

Extraction of oil samples was performed by means of a Solid Phase Extraction (SPE) method. 1 g of oil sample was dissolved in 2 to 3 ml of HPLC-grade n-pentane. The separation was performed using normal-phase cartridges packed with silica gel. All extractions were performed by employing a vacuum equipped with flow controller. The cartridges were previously conditioned with 5 ml of n-pentane at atmospheric pressure. Sample is passed through

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the cartridge under vacuum. Traces of oil retained on the packing were eluted with 5 ml of n-pentane.

The cartridge was dried by suction, maintaining the vacuum for 5 minutes. The retained Irgamet 39 was eluted with a mixture of HPLC grade Methanol. First 2 ml was collected in sample vials and filtered by iso-disc syringe-tip filter unit.

For quantitative and qualitative analysis of the extracts, reversed-phase HPLC was used in isocratic mode, at a temperature of 30 °C, using UV detection. The measurements were performed using a Waters instrument with Photodiode array UV detector. A Column (C-18) bonded phase is used with a flow rate of 1.0 ml/min. The eluent was identical to the one used for SPE. The injection volume was 20 µL. An all-glass filtration assembly was used in the experiments, with PTFE filter of diameter 25 mm and pore size 0.2 micron.

III. RESULTS AND DISCUSSIONS

Degradation of passivators were studied at two different temperatures of 140 °C and 150 °C under different experimental conditions.

A. Degradation of passivators at 140 °C

Degradation of passivators was studied during thermal ageing of paper covered copper conductors in passivated oil at 140°C in nitrogen atmosphere. The following samples were selected for understanding the role of passivators with and without sulphur compounds.

Sample 1: Transformer oil + 100 ppm of Irgamet 39

Sample 2: Transformer oil + 100 ppm of Irgamet 39 + 100 ppm of DBDS

Sample 3: Transformer oil + 100 ppm of BTA

Sample 4: Transformer oil + 100 ppm of BTA + 100 ppm of DBDS

In Fig.2 and 3 a comparative data on degradation of Irgamet and BTA independently and in presence of DBDS are shown. Though Irgamet 39 and BTA concentration decrease initially at a rapid rate; BTA concentration remains constant at 20 ppm from 150 to 784 hours of thermal ageing in the presence of DBDS as shown in Fig.4. The concentration of Irgamet 39 goes down up to 400 hours and it saturates around 6 ppm. Thus Irgamet 39 is observed to be consumed much more than BTA when oil is thermally aged at 140 ° C. It is observed that when Irgamet 39 is used either independently or along with 100 ppm of DBDS its concentration decreases to around 6 ppm at around 432 hours of thermal aging and remains constant over a period of 784 hours of thermal ageing. In case of BTA, its concentration decreases to around 20 ppm at 432 hour when there is no DBDS. However in presence of DBDS, concentration of BTA falls to 20 ppm after 120 hours of thermal aging which is much more rapid than the case when BTA alone is present. However, the concentration of BTA remains unaltered at 20 ppm up to a period of 784 hours. Degradation trends clearly indicate that minimum concentration of BTA at the end of the thermal ageing period is much more than the minimum concentration of Irgamet 39 under identical conditions of temperature and nitrogen bubbling.

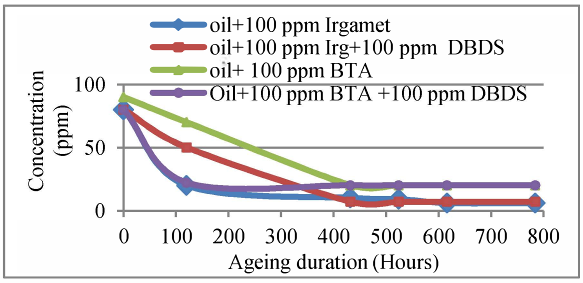

Fig.2. A comparison of degradation of Irgamet and BTA due to thermal ageing of oil

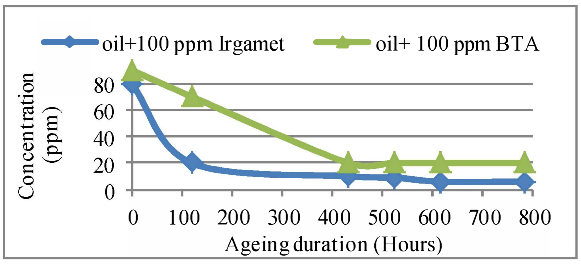

Fig.3. A comparison of degradation of Irgamet and BTA due to thermal ageing of oil (in absence of DBDS)

In Fig.4, results of decomposition of Irgamet 39 and BTA and DBDS with thermal ageing are shown for duration of 784 hours. It is observed that both Irgamet 39 and BTA show similar trends as in Fig.2. However DBDS concentration slightly increases and then starts decreasing up to 5 ppm and then increases to 66 ppm after 600 hours. Hence concentration of DBDS is unpredictable because of its cleavage and recombination during the thermal ageing cycles. It should be remembered that passivators have to protect the conductors from sulphur attacks and hence their concentrations are to be maintained consistently during the life of transformers.

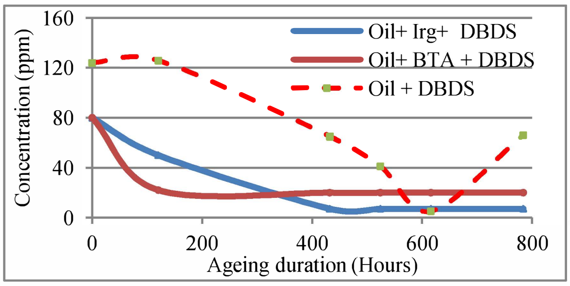

Fig.4.Degradation of Irgamet and BTA in presence of DBDS in oil

B. Degradation of passivators at 150°C

The degradation of Irgamet 39 and BTA has been studied under different conditions in nitrogen atmosphere and the results are shown in Fig.5. It is observed that Irgamet 39 concentration decreases to about 10 ppm when it is thermally aged in oil. When it is aged with paper covered copper

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conductors, its concentration decreases rapidly after 80 hours to below 10 ppm. Even when MBT is present, it is consumed and the variations are similar to that of Irgamet 39. Even in presence of DBDS, Irgamet 39 is continuously consumed. However, its consumption is faster in presence of copper conductor.

It is interesting to observe that when Irgamet and BTA are used, the MBT concentration goes down due to thermal ageing in an identical fashion at 150 ° C in nitrogen atmosphere as shown in Fig.6. Hence the results clearly point towards the fact that both Irgamet and BTA are equally effective in controlling sulphur attacks on copper conductor. Further, evidences show that even a higher starting concentration of MBT is reduced to 0.08 ppm and it is observed that there is no formation of sulphur on copper.

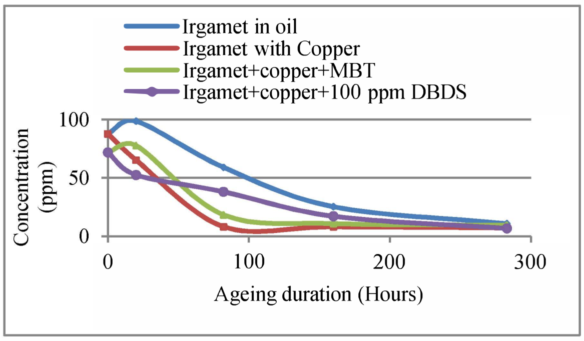

Fig. 5. Degradation of Irgamet 39 under thermal ageing at 150 ° C under different conditions

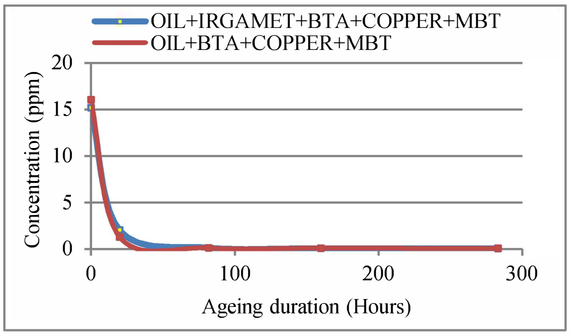

Fig. 6. Degradation of MBT due to thermal ageing at 150 ° C under different conditions in nitrogen

The variations in concentration of BTA in mineral oil, during thermal ageing at 150 ° C in nitrogen are shown in Fig.7. These experiments were carried out in the presence of copper conductors, MBT and DBDS. When BTA alone is used, its concentration reduces gradually to about 22 ppm after 280 hours of thermal ageing. When copper conductor is present, the concentration decreases only marginally as compared to the previous case when BTA alone was present in oil. When BTA, MBT and copper are present, the rate of decrease of BTA is initially faster but it is not different from the other two cases after 80 hours of thermal ageing. When MBT is replaced by 100 ppm of DBDS, BTA undergoes significant reduction with in 20 hours of thermal ageing and thereafter the rate of decrease of BTA follows the trend seen in the other three cases. Hence it is very important to follow the concentration of both the passivator and DBDS concentration in oil since BTA concentration reduces rapidly when higher concentrations of DBDS is present.

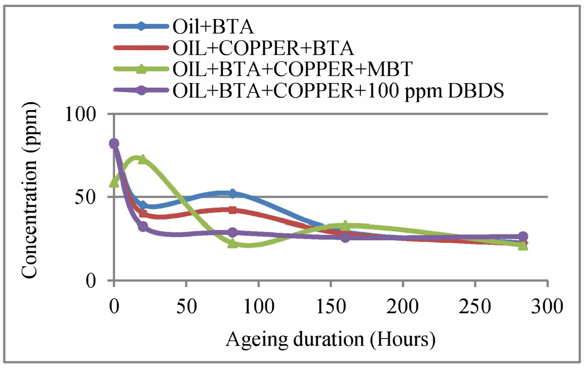

Fig.7. Degradation of BTA due to thermal ageing at 150 °C under different conditions

C. *Analysis of sulphur on copper using EDAX*

The elemental analysis of copper conductors was carried out using EDAX. When copper conductor was aged in oil at 140 ° C for 616 hours in presence of 100 ppm of DBDS and 100 ppm of Irgamet, there was no trace of sulphur on copper as depicted in Fig.8. Even copper conductor did not change in color to indicate the possible formation of Copper sulphide. Thus it is clear that even though there is decrease in concentration of Irgamet, it is able to protect the copper conductor from sulphur attacks. Since, passivators form a layer on copper conductors on a continual basis, their concentration decreases in oil due to thermal ageing.

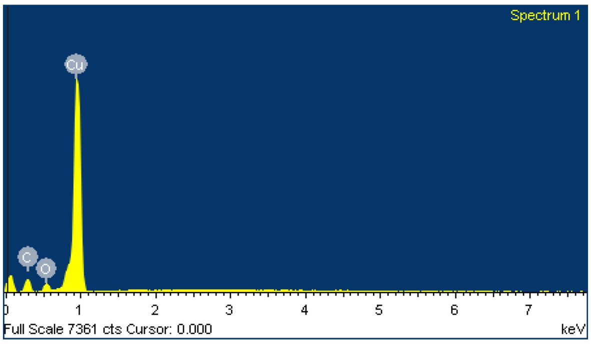

Fig.8. Copper aged in oil containing 100 ppm of DBDS and 100 ppm of Irgamet for 616 hours at 140 °C in nitrogen atmosphere

Similarly, oil containing copper conductor was aged in presence of 100 ppm of BTA and 100 ppm of DBDS at 140 ° C for 616 hours in nitrogen atmosphere. Even in this case, there was no trace of sulphur on copper conductors as shown in Fig.9. Thus it is very clear that both Irgamet and BTA are effective in controlling the formation of copper sulphide on copper conductors, though there are clear evidences to show that both BTA and Irgamet decrease in concentration when the oil is subjected to thermal ageing. It is also important to note that despite increase in DBDS due to its cleavage and

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recombination, its effect on copper to form copper sulphide is very much controlled [3-6].

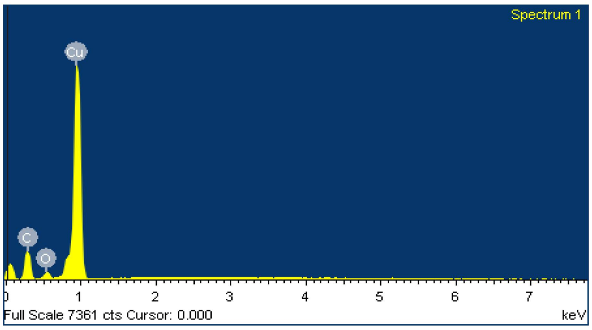

Fig.9. Copper aged in oil containing 100 ppm of BTA and 100 ppm of DBDS for 616 hours at 140 °C in nitrogen atmosphere

It is necessary to understand the impact of DBDS on copper conductors in the absence of passivators like BTA and Irgamet 39. Therefore mineral oil was aged at 140° C in nitrogen with addition of 100 ppm of DBDS for 616 hours. It is interesting to observe 1.75 weight % of sulphur on copper in this case as shown in Fig.10. Further, there were evidences of copper sulphide formation on conductor. Hence uses of metal passivators definitely help in mitigating the problems due to sulphur compounds in oil. However, the need to top up passivator appears to be very essential. Therefore it may be necessary to estimate the concentrations of metal passivators in oil and it would be safer to top up when it reaches saturation levels. However, one should look for other indicators like increase in Hydrogen and CO_2 liberation, since these parameters are also very important. However, during the course of this investigation, an increase in CO_2 concentration was partly observed but increase in Hydrogen concentration could not be conclusively proved because of low solubility of Hydrogen in mineral oil [5]. Since experiments were carried out in nitrogen atmosphere, some differences with results published by other workers have been observed.

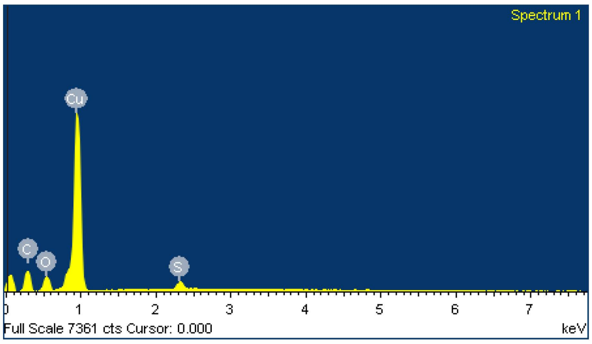

Fig.10. Copper aged in oil containing 100 ppm of DBDS for 616 hours at 140 °C in nitrogen atmosphere

IV. CONCLUSIONS

The following are some of the important conclusions of this study:

(1) Irgamet 39 and BTA are effective in protecting the copper conductors from sulphur attacks.

(2) Both BTA and Irgamet 39 undergo decomposition due to thermal ageing irrespective of the surrounding atmosphere. Hence it is necessary to monitor their concentration during the service life of transformers if they are added for mitigation of corrosive sulphur problems.

(3) Though the concentrations of BTA and Irgamet 39 deteriorate during thermal ageing, there are no signs of sulphur on copper conductors even though there are indications of increase in DBDS concentrations. However, it would be better to top up passivators when there is significant decrease in their concentration.

(4) Irgamet 39 concentration decreases much below the levels of BTA under identical conditions of thermal ageing.

(5) Both Irgamet 39 and BTA are effective in controlling sulphur attacks on copper in presence of MBT as well as DBDS.

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