Chapter 8

ANALYTICAL TECHNIQUES TO UNDERSTAND COPPER SULPHIDE FORMATION IN PAPER OIL INSULATION

8.1 INTRODUCTION

The formation of copper sulphide in transformer cellulose insulation has been studied throughout the world over past one and a half decades [1]. Number of power transformer failures has occurred since 2004 worldwide. It is obvious to expect sulphur compounds in transformer oil as it is of crude oil origin. However, because of recent changes in design of transformers, the amount of oil per kVA has significantly reduced when compared to old transformers which were designed 30 years ago. This has resulted in increased electric stresses even at operating temperatures and higher temperatures also transforms some useful sulphur compounds to reactive sulphur [2]. Diagnostics and proper monitoring of insulation system plays key role in life expectancy of Power transformers.

Sulphur compounds in transformers are grouped into five categories namely elemental sulphur, thiols, sulphides, disulphides and thiophenes. However, not all forms of sulphur are corrosive. Among all sulphur compounds present in transformer oil, Dibenzyl disulphide (DBDS) is considered to be highly reactive [3]. DBDS is introduced into the system either intentionally due to its autoxidizing nature [4] or accidently it gets
into oil. At elevated temperatures DBDS undergoes cleavage to form benzyl mercaptide in presence of copper and this ultimately leads to the formation of copper sulphide [5].

Further, the oil gets contaminated by the formation of moisture, sludge, acids and other compounds due to the ageing of insulation which changes the physical and chemical properties of oil. Apart from this, in a Power apparatus, high energy faults not only degrade the transformer’s insulation but can generate metal particles that will disperse within the mineral oil. These particles will be distributed throughout the transformer by oil circulation. Certain transformer components produce specific metal particles and these metal particles will be either found alone or in combinations with different concentrations. Analysis of the nature and number of particle will help to narrow the list of transformer components involved in the fault.

Metals that may be found in transformer oil are: aluminium, copper, iron, lead, silver, tin and zinc. For example, copper would be found in the windings and also any bronze or brass components. Lead is found in soldered joints, connectors and other peripheral components. Iron is located in the transformer core and tank, whereas aluminium can be found in the windings, corona shields and ceramic bushings. Lugs, bolts, connectors and some peripheral components may also contain tin, silver and zinc. Analysis of metals in oil would help to determine the fault type and pinpoint its location. Metals in oil can be analyzed using Atomic absorption spectroscopy (AAS). In this study AAS analysis is carried out in accordance with ASTM D3635-13 [8].

The various contamination levels in oil can be examined and verified using UV-Visible spectroscopy according to ASTM standard E-275-08 (2013) [9]. The analysis helps in identification and quantification of the impurities in transformer oil. This also helps in interpreting the dielectric response of insulation system by using light absorbing properties of the sample [10-12].

UV spectrometer is used to describe the relative level of impurities present in insulating oil of petroleum origin. It is reported [13] that new oil is almost transparent to the monochromatic beam of light in the visible spectrum. Increasing concentration of impurities in oil shifts the absorbance curve towards longer wavelengths.
Further, it is practically impossible to detect and analyze individually all sulphur compounds present in the transformer oil. However, DBDS in oil sample can be analyzed using gas chromatography equipped with mass spectrometry or gas chromatography equipped with atomic emission detector [3]. Detection limit of GC-MS is observed to be 0.1 ppm. Mercaptan sulphur or thiols present in the transformers or formed during thermal degradation of DBDS can be analyzed by potentiometric titration in accordance with ASTM D3227-04a [6]. Analysis of total sulphur content of the oil sample by Wavelength Dispersive X-Ray Fluorescence (WDXRF) in accordance with ISO 14596 [7] is also observed to be very useful.

In the present study, transformer oil samples which are subjected to thermal ageing in presence of 2-mercapto benzothiazole and DBDS under different experimental conditions are analyzed for their sulphur content, copper ion dissolution and extent of contaminations. Passivators added to mineral oil to suppress the formation of copper sulphide in transformers [14, 15]. Hence study is extended to understand the effects of passivators like Irgamet 39 (Ir 39) and Benzotriazole (BTA).

8.2 THERMO ANALYTICAL RESULTS OF ADDITIVES

Thermogravimetric analysis (TGA) of the additives gives information regarding their degradation when they are present individually. TGA of DBDS is shown in figure 8.1. It is well known that DBDS interacts with metal surface to form corrosive by-products. In transformer, DBDS reacts with copper conductors to form Cu-DBDS complex and finally copper sulphide. Hence it is very essential to understand the thermal behavior of DBDS and then attempts will be made to correlate its thermal properties to its reactions with copper in a transformer.

It is observed that degradation starts around 125 °C and about 20 % degradation takes place around 195 °C. A 60 % decrease in weight of DBDS is observed around 220 °C and 93.13 % degradation is seen around 225 °C. Hence complete degradation of DBDS takes place at a temperature of 225 °C when it is heated alone. However, degradation may vary slightly when it is present in mineral oil.
Thermogram of 2MBT is shown in figure 8.2. Degradation of 2MBT starts at a temperature of 170 °C. About 80 % reduction in weight is observed at around 225 °C. Further, weight reduces to 10 % in around 285 °C and 98.43 % loss in weight is observed around 300 °C and no further reduction in weight is observed even after heating to a temperature of 375 °C. Hence, 2MBT appears to be more stable than DBDS when they are present individually.

Thermogram of passivator BTA is shown in figure 8.3. Degradation of BTA starts around 150 °C and a decrease in weight of 80 % is observed at around 210 °C which
appears to be more stable than DBDS and 2MBT. About 99.71% reduction in weight is observed in around 250 °C.

Figure 8.3 Thermogram of BTA

Differential Scanning Calorimetric (DSC) analysis of DBDS, 2MBT and BTA are studied and differential thermogram of DBDS is furnished in figure 8.4. Typical thermograms display the difference in heat flow or heat flux on the Y axis, while temperature is plotted along X axis. Parameters analyzed are onset of melting peak, summit of melting peak, enthalpy of melting.

Figure 8.4 Differential thermogram of DBDS
Onset of melting peak is observed at 180.91 °C where phase transition starts and summit of peak is observed at 184.12 °C and it is the temperature at which the phase change peak displays the highest heat flow value where at least half of the compound has gone through phase change. The area under the peak corresponds to the enthalpy of the phase transition and it is 227.58 mJ.

Differential thermogram of 2MBT is shown in figure 8.5. Onset of melting in case of 2MBT starts at 71.57 °C and peak appears at 74.11 °C. Enthalpy of transition is 324.10 mJ.

Differential thermogram of BTA is shown in figure 8.6. Onset of melting in case of 2MBT starts at 96.80 °C and summit of peak appears at 102.36 °C. Enthalpy of transition is 615.31 mJ.
8.3 ATOMIC ABSORPTION AND UV-VISIBLE SPECTRAL ANALYSIS OF MINERAL OILS

Thermal ageing of oil containing sulphur compounds (2MBT and DBDS) and passivators (Irgamet 39 and BTA) in presence of pigtail sample were studied and the oil after thermal ageing was evaluated for dissolved copper and for the presence of contaminations. Atomic absorption spectra for the oil would furnish dissolved copper content whereas value of absorption obtained from UV-Visible spectra shows the extent of contamination of the oil in presence of additives.

8.3.1 UVV and AAS of oil in presence of mercaptan sulphur

A UV-Visible spectrum of transformer oil containing 10 ppm of MS aged in presence of pigtail sample at a temperature of 100 °C for 976 hours in air is shown in figure 8.7. The maximum absorbance observed in this case is 3.123 which is around 340 nm. However, UV-Visible spectrum of transformer oil containing 20 ppm of MS aged in presence of pigtail sample at a temperature of 100 °C for 976 hours in air is shown in figure 8.8 and maximum absorption is 3.883. Slight increase in absorbance is observed with increasing concentration of MS. Further, the difference in two spectra is very small.
and it is observed in the region of 300 to 400 nm. Results of oil conductivity as determined from Frequency Domain Spectra (FDS) showed that sample with 10 and 20 ppm of MS had oil conductivity of 10 fS/m and 37 pS/m respectively. There is drastic increase of oil conductivity upon increasing concentration of MS. Thus increase in absorbance is essentially due to presence of more acids when 20 ppm of MS is used.

**Figure 8.7** UV-Visible spectra of transformer oil containing 10 ppm of MS aged in presence of pigtail sample for 976 hours at 100 °C in air

**Figure 8.8** UV-Visible spectrum of transformer oil containing 20 ppm of MS aged in presence of pigtail sample for 976 hours at 100 °C in air
UV-Visible spectrum of transformer oil containing 20 ppm of MS aged in presence of pigtail sample for 600 hours at 140 °C in air is shown in figure 8.9. Maximum absorbance of 4.377 is observed which is slightly higher when compared to sample aged at 100 °C. Further, broadening of the spectra in the region of 300-400 nm is also evident. Oil conductivity is observed to be 310 pS/m. Hence, increase in temperature of ageing is seen in terms of increase in oil conductivity which in turn results in increase in absorbance.

![Figure 8.9](image)

**Figure 8.9** UV-Visible spectra of transformer oil containing 20 ppm of MS aged in presence of pigtail sample for 600 hours at 140 °C in air

Table 8.1 summarizes the results of UV-Visible and AAS of oil samples aged in presence of 2MBT in air. It is observed that there is slight increase in maximum absorbance with increasing concentration and increasing temperature.

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Sample ageing temperature and duration condition</th>
<th>MS (ppm)</th>
<th>Maximum Absorbance</th>
<th>Copper Content (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10 ppm of MS+100°C+aged for 976 hours + air</td>
<td>0.15</td>
<td>3.123</td>
<td>1.1</td>
</tr>
<tr>
<td>2</td>
<td>20 ppm of MS+100°C+aged for 976 hours+ air</td>
<td>0.13</td>
<td>3.883</td>
<td>1.3</td>
</tr>
<tr>
<td>3</td>
<td>20 ppm of MS+140°C+aged for 600 hours+ air</td>
<td>0.19</td>
<td>4.377</td>
<td>1.5</td>
</tr>
</tbody>
</table>
Dissolved copper of 1.1 to 1.5 ppm is observed in all the cases considered. However, result of figure 8.9 also indicates considerable changes in the spectra in the vicinity of 400 nm.

### 8.3.2 UVV and AAS of oil in presence of DBDS

DBDS in mineral oil is the main culprit for copper corrosion in transformers. Thermal degradation of DBDS in mineral insulating oil in presence of copper conductors is very complex. Analysis of thermally aged oil in presence of DBDS and copper furnishes details regarding copper sulphide formation in transformers. Various possible approaches are tried to analyze copper corrosion in transformers.

UV-Visible spectra and AAS results of mineral oil after thermal ageing at different temperatures in presence of DBDS of different concentration gives valuable information about contamination of the oil and dissolved copper in oil after different duration of ageing.

UV-Visible spectra of transformer oil containing 50 ppm of DBDS aged in presence of pigtail sample for 1063 hours at 100 °C in nitrogen are shown in figure 8.10. UV-Visible spectra of transformer oil containing 300 ppm of DBDS aged in presence of pigtail sample aged for 1063 hours at 100 °C in nitrogen is shown in figure 8.11.

From figure 8.10, the maximum absorbance observed is 4.515 for 50 ppm of DBDS in oil and it is 2.855 in case of 300 ppm of oil. AAS analysis showed that results of concentration of copper in oil are 1.5 and 1.1 ppm respectively. Though absorbance of oil with 300 ppm of DBDS is very less, dissolved copper in both the cases are almost same. Thus disintegration of 50 ppm and 300 ppm of DBDS results in nearly same amount of copper. However, degree of contamination of paper would be larger in case of 300 ppm of DBDS due to formation of copper sulphide. It is clear that rate of disintegration of DBDS is proportional to concentration of DBDS but its reaction with copper appears to be same to form copper ions of 1 to 1.5 ppm. However, this result may also be due to formation of copper sulphide in case of 300 ppm of DBDS.
UV-Visible spectra of transformer oil containing 50 ppm of DBDS aged in presence of pigtail sample for 1063 hours at 100 °C in nitrogen are shown in figure 8.10 to 8.15 respectively. Maximum absorbance of 4.588, 4.375, 0.487 and 4.66 are seen for oil with 50, 100, 200 and 300 ppm of DBDS respectively. Corresponding dissolved copper from AAS spectra are 1.1, 1.2, 0.1 and 1.2 ppm respectively for 50, 100, 200 and 300 ppm of DBDS in oil. Oil conductivity values for these 4 samples are
determined using Frequency Domain Spectroscopy (FDS). Oil conductivity of samples with 50, 100, 200 and 300 ppm of DBDS are 950, 240, 580 and 12 pS/m respectively. Thus in case of thermal ageing at 100 °C for 1735 hours, considerable increase in conductivity is observed which can be due to moisture as well as acids. Since absorbance has decreased considerably, it appears that moisture content is higher.

Figure 8.12 UV-Visible spectra of transformer oil containing 50 ppm of DBDS aged in presence of pigtail sample for 1735 hours at 100 °C in nitrogen

Figure 8.13 UV-Visible spectra of transformer oil containing 100 ppm of DBDS aged in presence of pigtail sample for 1735 hours at 100 °C in nitrogen
A UV-Visible spectrum of transformer oil containing 100 ppm of DBDS aged in presence of pigtail sample for 616 hours at 140 °C in nitrogen is shown in figure 8.16. From the figure maximum absorbance observed is 3.583. Result of AAS for dissolved copper showed 1.1 ppm. Hence degree of contamination appears to be higher in this case.
UV-Visible spectrum of transformer oil containing 200 ppm of DBDS aged in presence of pigtail sample for 370 hours at 140 °C in nitrogen is shown in figure 8.16. Maximum absorption observed is 3.259. ASS analysis showed the presence of 1.3 ppm of dissolved copper.

The results of thermal ageing of oil in presence of DBDS of different concentrations at different temperatures, resulting maximum absorption and dissolved
copper in oil are summarized in table 2. Oil samples with DBDS of 50 and 300 ppm aged at 100 °C for 1063 hours are shown under serial numbers 1 and 2 respectively. It is observed that maximum absorption as well as dissolved copper in oil is comparatively less in case of oil containing 300 ppm of DBDS. This indicates that the oil with 300 ppm of DBDS appears to be less contaminated. This is explained by the probable adhesion of formed copper sulphide on paper surface. Higher the concentration of sulphur compounds, higher is the dissolution of copper. It is also observed that concentration of DBDS after thermal ageing of 1060 hours are 0.1 and 97 for samples with starting concentration of 50 and 300 ppm of DBDS.

Transformer oil samples identified as 3 to 6 were aged for 1735 hours at 100°C with initial concentration of 50, 100, 200 and 300 ppm of DBDS. Prolonged ageing of the samples containing lower concentration of DBDS does not lead to further increase of contamination with dissolved copper. However, with higher concentration of DBDS in oil samples, prolonged ageing leads to increase in concentrations of acids, ketone etc., of the oil as well as increase in dissolved copper.

As dissolution of copper increases, movement of copper ions in the oil also increases with temperature and probability adsorption of copper over and paper increases. This result in the false indication of dissolved copper at a time when analysis is carried out and with further ageing of the insulation system, copper ions again comes back to the oil showing higher value of dissolved copper.

Oil samples identified by numbers 7 and 8 were aged at 140°C for lesser duration of 616 and 373 hours respectively. Contamination level and dissolved copper of these samples are almost same as those of corresponding samples aged at 100°C for longer durations of 1700 hours.
Chapter 8

Analytical techniques to understand copper sulphide formation in paper oil insulation

It is observed that degradation of DBDS in mineral oil in presence of air and nitrogen are different as discussed in chapter 5. Hence aged oil containing DBDS is analyzed using UV-Visible spectra and by AAS. UV-Visible spectrum of transformer oil containing 50, 100 and 200 ppm of DBDS aged in presence of pigtail sample for 976 hours at 100 °C in air is shown in figure 8.18, 8.19 and 8.20 respectively. For oil with 50 ppm oil, maximum absorbance is observed to be 1.024, for 100 ppm of DBDS it is 2.448 and for 200 ppm of oil, the observed maximum absorbance is 1.268. AAS analysis of the oils with 50, 100 and 200 ppm has shown the presence of 1.24 ppm, 2.5 ppm and 1.1 ppm of dissolved copper respectively.

Table 8.2 Effect of thermal ageing of mineral oil in presence of DBDS in nitrogen showing condition of DBDS, maximum absorbance, copper content and TS after specified ageing duration

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Sample ageing temperature and duration conditions</th>
<th>DBDS (ppm)</th>
<th>Maximum absorption</th>
<th>Copper in oil (ppm) by AAS</th>
<th>TS (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50 ppm DBDS+100 °C+ aged for 1063 hours+N2</td>
<td>0.1</td>
<td>4.515</td>
<td>1.5050</td>
<td>12</td>
</tr>
<tr>
<td>2</td>
<td>300 ppm DBDS+100 °C+ aged for 1063 hours+N2</td>
<td>97</td>
<td>2.855</td>
<td>1.0864</td>
<td>15</td>
</tr>
<tr>
<td>3</td>
<td>50 ppm DBDS+100 °C+ aged for 1735 hours+N2</td>
<td>0.1</td>
<td>4.588</td>
<td>1.1383</td>
<td>11.399</td>
</tr>
<tr>
<td>4</td>
<td>100 ppm DBDS+100 °C+ aged for 1735 hours+N2</td>
<td>0.1</td>
<td>4.375</td>
<td>1.2109</td>
<td>18.293</td>
</tr>
<tr>
<td>5</td>
<td>200 ppm DBDS+100 °C+ aged for 1735 hours+N2</td>
<td>17</td>
<td>0.487</td>
<td>0.9810</td>
<td>113.767</td>
</tr>
<tr>
<td>6</td>
<td>300 ppm DBDS+100 °C+ aged for 1735 hours+N2</td>
<td>6</td>
<td>4.66</td>
<td>1.1539</td>
<td>113.276</td>
</tr>
<tr>
<td>7</td>
<td>100 ppm DBDS+140 °C+ aged for 616 hours+N2</td>
<td>0.3</td>
<td>3.583</td>
<td>1.1383</td>
<td>50</td>
</tr>
<tr>
<td>8</td>
<td>200 ppm DBDS+140 °C+ aged for 370 hours+N2</td>
<td>22</td>
<td>3.259</td>
<td>1.3134</td>
<td>63.237</td>
</tr>
</tbody>
</table>
UV-Visible spectra of transformer oil containing 50 ppm of DBDS aged in presence of pigtail sample for 600 hours at 140 °C in air are shown in figure 8.21. Maximum absorbance is observed to be 0.964 and dissolved copper in the oil is 1.4 ppm. Oil conductivity as measured from FDS is observed to be 29 pS/m.
Table 8.3 shows the effect of thermal ageing of transformer oil in air and in terms of concentrations of DBDS, oil contamination and dissolved copper at after different ageing durations. It is observed that contamination of the oil and dissolved copper increase as DBDS concentration increases from 50 to 100 ppm. However, upon increasing its concentration to 200 ppm, contamination as well as dissolved copper in oil

**Figure 8.20** UV-Visible spectra of transformer oil containing 200 ppm of DBDS aged in presence of pigtail sample for 976 hours at 100 °C in air

**Figure 8.21** UV-Visible spectra of transformer oil containing 50 ppm of DBDS aged in presence of pigtail sample for 600 hours at 140 °C in air
tends to show lower values. This may be again due to adsorption of copper ions on paper during the time of sample analysis. Both the samples aged at 140°C for 600 hours and at 100°C for 976 exhibit similar values of maximum absorption and dissolved copper.

Table 8.3 Condition of thermal ageing in presence of DBDS in air and the results of DBDS content, maximum absorbance, copper content and TS after specified ageing duration

<table>
<thead>
<tr>
<th>Condition of Ageing</th>
<th>DBDS (ppm)</th>
<th>Maximum absorption</th>
<th>Copper in oil (ppm) by AAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 ppm DBDS+100 °C+ aged for 976 hours+O₂</td>
<td>1.5</td>
<td>1.024</td>
<td>1.2358</td>
</tr>
<tr>
<td>100 ppm DBDS+100 °C+ aged for 976 hours+O₂</td>
<td>18</td>
<td>2.448</td>
<td>2.448</td>
</tr>
<tr>
<td>200 ppm DBDS+100 °C+ aged for 976 hours+O₂</td>
<td>23</td>
<td>1.268</td>
<td>1.1274</td>
</tr>
<tr>
<td>50 ppm DBDS+140 °C+ aged for 600 hours+O₂</td>
<td>1.6</td>
<td>0.964</td>
<td>1.4072</td>
</tr>
</tbody>
</table>

8.3.3 UVV and AAS of oil in presence of both MS and DBDS

UV-Visible spectra of transformer oil containing 10 ppm of 2MBT and 50 ppm of DBDS aged in presence of pigtail sample for 600 hours at 140 °C in air is shown in figure 8.22. In addition, values of DBDS and MS concentrations and maximum absorption and dissolved copper after thermal ageing of 600 hours at 140°C in presence of 10 ppm of mercaptan sulphur as well as 50 ppm of DBDS are given in table 8.4.

Table 8.4 Condition of thermal ageing in presence of mercaptan sulphur and DBDS and the results of MS, DBDS, Maximum absorbance, copper content and TS after specified ageing duration

<table>
<thead>
<tr>
<th>Condition of Ageing</th>
<th>DBDS (ppm)</th>
<th>MS (ppm)</th>
<th>Maximum absorption</th>
<th>Copper in oil (ppm) by AAS</th>
<th>TS (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 ppm MS+50 ppm DBDS+140 °C+ aged for 600 hours+O₂</td>
<td>0.8</td>
<td>0.24</td>
<td>4.475</td>
<td>4.0131</td>
<td>93.778</td>
</tr>
</tbody>
</table>
It is observed that there is a large increase in absorption maximum of 4.475 when compared to the oil with DBDS alone in the previous case where it was 0.964. Dissolved copper also increases from 1.4072 ppm of previous case to 4.0131 ppm in presence of both the compounds. Hence, presence of mercaptan sulphur in transformer oil plays a significant role.

![UV-Visible spectra of transformer oil containing 10 ppm of 2MBT and 50 ppm of DBDS aged in presence of pigtail sample for 600 hours at 140 °C in air](image)

**Figure 8.22** UV-Visible spectra of transformer oil containing 10 ppm of 2MBT and 50 ppm of DBDS aged in presence of pigtail sample for 600 hours at 140 °C in air

### 8.3.4 Presence of passivators

Effect of passivators like Irgamet 39 and BTA on copper dissolution is studied by AAS and UV-Visible absorbance spectra. UV-Visible spectra of transformer oil containing 15 ppm of 2MBT and 100 ppm of Ir 39 aged in presence of pigtail sample for 160 hours and 283 hours at 150 °C in nitrogen are shown in figure 8.23 and 8.24 respectively. Maximum absorption in the two cases is observed to be 3.309 and 4.055 respectively. Dissolved copper at 160 hours of ageing was 1 ppm and 1.5 ppm respectively. Results indicate that maximum absorption and dissolved copper increase with thermal ageing in presence of Ir 39 and BTA.
UV-Visible spectra of transformer oil containing 100 ppm of DBDS and 100 ppm of Ir 39 aged in presence of pigtail sample for 160 and 283 hours at 150 °C in nitrogen is shown in figure 8.25 and 8.26. Maximum absorbances observed in the two cases are
2.564 and 4.284 respectively and dissolved copper in both the cases are around 1 ppm. Oil with 15 ppm of MS in oil results in more dissolved copper than 100 ppm of DBDS.

![Figure 8.25](image)

**Figure 8.25** UV-Visible spectra of transformer oil containing 100 ppm of DBDS and 100 ppm of Ir 39 aged in presence of pigtail sample for 160 hours at 150 °C in nitrogen

![Figure 8.26](image)

**Figure 8.26** UV-Visible spectra of transformer oil containing 100 ppm of DBDS and 100 ppm of Ir 39 aged in presence of pigtail sample for 283 hours at 150 °C in nitrogen

UV-Visible spectra of transformer oil containing 15 ppm of 2MBT and 100 ppm of BTA aged in presence of pigtail sample for 160 and 283 hours at 150 °C in nitrogen is shown in figure 8.27 and 8.28. Maximum absorbances observed in these cases are 3.653 and 3.895 respectively. Results of ASS showed the presence of 1 and 1.1 ppm of dissolved copper in oil respectively.
UV-Visible spectra of transformer oil containing 100 ppm of DBDS and 100 ppm of BTA aged in presence of pigtail sample for 160 and 273 hours at 150 °C in nitrogen is shown in figure 8.29 and 8.30 respectively. Maximum absorbance observed in the two cases is 1.767 and 4.49 respectively. Results of AAS showed the presence of 1 and 1.1 ppm of dissolved copper in oil.

Unlike in the presence of Irgamet 39, both MS and DBDS results in almost same quantity of dissolved copper in oil with BTA.
Transformer oil samples containing DBDS and 2MBT along with passivators were aged at 150°C for 283 hours and table 8.5 furnishes the details of condition of ageing, the results of UV-visible spectroscopy and AAS at two ageing durations of 160 and 283 hours. UV-visible spectroscopy results indicate the increased contamination of the oil in presence of mercaptan sulphur than with DBDS at 160th hour of ageing. Further, results shows that contamination of the oil increases with ageing and absorbance due to
DBDS is more than mercaptan sulphur at 283 hours of ageing. Further, maximum absorbance in presence of DBDS increases by 50% with an additional ageing of 123 hours where as in presence of MS increase in absorbance is not significant and hence the contamination of the oil appears to be less with MS.

From the data of table 8.5, it is observed that dissolved copper in oil at 160th hour of ageing is less in case of oil aged in presence of Irgamet 39 than in presence of BTA. However, at an ageing of 283 hours, copper dissolution increases and it is maximum for oil with Irgamet 39 and mercaptan sulphur. However, an important observation from sl no 7 of table 8.2, is that dissolution of copper is almost same in case of oil with passivator as well as in the absence of passivators. There is always time delay for action of passivators and DBDS is able to act much faster.

Table 8.5 Condition of thermal ageing in presence of passivators and the results
Maximum absorbance, copper content after specified ageing duration

<table>
<thead>
<tr>
<th>Condition of Ageing</th>
<th>Aged for 160 hours</th>
<th>Aged for 283 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Maximum absorption</td>
<td>Copper in oil (ppm) by AAS</td>
</tr>
<tr>
<td>15 ppm MS + 100 ppm Ir 39 + 150 °C + N₂</td>
<td>3.309</td>
<td>0.9580</td>
</tr>
<tr>
<td>100 ppm DBDS + 100 ppm Ir 39 + 150 °C + N₂</td>
<td>2.564</td>
<td>0.9876</td>
</tr>
<tr>
<td>15 ppm MS + 100 ppm BTA + 150 °C + N₂</td>
<td>3.653</td>
<td>1.0339</td>
</tr>
<tr>
<td>100 ppm DBDS + 100 ppm BTA + 150 °C + N₂</td>
<td>1.767</td>
<td>1.0324</td>
</tr>
</tbody>
</table>

In general, a linear correlation between dissolved copper and absorbance maxima is observed throughout the analysis which is in agreement with the report of Norazhar Abu Bakar [11].
8.3.5 Analysis of transformer oil for sulphur compounds

A comparative study is carried out with three samples of transformer oil containing 1) 20 ppm of MS, 2) 60 ppm DBDS and 3) 10 ppm MS and 50 ppm DBDS after thermal ageing at 140 °C for 600 hours in air. Results of MS, DBDS and TS at different duration of ageing are shown in table 8.6.

In all the three cases, concentration of MS becomes very low within 150 hours of aging which may be either due to the formation of copper sulphide or due to its disintegration within the system.

DBDS content of the oil shows decreasing trend in all the cases when ageing was carried out in air.

Table 8.6 Condition of thermal ageing and results of MS, DBDS and TS content of the oil at different ageing durations.

<table>
<thead>
<tr>
<th>Condition of Ageing</th>
<th>0 hours of ageing</th>
<th>144 hours of ageing</th>
<th>408 hours of ageing</th>
<th>528 hours of ageing</th>
<th>600 hours of ageing</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 ppm MS + 140 °C+ O₂</td>
<td>MS(ppm) 20.81</td>
<td>1.93</td>
<td>0.16</td>
<td>0.15</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>DBDS(ppm) 0.5</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>TS (ppm) 56.4135</td>
<td>42.622</td>
<td>82.748</td>
<td>33.585</td>
<td>75.7928</td>
</tr>
<tr>
<td>60 ppm DBDS + 140 °C+ O₂</td>
<td>MS(ppm) 0.35</td>
<td>0.09</td>
<td>0.36</td>
<td>0.20</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>DBDS(ppm) 57</td>
<td>19</td>
<td>17</td>
<td>14</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>TS (ppm) 51.546</td>
<td>50.088</td>
<td>51.659</td>
<td>42.909</td>
<td>53.169</td>
</tr>
<tr>
<td>10 ppm MS + 50 ppm DBDS+140 °C+ O₂</td>
<td>MS(ppm) 9.75</td>
<td>0.80</td>
<td>0.16</td>
<td>0.14</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>DBDS(ppm) 59</td>
<td>11</td>
<td>0.7</td>
<td>1.4</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>TS (ppm) 60.1705</td>
<td>42.602</td>
<td>34.753</td>
<td>33.023</td>
<td>93.778</td>
</tr>
</tbody>
</table>

TS content of the oil changes continuously with ageing which is due its adsorption or formation of copper mercaptide complex or as copper-DBDS complex over copper or paper surface at the time of measurement.

Total sulphur content of the transformer oils aged under different conditions in presence of passivators is given in table 8.7. TS content of the oil in absence of added sulphur compounds are observed to be 5 ±1 ppm. Total sulphur content of the oil without
added sulphur compounds shows increase in both the cases of Irgamet 39 and BTA. Increase of TS in case of Irgamet 39 is drastic when compared to that of BTA. However, when oil containing MS and DBDS are aged for 283 hours, TS content of the oil decreases. This may be explained by either of the two phenomenon listed below.

1. Attack of few of the sulphur compounds over copper surface leading to its decreased concentration in oil.
2. Possible escape of few of the sulphur species through the formation of gaseous sulphur oxides.

**Table 8.7** Condition of thermal ageing in presence of passivators and the results of total sulphur content at different ageing durations

<table>
<thead>
<tr>
<th>Condition of Ageing</th>
<th>TS (ppm) at 0 hour</th>
<th>TS (ppm) after 283 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 ppm Ir 39+150 °C+ N₂</td>
<td>6.005</td>
<td>29.755</td>
</tr>
<tr>
<td>15 ppm MS+100 ppm Ir 39+150 °C+ N₂</td>
<td>37.206</td>
<td>28.295</td>
</tr>
<tr>
<td>100 ppm DBDS+100 ppm Ir 39+150 °C+ N₂</td>
<td>51.658</td>
<td>35.01</td>
</tr>
<tr>
<td>100 ppm BTA+150 °C+ N₂</td>
<td>4.519</td>
<td>5.489</td>
</tr>
<tr>
<td>15 ppm MS+100 ppm BTA+150 °C+ N₂</td>
<td>35.73</td>
<td>16.669</td>
</tr>
<tr>
<td>100 ppm DBDS+100 ppm BTA +150 °C+ N₂</td>
<td>49.559</td>
<td>25.448</td>
</tr>
</tbody>
</table>

It is also observed that, decrease in total sulphur in presence of BTA is almost half of its initial value where as in presence of Irgamet 39 it is less. This indicates the efficiency of Irgamet 39 in controlling the attack of sulphur compounds on copper conductor and hence in controlling copper corrosion to a greater extent than that of BTA. TS appear to decrease in presence of BTA.

**8.4 CONCLUSIONS**

Some of the important conclusions of this study are

1. Concentration of mercaptan sulphur in mineral oil decreases drastically with thermal ageing.
2. Gradual decrease in concentration of DBDS is observed with thermal ageing of mineral oil.
3. UV-Visible spectral results reveal that maximum absorbance of the oil increase both with increase in temperature and concentration of sulphur compounds. However, increase in absorbance is more significant in case of mercaptan sulphur than with DBDS. Increase in absorbance with thermal ageing is observed in both the cases.
4. Dissolution of copper is more in case of mercaptan sulphur than that of DBDS.
5. Increase in total sulphur content of the oil after certain ageing duration which is beyond its initial value may be due to sulphur conversion from a dynamic state.
6. Irgamet 39 is observed to be effective in controlling copper dissolution than BTA.
7. DBDS/MS act much faster on copper than BTA or Irgamet 39 and this leads to increase in absorbance.
8. Dissolved copper in oil appears to be same irrespective of the presence of DBDS/MS/Irgamet 39/BTA.

REFERENCES

[2] “Impact on the worldwide electrical industry”, Together we power the world, Doble Engineering Company

[8] ASTM D3635-13 Standard Test Method for Dissolved Copper In Electrical Insulating Oil By Atomic Absorption Spectrophotometry


