

UNDERSTANDING THE EFFECTS OF COPPER SULPHIDE IN TRANSFORMER INSULATION BY DIFFERENT CHEMICAL AND ANALYTICAL TECHNIQUES

Ramachandra H.*¹, Akshatha A.² and Sundara J. R.²

1. Department of Chemistry, PET Research Foundation, PES College of Engineering, Mandya, Karnataka (INDIA)
2. R & D Management Division, Central Power Research Institute, Bangalore (INDIA)

*E-mail : ram63chandrah@gmail.com

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ABSTRACT

A number of power transformer failures have occurred worldwide since 2004 due to the formation of semiconducting copper sulphide and its accumulation in paper layers. Detecting and analyzing the copper sulphide in the beginning of its formation in mineral oil is a tedious task due to many factors like its slow formation rate which makes it difficult to detect in terms of usual electrical and dielectric measurements, its migration from paper to oil which makes it difficult to analyze accurately at any given instant of time. Hence, simultaneous use of different techniques has been made to understand the formation of copper sulphide in paper-oil insulation of transformers. Transformer oil samples containing different concentration of mercaptan sulphur ranging from 10 to 20 ppm, dibenzyl disulphide of 50 to 300 ppm and 100 ppm of metal passivators, are exposed to thermal ageing at temperatures of 100 to 150°C for different durations in presence of paper covered copper conductors. It is practically impossible to detect and analyze individually all sulphur compounds present in the transformer oil. However, Dibenzyl disulphide (DBDS) in oil can be analyzed using gas chromatography equipped with mass spectrometry. Mercaptan sulphur or thiols present in the transformers or formed during thermal degradation of DBDS is analyzed by potentiometric titration. Analysis of total sulphur content of the oil sample is carried out using Wavelength Dispersive X-Ray Fluorescence (WDXRF). Dissolved copper in oil is analyzed by Atomic Absorption Spectroscopy (AAS).

Key Words : Dibenzyl disulphide, Mercaptan sulphur, Total sulphur, Contamination, Absorption

INTRODUCTION

The formation of copper sulphide in transformers has been studied throughout the world over past two decades. A number of power transformer failures have occurred since 2004. 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 is significantly reduced when compared to old transformers which were designed 30 years ago. This has resulted in increased electric stresses even at operating temperatures due to conversion of some sulphur compounds to reactive species. Diagnostics and proper monitoring of insulation system plays key role in life expectancy of 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, Di-Benzyl Disulphide (DBDS) is considered to be highly reactive¹. DBDS is introduced into the system either intentionally due to its auto oxidizing nature² or accidentally get into oil. At elevated temperatures DBDS undergo cleavage to form benzyl mercaptide in presence of copper and this ultimately leads to the formation of copper sulphide³.

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 spectrometry¹. Detection limit of GC-MS is observed to be 0.1 ppm. Mercaptan sulphur or thiols present in the

*Author for correspondence

transformers or formed during thermal degradation of DBDS is analyzed by potentiometric titration in accordance with ASTM D3227-04a⁴. Analysis of total sulphur content of the oil sample by Wavelength Dispersive X-Ray Fluorescence (WDXRF) in accordance with ISO 14596⁵ is also observed to be very useful.

In a Power apparatus, high energy faults not only degrade the transformer's insulation but generate metal particles that will disperse in mineral oil. These particles will be distributed throughout the transformer by oil circulation. Analysis of such particles will help to narrow the list of transformer components involved in the fault.

Metals that may be found in transformer oil are : aluminum, copper, iron, lead, silver, tin and zinc. For example, copper would be found in the windings in addition to 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 aluminum 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. Metal in oil analysis will help determine the fault type and pinpoint its location. Metals in oil can be analyzed using Atomic Absorption Spectroscopy (AAS). Analysis is carried out in accordance with ASTM D3635-13⁶.

The various contamination levels in oil can be examined and verified using UV-visible spectroscopy according to ASTM standard E-275-08 (2013)⁷. The analysis would help in identification and quantification of the impurities in transformer oil with respect to contaminations present. This also helps in the dielectric response of insulation system and these particles can also use light absorbing properties of the sample and would help in analysis of impurities by using light absorbing properties of the sample⁸.

AIMS AND OBJECTIVES

In the present study, transformer oil samples are subjected to thermal ageing in presence of 2-mercapto benzothiazole (2MBTA) and DBDS and the oil is analyzed for sulphur content, copper ion dissolution and extent of contaminations. Passivators are added to mineral oil to suppress the formation of copper sulphide in transformers^{9,10}. Hence study is

extended to understand the effects of passivators like Irgamet 39 (Ir 39) and Benzotriazole (BTA).¹¹

MATERIAL AND METHODS

Transformer oil samples containing different concentration of mercaptan sulphur ranging from 10 to 20 ppm, DBDS of concentration of 50 to 300 ppm and 100 ppm of metal passivators are exposed to thermal ageing at temperatures of 100 to 150°C for different durations in presence of conventional pigtail sample¹²⁻¹⁵. Variation in concentration of mercaptan sulphur, DBDS and total sulphur content of the samples at different duration of thermal ageing have been studied. The concentrations of these compounds are determined using UV visible spectroscopy.¹⁶⁻¹⁸ Higher the value of absorption maxima, higher is the level of contamination. Dissolved copper in aged oil samples were also analyzed by AAS.¹⁹⁻²¹

Methods used for analysis of the oil samples are explained below.

Mercaptan sulphur analysis

The hydrogen sulphide free mineral oil sample is dissolved in an alcoholic sodium acetate titration solvent and titrated potentiometrically with alcoholic silver nitrate (AgNO₃) solution. The titration has to be continued till there cognition the End Point (EP). After getting the end point, titration has to be stopped automatically by setting the value of stop volume and the value of mercaptan sulphur is obtained.

Total sulphur analysis

Total sulphur content of the oil is determined by using wavelength dispersive X-ray fluorescence. In WDXRF spectrometry, the polychromatic beam emerging from a sample surface is dispersed into its monochromatic constituents by the use of an analyzing crystal according to Bragg's Law. The wavelength for any measured line is computed from knowledge of the crystal parameters and diffraction angle. In a simultaneous WDXRF spectrometer one or more detectors are placed at the certain angle for an element and so it is possible to measure different elements simultaneously.

Gas chromatography-mass spectrometry

DBDS in insulation oil is determined using GC-MS. The method involves the solid phase

extraction of DBDS with active alumina followed by gas chromatography equipped with mass spectrometry. Separation of DBDS and oil constituents is achieved with a suitable fused silica column with 5% phenyl 95% methyl polysiloxane. DBDS is monitored with a mass spectrometer and with the internal standard.

UV-Visible spectroscopy

UV-Visible spectroscopy is used to investigate contaminations in the transformer oil by using light absorbing properties of a sample. The spectral response of given transformer oil is observed and analyzed using this method. The contamination level of the oil is determined based on the maximum absorbance of the spectral response. The oil is said to be more contaminated if the absorbance peak is high and vice-versa.

Atomic Absorption Spectroscopy

In this technique, the metal particles contained in the sample are burnt at high temperatures to produce free metal atoms. The presence of these metal atoms in flame is quantified by measuring the absorption of discrete frequencies in the radiation spectrum by the

free metal atoms against a known standard.

RESULTS AND DISCUSSION

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

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 **Fig. 1**. 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 **Fig. 2** and maximum absorption is observed to be 3.883.

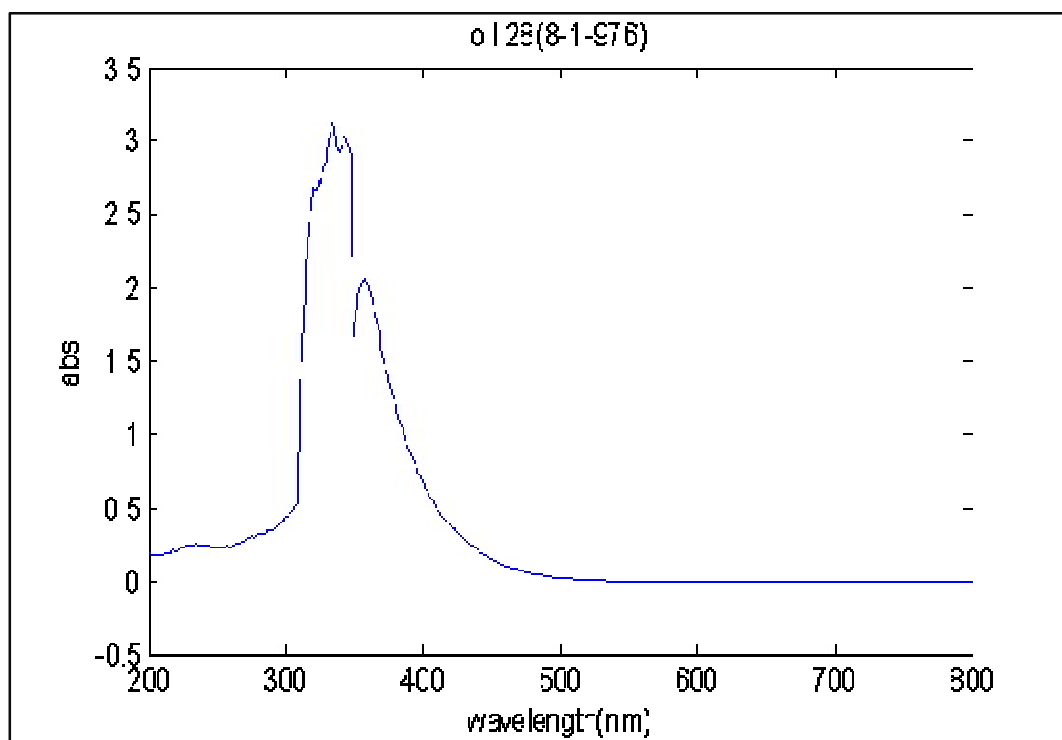


Fig. 1 : UV-Visible spectra of transformer oil containing 10 ppm of MS aged in presence of pigtail sample for 976 hours at 100°C in air

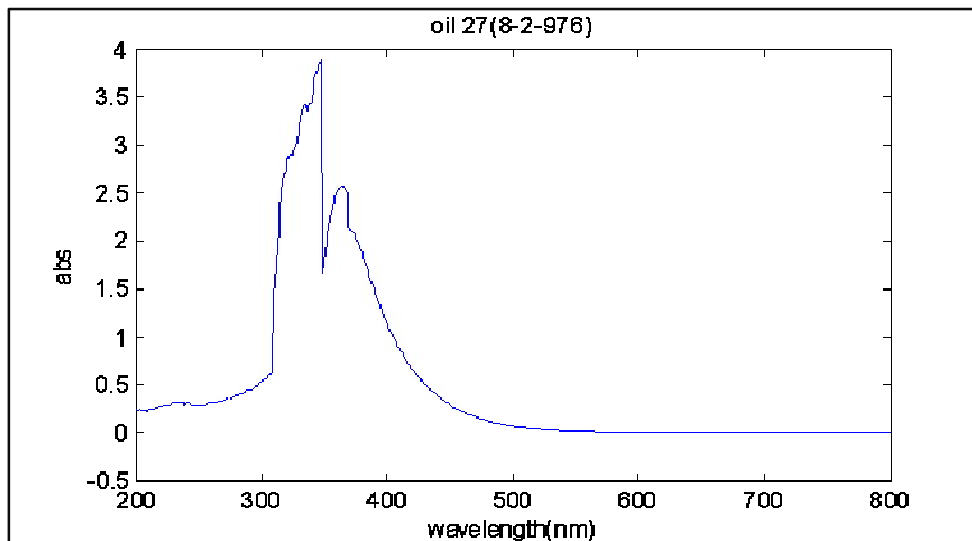


Fig. 2 : UV-Visible spectrum of transformer oil containing 20 ppm of MS aged in presence of pigtail sample for 976 hours at 100 °C in air

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 pS/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.

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 **Fig. 3**. 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. **Table 1** summarizes the results of UV-Visible and AAS of oil samples aged in presence of 2MBT in air.

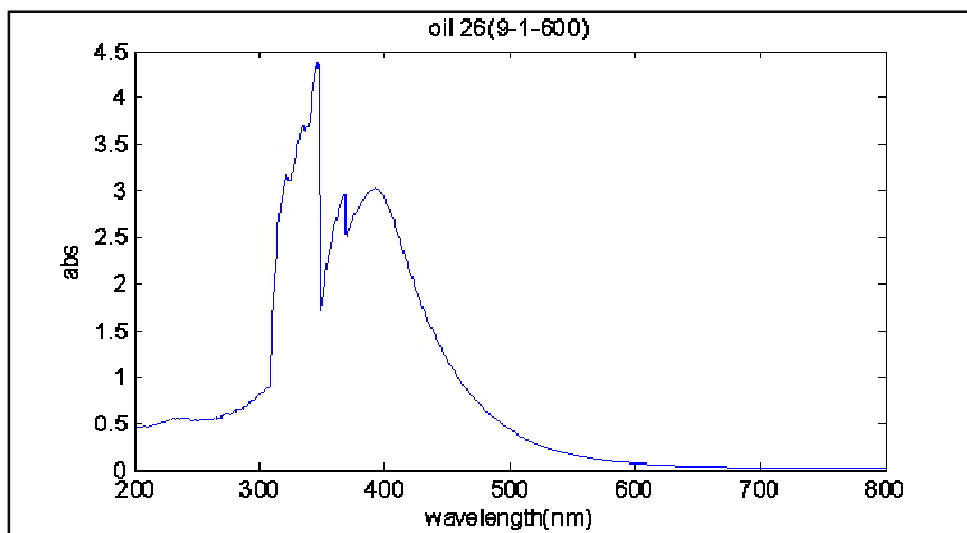


Fig. 3 : UV-Visible spectra of transformer oil containing 20 ppm of MS aged in presence of pigtail sample for 600 hours at 140°C in air

Table 1 : Effect of thermal ageing of mineral oil in presence of mercaptan sulphur shows the results of MS, maximum absorbance and copper content after thermal ageing

S/N	Sample ageing temperature and duration condition	MS (ppm)	Maximum absorbance	Copper content (ppm)
1	10 ppm of MS+100 ⁰ C+aged for 976 hours + air	0.15	3.123	1.1
2	20 ppm of MS+100 ⁰ C+aged for 976 hours+ air	0.13	3.883	1.3
3	20 ppm of MS+140 ⁰ C+aged for 600 hours+ air	0.19	4.377	1.5

It is observed that there is slight increase in maximum absorbance with increasing concentration and increasing temperature. Dissolved copper of 1.1 to 1.5 ppm is observed in all the cases considered.

UVV and AAS of oil in presence of DBDS

Presence of DBDS in mineral oil is considered to be the main reason 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 of 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 100⁰C in nitrogen are shown in **Fig. 4**. UV-Visible spectra of transformer oil containing 300 ppm of DBDS aged in presence of pigtail sample for 1063 hours at 100⁰C in nitrogen is shown in **Fig. 5**.

From **Fig. 5**, 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.

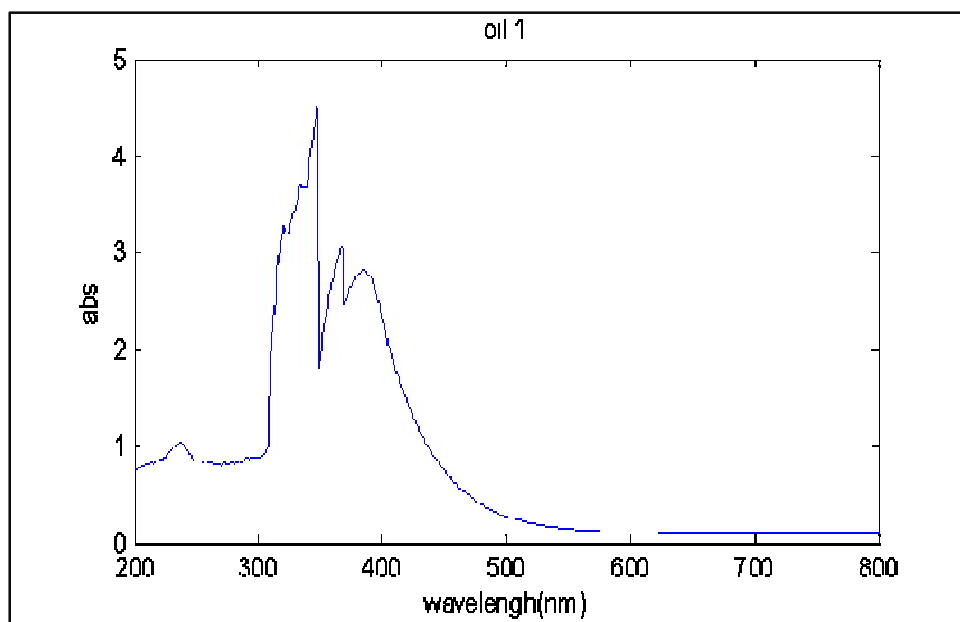


Fig. 4 : UV-Visible spectra of transformer oil containing 50 ppm of DBDS aged in presence of pigtail sample for 1063 hours at 100⁰C in nitrogen

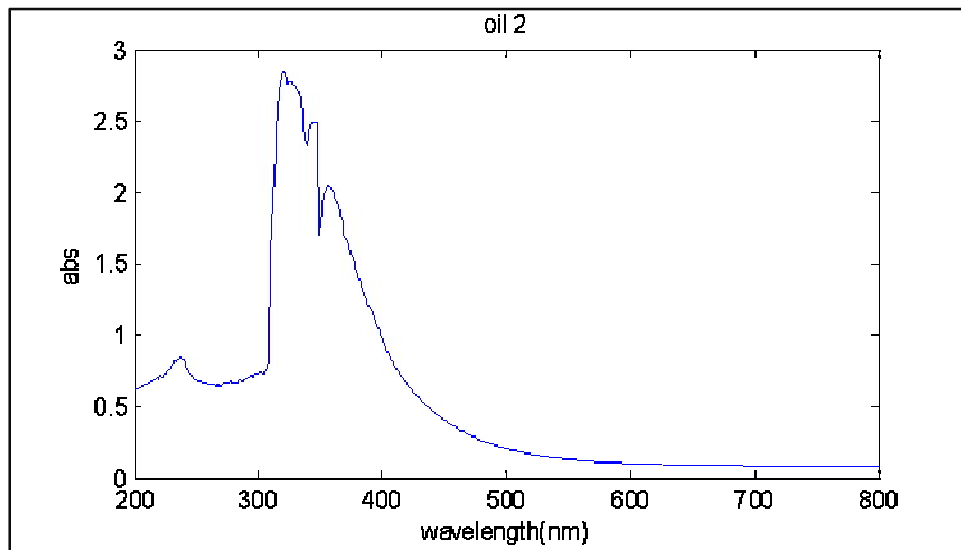


Fig. 5 : UV-Visible spectra of transformer oil containing 300 ppm of DBDS aged in presence of pigtail sample for 1063 hours at 100⁰C in nitrogen

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 50,100, 200 and 300 ppm of DBDS aged in presence of pigtail sample for 1735 hours at 100⁰C in nitrogen are shown in **Fig. 6** to **Fig. 9** 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.

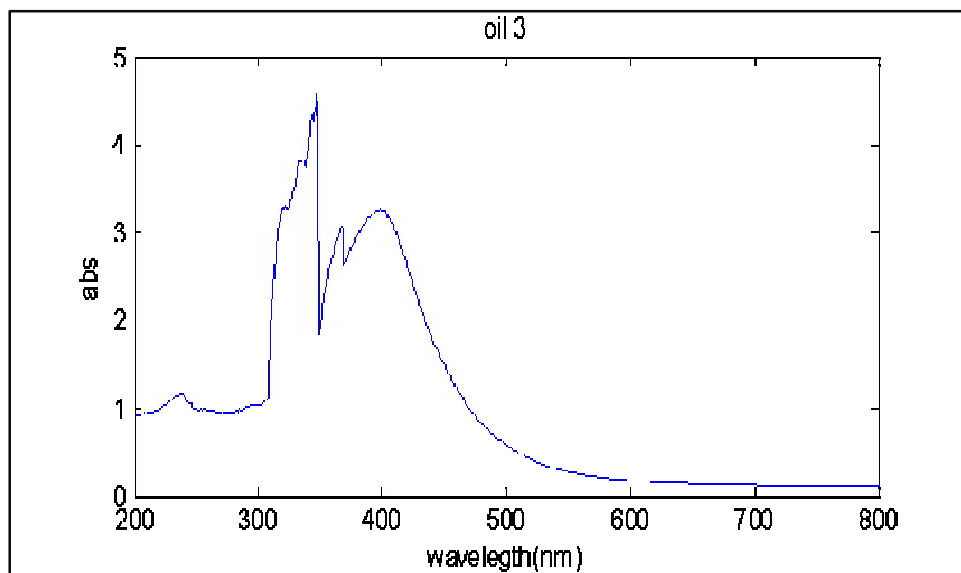


Fig. 6 : UV-Visible spectra of transformer oil containing 50 ppm of DBDS aged in presence of pigtail sample for 1735 hours at 100⁰C in nitrogen

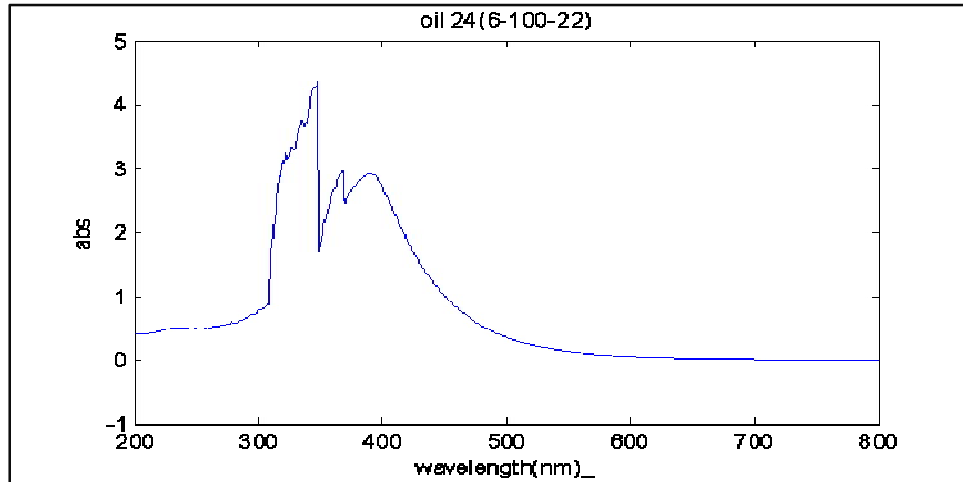


Fig. 7 : UV-Visible spectra of transformer oil containing 100 ppm of DBDS aged in presence of pigtail sample for 1735 hours at 100°C in nitrogen

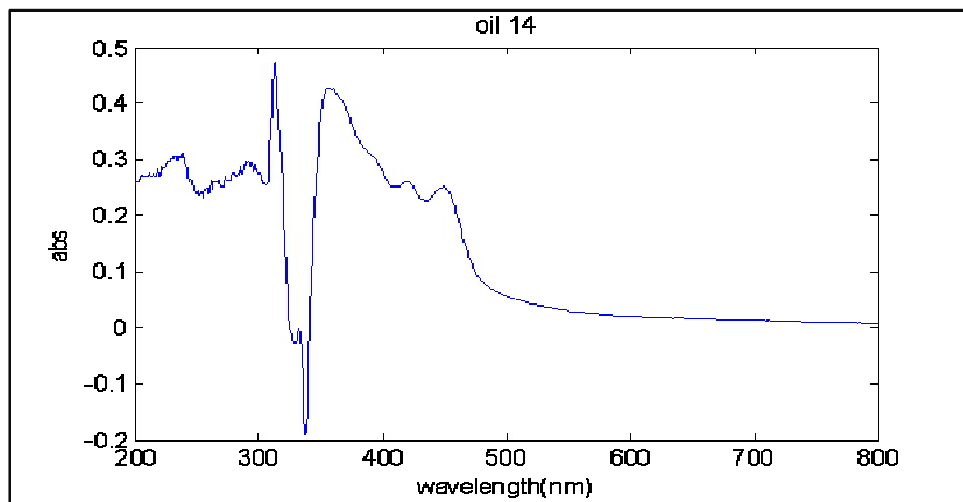


Fig. 8 : UV-Visible spectra of transformer oil containing 200 ppm of DBDS aged in presence of pigtail sample for 1735 hours at 100°C in nitrogen

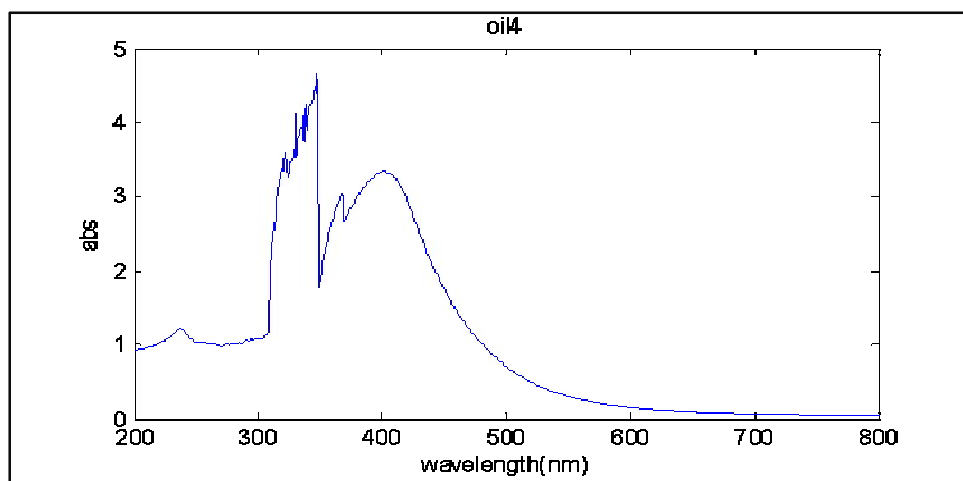


Fig. 9 : UV-Visible spectra of transformer oil containing 300 ppm of DBDS aged in presence of pigtail sample for 1735 hours at 100°C in nitrogen

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.

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 **Fig. 10**. 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 **Fig. 11**. Maximum absorption observed is 3.259. ASS analysis showed the presence of 1.3 ppm of dissolved copper.

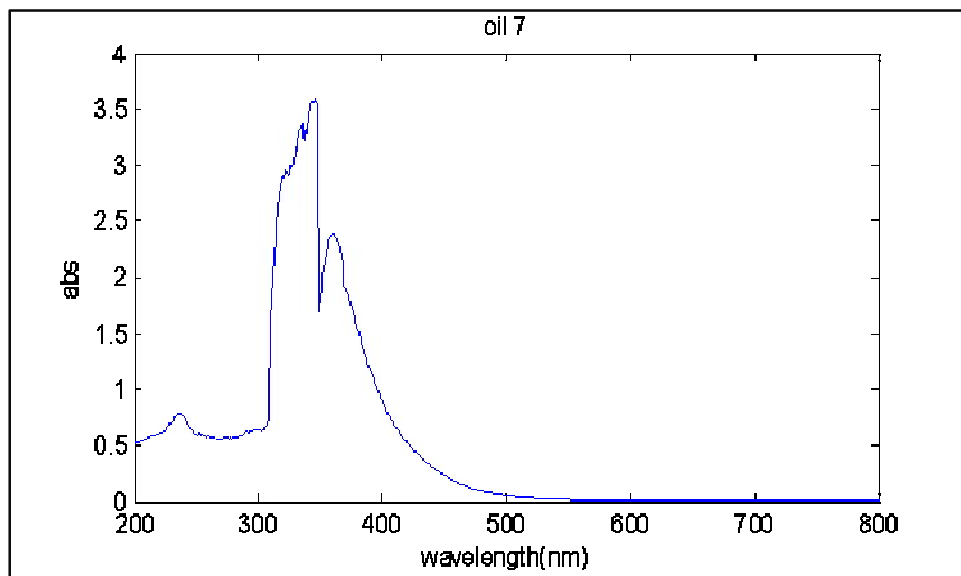


Fig. 10 : UV-Visible spectra of transformer oil containing 100 ppm of DBDS aged in presence of pigtail sample for 616 hours at 140°C in nitrogen

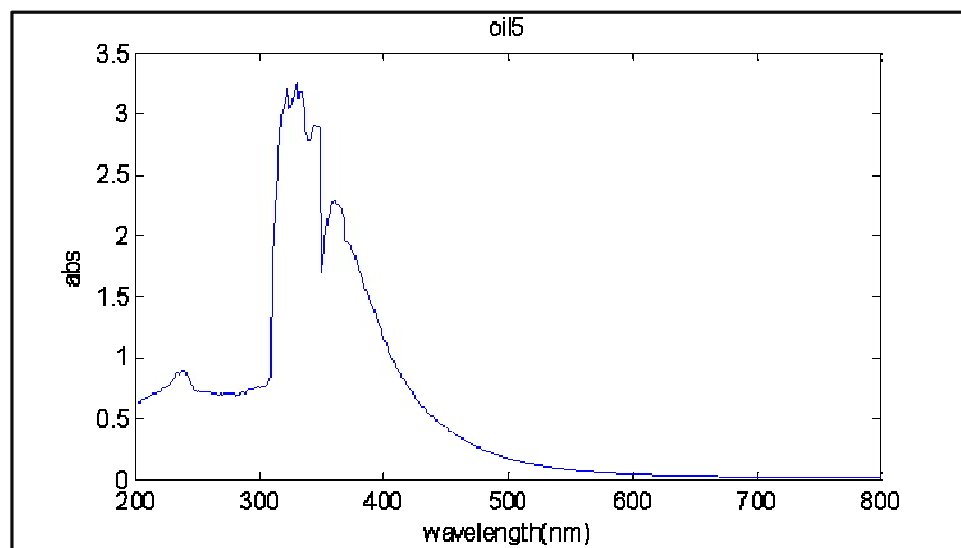


Fig. 11 : UV-Visible spectra of transformer oil containing 200 ppm of DBDS aged in presence of pigtail sample for 370 hours at 140°C in nitrogen

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.

Table 2 : Effect of thermal ageing of mineral oil in presence of DBDS in nitrogen shows condition of DBDS, max absorbance, copper content and TS after specified ageing duration

S/N	Sample ageing temperature and duration conditions	DBDS (ppm)	Maximum absorption	Copper in oil (ppm) by AAS	TS (ppm)
1	50 ppm DBDS+100°C+ aged for 1063 hours+N ₂	0.1	4.515	1.5050	12
2	300 ppm DBDS+100°C+ aged for 1063 hours+N ₂	97	2.855	1.0864	15
3	50 ppm DBDS+100°C+ aged for 1735 hours+N ₂	0.1	4.588	1.1383	11.399
4	100 ppm DBDS+100°C+ aged for 1735 hours+N ₂	0.1	4.375	1.2109	18.293
5	200 ppm DBDS+100°C+ aged for 1735 hours+N ₂	17	0.487	0.9810	113.767
6	300 ppm DBDS+100°C+ aged for 1735 hours+N ₂	6	4.66	1.1539	113.276
7	100 ppm DBDS+140°C+ aged for 616 hours+N ₂	0.3	3.583	1.1383	50
8	200 ppm DBDS+140°C+ aged for 370 hours+N ₂	22	3.259	1.3134	63.237

It is observed that degradation of DBDS in mineral oil in presence of air and nitrogen are

different. Hence, oil containing DBDS aged in air 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 100⁰C in air is shown in **Fig. 12** to **Fig. 14** 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. ASS 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.

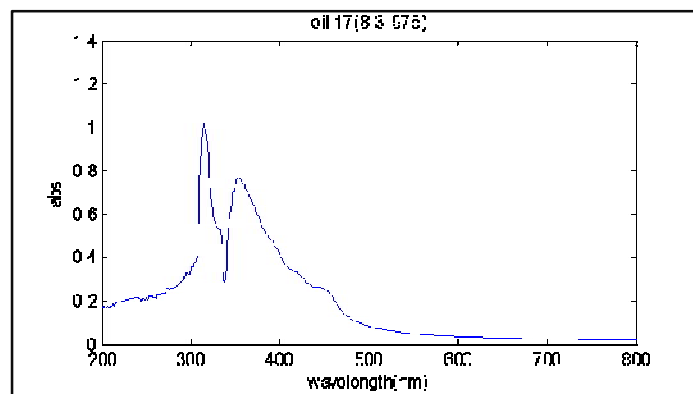


Fig. 12 : UV-Visible spectra of transformer oil containing 50 ppm of DBDS aged in presence of pigtail sample for 976 hours at 100⁰C in air

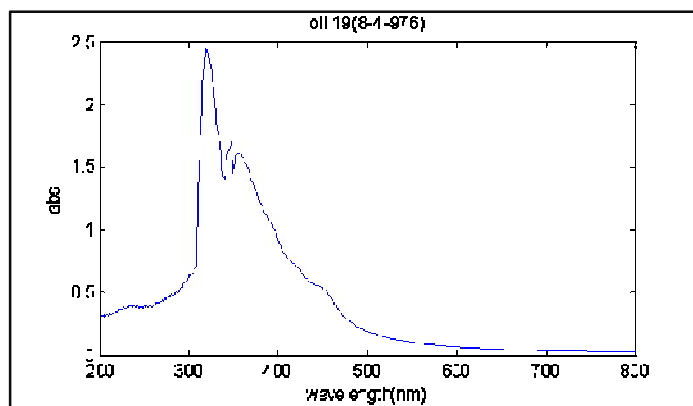


Fig. 13 : UV-Visible spectra of transformer oil containing 100 ppm of DBDS aged in presence of pigtail sample for 976 hours at 100⁰C in air

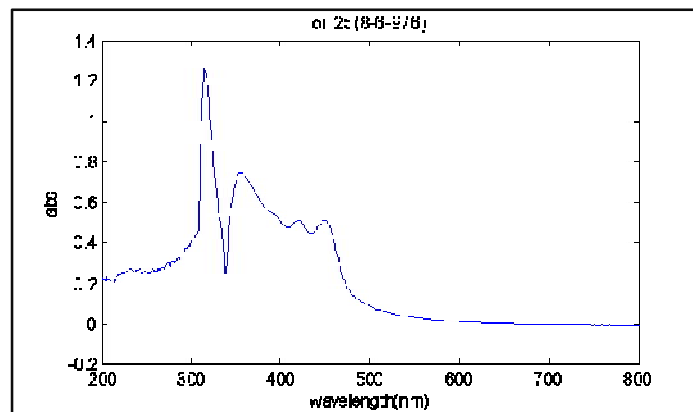


Fig. 14 : UV-Visible spectra of transformer oil containing 200 ppm of DBDS aged in presence of pigtail sample for 976 hours at 100⁰C in air

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 **Fig. 15**. 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 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 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.

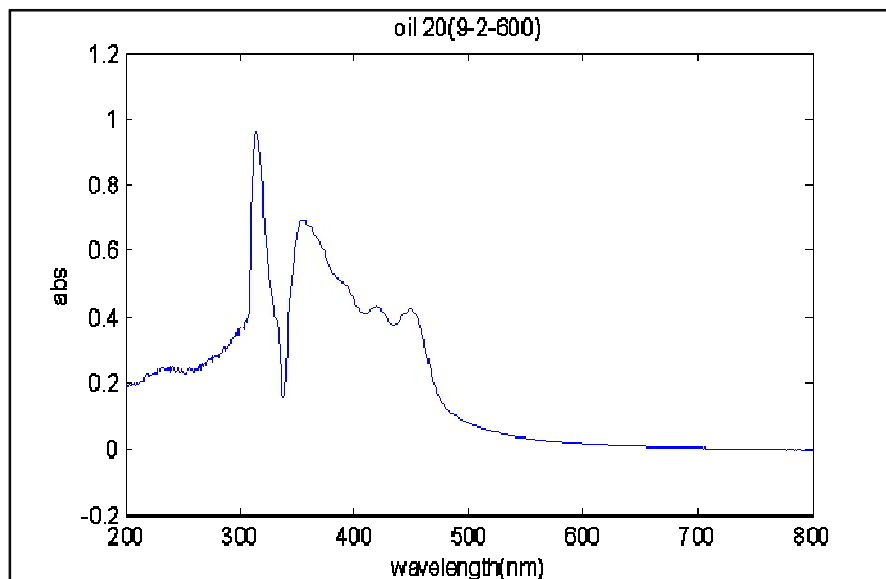


Fig. 15 : UV-Visible spectra of transformer oil containing 50 ppm of DBDS aged in presence of pigtail sample for 600 hours at 140°C in air

Table 3 : Condition of thermal ageing in presence of DBDS in air and the results of DBDS content, max. absorbance, copper content and TS after specified ageing duration

Condition of ageing	DBDS (ppm)	Maximum absorption	Copper in oil (ppm) by AAS
50 ppm DBDS+100°C+ aged for 976 hours+O ₂	1.5	1.024	1.2358
100 ppm DBDS+100°C+ aged for 976 hours+O ₂	18	2.448	2.448
200 ppm DBDS+100°C+ aged for 976 hours+O ₂	23	1.268	1.1274
50 ppm DBDS+140°C+ aged for 600 hours+O ₂	1.6	0.964	1.4072

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 **Fig. 16**.

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 4**.

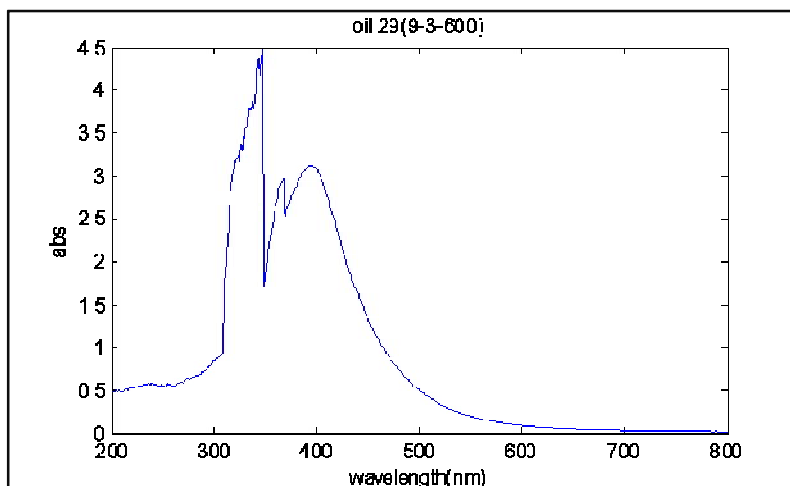


Fig. 16 : UV-Visible spectra of transformer oil containing 10 ppm of 2MBT and 50 ppm of DBDS aged in presence of pigtail sample for 600 hours at 140°C in air

Table 4 : Condition of thermal ageing in presence of mercaptan sulphur and DBDS and results of MS, DBDS, max absorbance, copper content and TS after specified ageing duration

Condition of ageing	DBDS (ppm)	MS (ppm)	Maximum absorption	Copper in oil (ppm) by AAS	TS (ppm)
10 ppm MS+50 ppm DBDS+140°C+ aged for 600 hours+ O ₂	0.8	0.24	4.475	4.0131	93.778

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.

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 already shown in **Fig. 15** and **Fig. 16** 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.

Transformer oil samples containing DBDS and 2MBT along with passivators were aged at 150°C for 283 hours and **Table 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 160hour 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 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 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 5 : Condition of thermal ageing in presence of passivators and results max absorbance, copper content after specified ageing duration

Condition of ageing	Aged for 160 hours		Aged for 283 hours	
	Maximum absorption	Copper in oil (ppm) by AAS	Maximum absorption	Copper in oil (ppm) by AAS
15 ppm MS+100 ppm Ir 39+150 ⁰ C+ N ₂	3.309	0.9580	4.055	1.5586
100 ppm DBDS+100 ppm Ir 39+150 ⁰ C+ N ₂	2.564	0.9876	4.284	1.0877
15 ppm MS+100 ppm BTA+150 ⁰ C+ N ₂	3.653	1.0339	3.895	1.1416
100 ppm DBDS+100 ppm BTA +150 ⁰ C+ N ₂	1.767	1.0324	4.49	1.1805

CONCLUSION

Concentration of mercaptan sulphur in mineral oil decreases significantly with thermal ageing. Gradual decrease in concentration of DBDS is observed with thermal ageing of mineral oil. 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. Dissolution of copper is more in case of mercaptan sulphur than that of DBDS. Increase 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. Irgamet 39 is observed to be effective in controlling copper dissolution than BTA. DBDS/MS act much faster on copper than BTA or Irgamet 39 and this leads to increase in absorbance. Dissolved copper in oil appears to be same irrespective of the presence of DBDS/MS/Irgamet 39/BTA.

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