Studies on Chemical and Dielectric Phenomena in Paper - oil insulation due to sulphur compounds in mineral oil

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***Abstract*—This paper presents the results of thermal ageing of paper oil insulation at 140° C when DBDS and mercaptan sulphur are present in oil. It discusses the effects of simultaneous presence of DBDS and mercaptan sulphur at higher temperatures. It is observed that DBDS and Mercaptan sulphur increase copper corrosion. Dielectric response using Frequency Domain Spectroscopy and Polarization/depolarization current in presence of DBDS and Mercaptan sulphur in oil during thermal ageing was studied and the results are discussed.**

Keywords— Mercaptan Sulphur; Dibenzyl disulphide; Total Sulphur; Frequency Domain Spectroscopy

I. INTRODUCTION

Presence of corrosive sulphur compounds in insulating liquids affects the long term performance of transformers. Though many sulphur compounds are present in mineral insulating oil, only a few of them function as antioxidants. Further, few sulphur compounds are highly corrosive and react with copper to form copper sulphide. The total sulphur content of mineral oil would therefore depend on the origin of oil, method and degree of refining which is adopted in the manufacture of mineral transformer oil. Sulphur compounds like mercaptan sulphur (MS) and dibenzyl disulphide (DBDS) are major contributors for corrosion of copper conductors of transformers [1-5].

A few mineral oil manufacturers use DBDS to improve the performance of mineral oil. DBDS is an antioxidant at lower temperature but turns corrosive at higher temperatures. At higher temperatures (> 90° C), DBDS reacts with copper conductor to ultimately form copper sulphide (Cu_2S), which is a semiconducting compound. The copper sulphide formed on copper surface then migrates towards paper insulation over a period of time and causes internal discharges and short circuit faults which ultimately lead to breakdown of insulation [3- 4].

Risk assessment and risk mitigation techniques for transformers require deeper understanding of Cu_2S formation and migration in paper oil insulation. Metal passivators are used to prevent the formation of Cu_2S. Benzotriazole (BTA) and Aminomethyl substituted toluyl Benzotriazole (TTA) or Irgamet 39 and Disalicylidenediamine (DSDA) derivatives are the commonly used metal passivators. The passivators prevent corrosion by averting the attack of sulphur species on copper. However, long term effectiveness of metal passivators is not yet fully understood. Further, presence of passivator does not eliminate or reduce DBDS concentration in mineral oil [6].

Though copper corrosion is physiochemical phenomenon, electric field across paper insulation is disturbed by migration of Cu_2S into different paper layers. Hence this study attempts to understand the process of copper corrosion using both chemical and electrical methods.

The methods currently available for detection of corrosion are qualitative and are based on visual observations. In this study, experimental investigations were based on thermal ageing of paper-oil insulation, visual inspection of copper conductors, quantitative determination of total sulphur, mercaptan sulphur and DBDS [7] and these results are supported by data of Energy Dispersive X-Ray Analysis (EDAX) [8].

Under electrical methods, dielectric response measurements over a range of frequency were used for estimation of moisture content of paper–oil insulation [9-10]. Attempts were also made to understand the effects of copper corrosion on the results of frequency domain spectroscopy (FDS) and polarization depolarization current measurements (PDC), keeping typical dry paper oil insulation system as the benchmark.

II. EXPERIMENTAL PROCEDURE

The studies were carried out on transformer oil containing (i) 20 ppm of mercaptan sulphur (ii) 50 ppm of DBDS and (iii) combination of 10 ppm of mercaptan sulphur and 50 ppm of DBDS. The samples were aged in presence of conventional pigtail sample [10] in a hot air circulating oven at 140°C. The mineral oil samples after different intervals of thermal ageing were analyzed for mercaptan sulphur (MS), total sulphur (TS) and DBDS content. Mineral oil was also analyzed for dissolved copper using Atomic Absorption technique.

FDS measurement was carried out to estimate moisture content and the PDC method was used for understanding the effect of DBDS and MS on polarization and depolarization current after thermal ageing. In addition, copper conductor and

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paper samples were analyzed using EDAX for the presence of sulphur on copper and copper and sulphur on paper insulation.

A. Experimental methods

Experiments were carried out to estimate the concentration of MS, DBDS and TS content of transformer oil during the process of thermal ageing. Decomposition of DBDS and MS and variations in TS were studied over a period of 600 hours. The chemical techniques of measurement are explained in brief:

1) Total Sulphur and copper analysis:

In Wavelength Dispersive X-ray fluorescence (WDXRF) spectrometry, a 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. Analysis of total sulphur in transformer oil is carried out according to IP 447/ISO 14596 [11] method.

2) Mercaptan sulphur analysis:

The measurement is carried out according to ASTM D3227 [12]. About 50 g of oil sample is dissolved in 100 ml of alcoholic sodium acetate titration solvent and titrated potentiometrically with silver nitrate ($AgNO_3$) solution. The assessment is continued till the recognition of the end point (EP) using software support. At end point, mercaptan sulphur content of the oil sample is estimated in ppm.

3) Gas chromatography–mass spectrometry (GC-MS):

It is an analytical method that combines the features of gas-liquid chromatography and mass spectrometry to identify different substances within a sample. It is the highly sensitive method for detection of DBDS in transformer oil [12]. The method allows detection limit of 0.1 ppm of DBDS in transformer oil.

The oil sample is diluted approximately in the ratio of 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 × 0.25 mm (ID) fused silica column with 5% phenyl and 95% methyl polysiloxane stationary phase using helium as carrier gas. Separation is facilitated through temperature programming over a suitable temperature range. DBDS is monitored with the detector and quantified with an internal standard.

4) FDS/PDC measurements:

In FDS method, a 200 V ac is applied to the insulation system. Power factor/dissipation factor is measured as a function of frequency from 0.0001 Hz to 1 kHz. In PDC method, a DC voltage is applied to the specimen and polarization current is measured for 10000 seconds. The specimen is shorted and depolarization current is also measured for 10000 seconds. Since there were no significant variations beyond 2000 seconds, results are only shown only up to 2400 seconds. These investigations help in assessment of (1) Moisture Content, (2) Moisture saturation (classified as dry, wet and very wet) and (3) Oil conductivity.

III. RESULTS AND DISCUSSIONS

A. Results of MS,TS and DBDS

Fig. 1 shows the variations in concentration of MS and DBDS with thermal ageing for oil with a starting concentration of 20 ppm of MS and traces of DBDS. Fig. 2 depicts variation in concentration of TS and other sulphur compounds (other than MS and DBDS) in oil.

MS in oil undergoes complete degradation to less than 1 ppm within 200 hours of thermal ageing. However, there is no formation of DBDS during this ageing period. From Fig. 2, it is observed that TS consists of MS and DBDS up to thermal ageing of 180 hours. Beyond this duration, other forms of sulphur are formed, since MS and DBDS concentration are very much reduced in 180 hours of thermal ageing.

Fig. 3 shows the variations in concentration of MS and DBDS during thermal ageing of oil containing 50 ppm of DBDS and no added MS. In Fig. 4, the corresponding variations in other sulphur compounds and TS are shown.

From Fig. 3, it is observed that DBDS undergoes degradation up to 180 hours and its concentration remains unchanged at 18 ppm from 200 to 500 hours. Further, after 500 hours, it reduces and reaches low levels at 600 hours of ageing. However, MS remains constant below 1 ppm during thermal ageing.

From Fig .4, it is observed that concentration of TS remains at an average value of 50 ppm till 400 hours of ageing. Between 400 hours and 530 hours, it decreases from 50 ppm to around 42 ppm and starts increasing again to reach 50 ppm at 600 hours. It is interesting to observe that concentration of other sulphur compounds increases to 30 ppm after 150 hours of ageing, but remains constant from 150 hours to 400 hours and then decreases to 28 ppm after 520 hours and starts increasing thereafter to reach 50 ppm. Thus, it is evident that in the presence of DBDS, there is significant increase in other forms of sulphur.

Fig. 5 shows the variations in concentration of MS and DBDS during thermal ageing of oil containing 50 ppm of DBDS and 10 ppm of MS and Fig. 6 depicts the variations in concentration of TS and other sulphur compounds.

Results shown in Fig. 5 indicate that both MS and DBDS undergo decomposition to very low levels after 400 hours of thermal ageing. From Fig. 6 it is observed that, there is an increase in the concentration of other forms of sulphur when DBDS and MS undergo degradation. When concentration of DBDS and MS is very low, contribution to TS is mainly from other sulphur compounds. The concentration of other sulphur species increases gradually during thermal ageing and reaches 35 ppm after 200 hours and remains at this level up to 430 hours and starts increasing after 530 hours of thermal ageing.

The reasons for observed results may be the possible migration of sulphur compounds towards copper and paper leading to decrease of sulphur concentration in oil. As ageing progresses, only few reactive sulphur species among them react with copper forming copper sulphide and remaining sulphur compounds go back to oil leading to increased TS value. The sulphur compound formed is not necessarily DBDS, since other forms of sulphur show increasing trend.

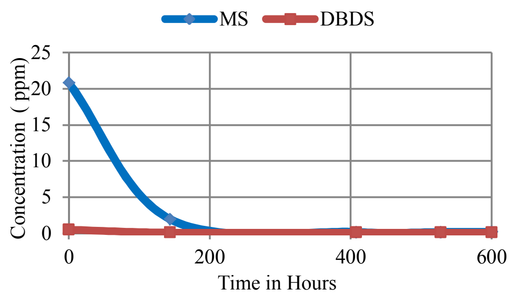

Fig.1. Variation of concentration of DBDS and MS in oil with 20 ppm of MS and traces of DBDS during thermal ageing

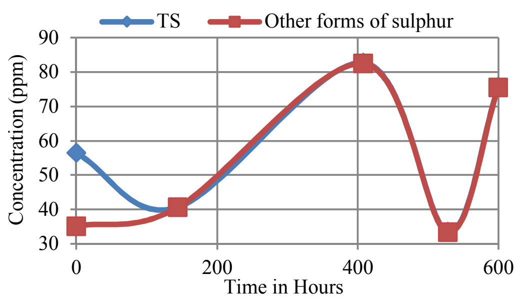

Fig.2. Variation of concentration of TS and other sulphur compounds during thermal ageing

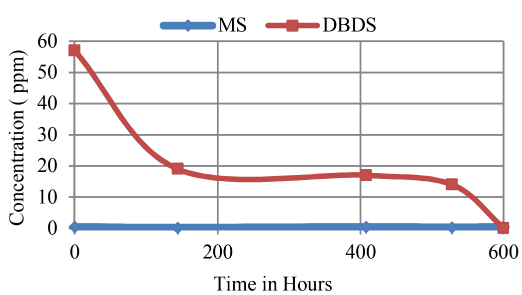

Fig.3. Variation of concentration of DBDS and MS in oil with 50 ppm of DBDS and no added MS during thermal ageing

B. EDAX Analysis

EDAX analysis of copper aged in transformer oil containing 20 ppm of MS and traces DBDS shows 1.05% of sulphur whereas oil containing 50 ppm of DBDS and no added MS shows 0.81% of sulphur on copper. However, copper in oil containing 10 ppm of MS and 50 ppm of DBDS shows 1.26 % of sulphur after 600 hours of thermal ageing. This indicates that MS and DBDS are more corrosive compounds when present together than the individual MS and DBDS compounds. Measurement of copper in oil by WDXRF shows similar trend with 15.9 ppm of copper in oil with 20 ppm of MS, 6.5 ppm of copper in oil with 50 ppm of DBDS and 79.1 ppm of copper in oil with both MS and DBDS. Atomic Absorption studies have shown copper ion concentration of 20 to 25 ppm in oil containing 50 ppm of DBDS which was aged for 600 hours at 140 º C.

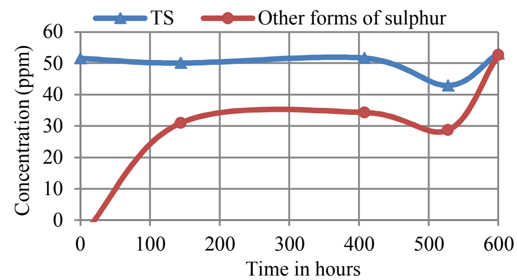

Fig. 4 Variation of concentration of TS and other sulphur compounds during thermal ageing of oil with 50 ppm of DBDS

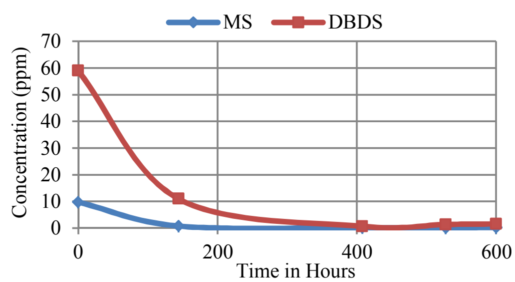

Fig. 5 Variation of concentration of DBDS and MS in oil with 50 ppm of DBDS and 10 ppm of MS during thermal ageing

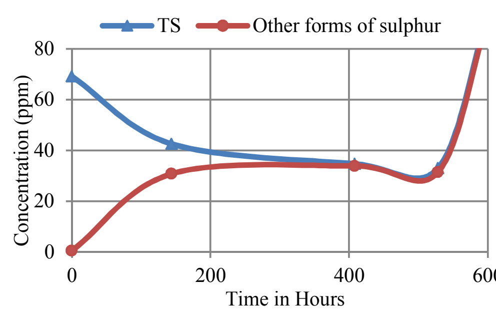

Fig.6. Variation of concentration of TS and other sulphur compounds during thermal ageing of oil with 50 ppm of DBDS and 10 ppm of MS

EDAX analysis of paper aged in oil containing 50 ppm of DBDS does not indicate the possible deposition of sulphur or copper on paper whereas in oil containing 10 ppm of MS and 50 ppm of DBDS 1.51% of sulphur and 5.26% of copper on paper are observed. Thus EDAX studies have shown that when 10 ppm of MS and 50 ppm of DBDS are present, paper shows presence of both sulphur and copper on it. Therefore, formation of copper sulphide is very evident in oil containing 10 ppm of MS and 50 ppm of DBDS. From the understanding of thermal ageing behavior of paper oil insulation, it is clear that if 10 ppm of MS and 50 ppm of DBDS are present, the performance of insulation is not much affected when temperature is 90ºC or below. But, if the temperature increases to 140º C, in about 25 days, migration of Cu_2S is evident.

C. FDS and PDC Analysis

The FDS result of paper oil insulation with 20 ppm of MS in oil aged for 600 hours is shown in Fig. 7. The results show that there are changes in the oil conductivity region which is between 0.01 to 1 Hz in a dry paper oil insulation. Since oil conductivity increases when mineral oil is aged in presence of DBDS, there are definite changes in the frequency region of oil conductivity. In Fig. 8, the power factor variations with frequency are shown for oil with 50 ppm of DBDS after thermal ageing for 600 hours at 140º C. The results are similar to the variations observed with 20 ppm of MS. Even in this case, there are changes in the spectra corresponding to the oil conductivity region. These changes are evident between 0.1 and 1 Hz of the data shown in Fig. 7 and 8.

The result of thermal ageing for 600 hours after addition of 10 ppm of MS and 50 ppm of DBDS to oil is shown in Fig 9. The results are closer to the data shown in Fig. 7 and hence MS is observed to be more dominant than DBDS in increasing oil conductivity. The impact of these results on oil condition, moisture content and levels of moisture are summarized in Table I. Addition of 20 ppm of MS leads to higher oil conductivity of 310 ps/m and the state of oil is not satisfactory and a moisture content of 4.3% indicates that the insulation is wet.

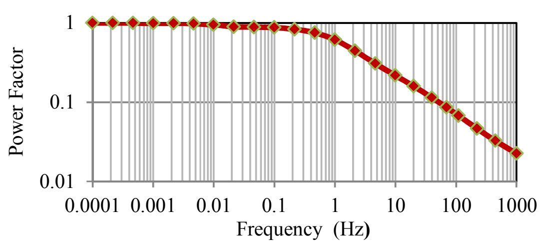

Fig.7. FDS of pigtail sample with starting concentration of 20 ppm of MS in oil aged for 600 hours

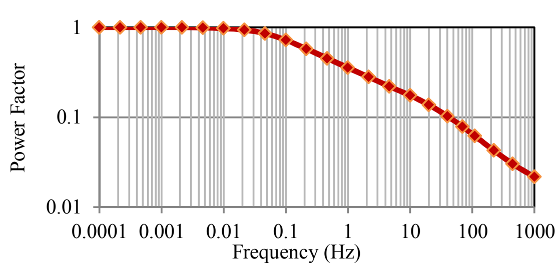

Fig.8. FDS of pigtail sample in oil having 50 ppm of DBDS, aged for 600 hours

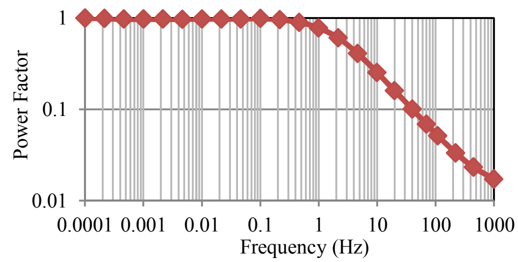

Fig.9. FDS of pigtail sample in oil with 20 ppm of MS and 50 ppm of DBDS aged for 600 hours

TABLE I. CONDITION OF PAPER - OIL INSULATION IN PRESENCE OF MS AND DBDS

Oil Sample	**Oil conductivity**	**Oil condition**	**Moisture content**	**Moisture category**
Clean oil	860 fs/m	Very good	1.2%	Dry
20 ppm of MBT	310 ps/m	Un satisfactory	4.3%	wet
50 ppm of DBDS	29 ps/m	Satisfactory	5.1%	Wet
10 ppm of MBT+ 50 ppm of DBDS	47 ps/m	Satisfactory	4.9%	wet

With addition of 50 ppm of DBDS, it is interesting to observe reduction in oil conductivity to 29 ps/m but the insulation has a very high moisture content of 5.1%. The insulation is observed to be wet. Further, when 10 ppm of MS and 50 ppm of DBDS is present, the oil conductivity is 47 ps/m and moisture content is 4.9% .The condition of insulation is observed to be wet in this case also.

From the data discussed, it is clear that average moisture content alone is not sufficient to judge the state of insulation. Hence there is a need to consider both oil conductivity and moisture levels due to presence of MS and DBDS in oil which is thermally aged.

The variation of polarization and depolarization current with time are shown in Fig. 10 for thermal ageing period of 600 hours with 20 ppm of MS, in Fig. 10, for 50 ppm of DBDS in Fig. 11 and for 10 ppm of MS and 50 ppm of DBDS in oil in Fig. 12.

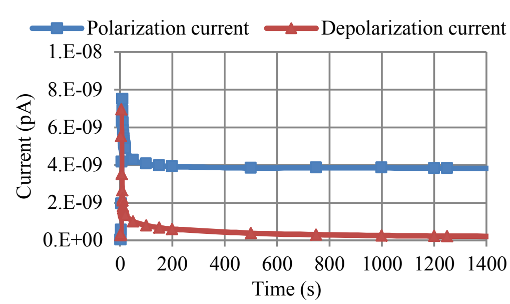

Fig. 10. Variation of polarization and depolarization current with time for oil with initial MS concentration of 20 ppm, aged for 600 hours

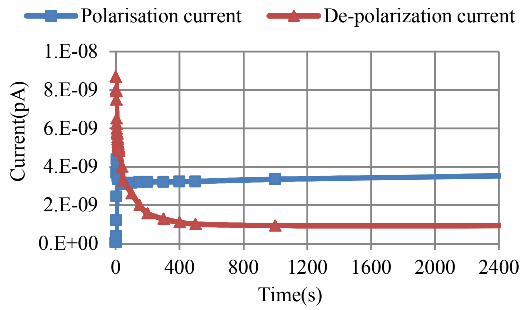

Fig.11. Variation of polarization and depolarization current with time for oil with initial DBDS concentration of 50 ppm, aged for 600 hours

There is not much of a difference in magnitude of polarization and depolarization current variations of the three cases. However in case of 20 ppm of MS (Fig. 10), both polarization and depolarization currents reach steady state levels in 10 seconds.

The PDC results with 50 ppm of DBDS looks different and formation of Cu_2S may be responsible for this characteristic. The polarization current magnitude in case of oil 10 ppm of MS and 50 ppm of DBDS (Fig. 12) is relatively higher than the two previous cases possibly due to the formation of Cu_2S and presence of copper ions in oil.

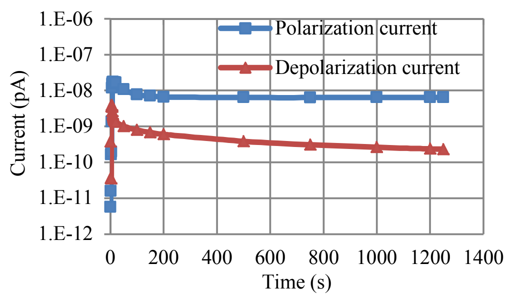

Fig.12. Variation of polarization and depolarization current with time for oil with initial DBDS concentration of 50 ppm and MS of 10 ppm aged for 600 hours

IV. CONCLUSIONS

The following are the important conclusions of this study:

1. The presence of copper ions in oil and Cu_2S on paper is observed when both DBDS and MS are present.
2. DBDS degrades at a much faster rate in presence of MS, than when it is alone, at 140 º C .
3. Chemical reactions leading to dissolved copper and copper sulphide are observed to be vigorous when both MS and DBDS are present in oil.
4. Thermal ageing of oil containing mercaptan sulphur and DBDS leads to increase in formation of other sulphur compounds.
5. The observed decrease in total sulphur concentration during thermal ageing may be due to the formation of Cu_2S.
6. FDS results indicate that in presence of MS and DBDS, there is increase in moisture content as well as increase in oil conductivity during thermal ageing of insulation.
7. PDC measurements show clear differences between polarization and depolarization current variations with time due to presence of MS and DBDS, under thermal ageing.

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REFERENCES

[1] V. Tumiatti, Carlo Roggero, Michela Tumiatti, Stefano Di Carlo, Riccardo Maina, Shubhen Kapila, "IEC 62697-2012: State of the art methods for quantification of DBDS and other corrosive sulphur compounds in unused and used insulating liquid," IEEE transaction on dielectrics and electrical insulation, vol. 19, no. 5, October 2012.

[2] S.Toyama, J. Tanimura, N. Yamada, E. Nagao, "Highly sensitive detection method of dibenzyl disulphide and the elucidation of the mechanism of copper sulphide generation in insulating oil," IEEE transaction on dielectrics and electrical insulation, vol. 16, no. 2, April 2012.

[3] G. A. Oweimreen, A. M.Y Jaber, A.M Abilkibash, N.A Mehanna, "The depletion of dibenzyl disulphide from a mineral transformer insulating oil," IEEE transaction on dielectrics and electrical insulation, vol. 19, no. 6, December 2012.

[4] Jelena M. Lukic, Draginja Nikolic, Valentina Mandic, Sandra B. Glisic, Dusan Antonovic, Aleksandar M. Orlovic, "Degradation of insulating system of Power transformers by copper sulphide Deposition: influence of oil oxidation and presence of metal passivators," Industrial and engineering chemistry research, 51, 4472-4477,ACS Publications-2012.

[5] Maria Augusta G. martins and R. Gomes, "Experimental study of the role played by dibenzyl disulphide in insulating oil corrosivity-Effect of passivator irgamet 39," IEEE transaction on dielectrics and electrical insulation, Vol.26, No. 4, August 2010.

[6] Maik Koch, Thomas Prevost, "Analysis of dielectric response measurements for condition assessment of oil-paper transformer insulation," IEEE transaction on dielectrics and electrical insulation, vol. 19, no. 6, December 2012.

[7] V. Tumiatti, Carlo roggero, Michela Tumiatti, Stefano Di Carlo, Riccardo Maina, shubhen Kalipa, "IEC 62697-2012: State of the art methods for quantification of DBDS and other corrosive sulphur compounds in unused and used insulating liquids," IEEE transaction on dielectrics and electrical insulation, vol. 19, no. 5, October 2012.

[8] Lance Lewand "The role of corrosive sulphur in transformer and transformer oil," Doble Engineering Company, 69th Annual international Doble client conference, 2002.

[9] Lance Lewand, Scott Reed, "Destruction of dibenzyl disulfide in transformer oil," Doble Engineering Company -75th Annual International Doble Client Conference, 2008.

[10] F. Kato, T. Amimoto, E. Nagao, N. Hosokaw, S. Toyama, J. Tanimura, "Effect of DBDS concentration and heating duration on copper sulphide formation in oil immersed transformer insulation," IEEE transaction on dielectrics and electrical insulation, Vol. 18, No.6, Dec-2012.

[11] IP 447: Petroleum products - Determination of sulfur content - Wavelength-dispersive X-ray fluorescence spectrometry, (Approved 2013), Published: January 2008, REF/ISBN: IP 447-2934869, IP: 447, BSI: 2000: 447, ISO: 14596, EN: 14596

[12] ASTM D 2337-13: Standard test method for (thiol mercaptan) sulphur in gasoline, kerosene, aviation turbine and distillate fuels (Potentiometric method).