The Journal of CPRI,
Vol. 13, No. 3, September 2017 pp. 387-396

Evaluation of mineral insulating oil by rapid small scale oxidation test

Ann Pamla Cruze* Lokesh K.S.**

Mineral oils are used in transformers as insulants and coolants. The long term performance of theses oils depends on their stability to oxidation of the oil. This characteristics is usually termed as resistance to oxidation process or oxidation stability. To assess oxidation stability of the insulating oils, every manufactured batch or sample is subjected to laboratory tests, by simulating the factors that influence the process of oxidation. One of the popular method followed is the oxidation stability test, where the oil is put to accelerated oxidation process by bubbling zero air over a duration of 164 to 500 hours as per IEC 61125 norms and by Rotating Pressure Vessel Oxidation Test method (RPVOT) as per ASTM D2112. Each of these procedures measure, different parameters to asses the oxidation stability of oil, depending on the test method. Experiments on same sample of insulating oils are also carried out by using a new method called Rapid Small Scale Oxidation Test method (RSSOT) ASTM D7545. The results are compared to assess the suitability of rapid small scale method for analysing the stability of insulation oils. RSSOT method has main advantage of rapid deliverance of test results and small quantity of sample. It is found that the rapid small scale method is comparable to the existing methods of oxidation stability characteristics of the oils.

Keywords: *Insulating Oils, Oxidation stability, Induction period , Rapid small scale method*

1.0 INTRODUCTION

Insulation materials are important component in the transformers, Life of the electrical equipment depends on the quality of solid and liquid insulating materials. For over five decades these mineral oils are used, which is known for excellent heat transfer characteristic and economic factors.in the transformer (1-2). A good insulation is considered, when insulation is more stable to oxidation process during its use in the transformer, During prolonged service in the electrical apparatus these oils undergo deterioration process mainly due to the continuous reaction of oxidation (1-3). The rate of reaction of oxidation process is increased when these oils are subjected electrical, thermal and mechanical stresses during service in transformer(1-4) Hence the quality of the insulation is highly dependent on the stability of the insulation oils to retain the original properties of oil. (1-4). The performance of oxidation better stability results indicates longer life of the insulating oils and good performance and stability of insulating oils are required to be analysed for every new batch or sample. Different test methods are adopted for evaluation of oxidation stability of insulating oils. At the laboratory real time factors are simulated to accelerated conditions like elevated temperature, external supply of oxidising agent (1-4). Under the influence of the accelerated conditions, the these oils undergo its physical and chemical changes due to the formation of oxidation products which is determined by laboratory methods

*Engineering Officer,Central Power Research Institute, Bengaluru, mobile no.:+919945761015 email: pamla@cpri.in,
**Professor & Registrar,JSS Science and Technology University, Mysuru, mobile no.+919481821960 email: registrarjssstu@gmail.com,

2.0 MECHANISM OF OXIDATION REACTION IN MINERAL OIL

Mineral insulating oils undergoes a series of oxidation reaction during its service in transformer or electrical equipment. Some of the factors that influence the rate of oxidation of the oil are increase in temperature, source of oxidizing agent, interference of light, oxidation duration and role of copper catalyst. The rate of deterioration of insulating oils, depends on the electrical stress, thermal stress, chemical stress and mechanical stress during its use of these oils in electrical equipment. The rate of reaction is greatly influenced by intensity and duration of contact of insulating oil with the factors affecting the reaction. It is understood that the oxidation takes place due to breakdown of molecules and reduction reaction. At temperatures below $100^{O}C$ hydro peroxides are formed, during oxidation and also auto oxidation process(4-5). Hydrogen peroxide (H2O2) is one of the most powerful oxidizers. Further the presence of oxygen enhances the chemical stress thereby increasing the rate of oxidation process (4-5). Such reaction, that involves an ionic compound in presence of water molecule, is very rapid. Oxidative reaction accelerates in oils, when metals or other catalysts cause unsaturated oil molecules to convert into free radicals are given as below:

- R-H → R Initiation reaction by heat
- R → R-O-O Reaction with triplet oxygen
- R-O-O → R-O-O-H+R Hydro peroxide Formation
- 2R-O-O →Formation of products like Alcohol Aldehyde/ Ketones, esters carboxylic acid and CO2 and auto decomposition can be represented overall as 2H2O2 → 2H2O + O2 (5)
- The above hydrocarbons decompose yielding to two active reactants ROOH → RO +OH which can initiate further reactions thus increasing the rate of oxidation.(6)

3.0 EXAMPLES OF OXIDATION OF HYDROCARBONS

Some of the typical examples of hydrocarbon molecules reactions of leading to oxidation are shown below:

CH3O + O → O2 + CH3

CH3O2 + CH3O2 → CH3O + CH3O + O2

C3H6 + OH → C3H5 + H2O

C4H6 + O → C2H4 + CH2CO

C6H5CH3 + OH →C6H5CH2 + H2O

C6H5CH3 + H → C6H5CH2 + H2

C6H5CH3 + O2 → C6H5CH2 + HO2

These reactions propagate to give raise to formation of insoluble oxidative products called as sludge. The sludge particles are solids, usually in suspended form and deposits on the solid insulating paper. These deposits affects the heat transfer characteristics of the insulating oils (7-9). Hence, at this point the oils is not fit for use. To retard the process of oxidation reaction, the finished products are added with antioxidants upto 0.5% by weight of oil. Oils without addition of antioxidants are termed as 'Uninhibited oils' and with antioxidants are termed as 'Inhibited oils' (14-15).

4.0 EXPERIMENTAL METHODS OF ANALYSIS FOR OXIDATION STABILITY OF INSULATING OILS

The long term performance of insulating oils is analysed by different methods viz., oxidation stability by zero air bubbling with accelerated temperature and copper catalyst as per IEC 61125 method C and Rotating Pressure Vessel Oxidation Stability (RPVOT) as per ASTM D 2112. Both uninhibited and inhibited type of oils are analysed by conventional method viz, Zero air bubbling method and RPVOT. Such oils are also analysed by Rapid Small Scale Oxidation Test (RSSOT) method as per ASTM D7545(10-13).

4.1 Oxidation stability by zero air bubbling method (IEC 61125)

Insulating oils are subjected to accelerated conditions that influence the rate of oxidation process, where the appreciable amount of oils is put to high temperature, with copper catalyst, and oxidizing gas bubbled through the oil during the conditioning period. The conditioning period is 164 hours for uninhibited oils, 332 hours for trace inhibited oils and 500 hours for inhibited oils. During the process the saturated and or long chain molecules of the oil undergo breakdown due to the constant and prolonged thermal stress. This gives a change in process which increases the total acidity and Dissipation Factor(Tan δ) value and also formation of sludge products depending on the quality of oil.

The oils after such conditioning is tested for parameters such as Dissipation Factor, Sludge content and Total acidity.

4.1.1 Dissipation Factor (Tan δ)

Dissipation factor (Tan δ) indicates the power loss characteristics of liquid insulation. DDF is usually measured by using Schering bridge as per test method described in IEC 60247. Numerically this property is low for new oils. As the oil deteriorates the (Tan δ) value increases indicating the extent of deterioration levels.

4.1.2 Sludge content

The analysis of sludge is carried out by precipitate formation in the sample, when dilution with 300 ml n-heptane as per the test method described in IEC 61125 and settling time for 18 hours. The precipitated sludge is filtered through G4 glass sintered crucibles.

The washings of the filtrate with n- heptane is made up to 500 ml. The sludge is quantified in terms of weight percentage.

4.1.3 Total Acidity

Total acidity of oil is analysed by developing colour and titration a base as mentioned in (IEC 61125). The filtrate collected after measuring the sludge is analysed for total acidity by colorimetric titration method by using a solvent mixture of toluene and ethanol in the ratio of 3:2 with alkali blue as indicator. The sample is neutralised with alcoholic KOH. The results are expressed in mg KOH/g.

4.2 Oxidation stability by rotating pressure vessel oxidation test (RPVOT)- ASTM D 2112

In RPVOT method, the sample is subjected to laboratory conditions with factors influencing to accelerate the rate of reaction. The pressure vessel is loaded with 50 $\pm$ 0.1 gms of sample in a glass container and 5 ml distilled water is added to maintain uniform temperature and also to accelerate to oxidation process. The pressure vessel is pressurized with oxygen of 99.999% purity and locked at 90 psi. The pressurized vessel is put in constant temperature oil bath at 140^{O}C, as long as the oil resists oxidation. The oxidation stability of the oil is measured as induction period in minutes.(8)

4.3 Oxidation stability by rapid small scale oxidation test (RSSOT) - ASTM D7545

The rapid small scale oxidation test method also utilizes the factors influencing oxidation. The sample quantity used is about 6ml and sample temperature is elevated to 140^{O}C in the test chamber. The sample cup is lined with inert metal coating. The sample compartment is filled with oxygen as oxidizing agent at a initial pressure of 700kPa (101.5 psi) and sealed hermetically. The temperature of the test chamber is increased to 140^{O}C.

5.0 RESULTS AND DISCUSSION

Interpretation of results of different test methods, to analyse assess the oxidation stability will be

discussed based on the experimental observations and the reference with acceptable values.

5.1 oxidation stability by zero air bubbling method IEC 61125 - method C

Inhibited and Uninhibited insulation oils were selected for analysis as per the conventional method ie, by oxidation stability analysis as per IEC 61125 Method C. During long duration conditioning, the oil undergoes a series of accelerated oxidation reaction thus tending to deteriorate its original parameters. The deterioration levels are evaluated by measuring Dielectric Dissipation factor DDF(Tan δ) as per IEC 60247 by using three terminal cell, Quantity of sludge is analysed as per the method IEC 61125 and increase in acid content IEC 61125 by solvent titration method. The following are the results obtained

TABLE 1

RESULTS OBTAINED BY IEC 61125 PROCEDURE

SAMPLE CODE	TYPE OF OIL	DDF	SLUDGE WT%	ACIDITY, MG KOH/G
S1	Uninhibited oils – IEC 61125 - 164 hrs	0.235	0.0024	3.12
S2		0.0095	0.0004	0.01
S3		0.063	0.11	0.77
S4		0.0054	0.0004	0.0052
S5	Inhibited oils -IEC 61125-500 hrs	0.0045	0.0036	0.0092
S6		0.0009	0.0008	0.01

Uninhibited oils are conditioned for 164 hours and Inhibited oils are conditioned for 500 hours.

Sample S1 measures high Dissipation factor, high acidity and the values are beyond the limiting values, During oxidation sample conditioning process the oil was giving out pungent odour. The results of S1 oil was not meeting the limiting values as per IEC 60296 (Product specification for unused mineral insulating oil). The following are the acceptable values for the insulating oils for both uninhibited and inhibited oils as per IEC 60296 – 2012.

TABLE 2

OXIDATION STABILITY -ACCEPTANCE VALUES

SL NO.	PROPERTY	LIMITING VALUES
1.	Dissipation Factor (Tan δ) , (max)	0.50
2.	Sludge content, wt % , (max)	0.8
3.	Total Acidity, mgKOH/g , (max)	1.2

Sample S2 and S4 indicates low dissipation factor, low acidity and low sludge content, which indicates higher stability of oxidation. Sample S3 has slightly higher dissipation factor, appreciable increase in total acid content and sludge content, but within limiting values. Sample S1,S2,S3,S4 are uninhibited oil. Sample S5 and S6 are inhibited with anti-oxidant oil which shows better results of oxidation stability analysis. .

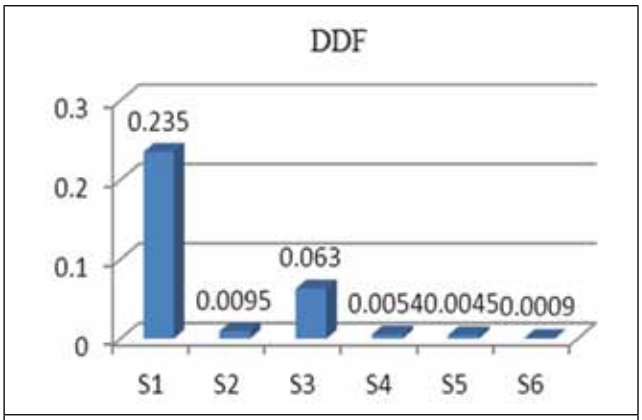

FIG 1: BAR CHART FOR DDF (TAN DELTA)

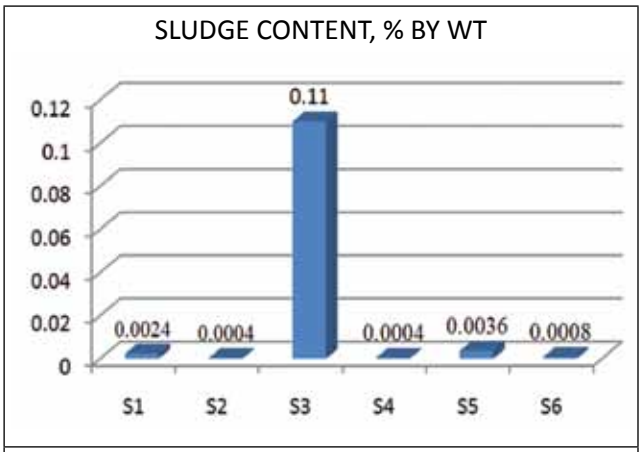

FIG 2: BAR CHART FOR SLUDGE CONTENT

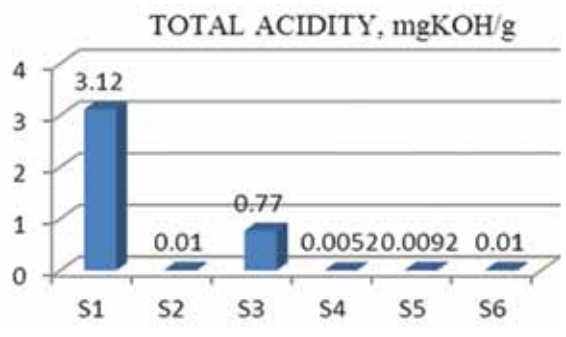

FIG 3: BAR CHART FOR TOTAL ACIDITY

5.2 Oxidation stability by rotating pressure vessel oxidation test (RPVOT) - ASTM D2112

The experimental requirements, 56 cm^2 copper catalyst put into the oxidation vessel along with 50 gms sample and 5 ml of water is put in stainless steel pressure vessel which is capable of withstanding up to 200 psi. It is very important to check the pressure vessel for leakage at room temperature. Once leakage is ascertained the pressure vessels is loaded into the oil bath maintained at 140^{O}C and fixed to the sample for the rotation at 100 rpm. Rotating pressure vessel oxidation induction period (OIP), measured in terms of minutes is obtained through graph as show in figure.

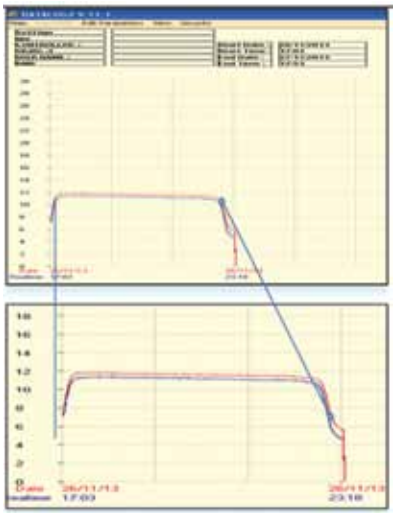

FIG 4: GRAPH OBTAINED BY RPVOT

The graph indicates the initial pressure at 90 Psi at the start of the experiment. The increased pressure indicates the expansion of oxygen pressure with the pressure vessel when the oil is subjected to high temperature of 140^{O}C. As the temperature of the oil in the pressure vessel increases the oxygen pressure rises to about 125 psi. The expanded pressure remains constant as long as the oil and along with oxidative additives, has the ability to resist to oxidation. Once the oxidation inhibitors have been consumed the oils begins to oxidize at a rapid rate. At this juncture the oxygen pressure drops from the elevated constant pressure. A drop by 25 psi is considered to be the end point. The time taken for the oil to remain at plateau pressure to the end point is considered as the oxidation induction period (OIP). The above mentioned conditions are very severe and Cigre A2-35 21 recommends this test more suitable for Inhibited mineral insulating oils.

Both inhibited and uninhibited oils are evaluated by RPVOT method, The results obtained for different samples is shown in tabular form and bar chart.

TABLE 3

INDUCTION PERIOD OBTAINED BY RPVOT

SAMPLE CODE	TYPE OF OIL	RPVOT, MIN
S1	uninhibited oils	45
S2		253
S3		115
S4		200
S5	inhibited oils	370
S6		540

Limiting values for inhibited oils as per IS:12463 (Product standards for inhibited mineral insulating oils) is 195 minutes (14-15).

The bar chart indicates the oxidation induction period (OIP) of same sample that were analysed by zero air bubbling method (IEC 61125 method C). The induction period for sample S1 is the least at 45 min. and it is also indicated in the zero air bubbling method where the results of DDF, acidity and is out of acceptable range. The induction period of sample S3 is less than 195 min, where as the zero air method indicates clear deterioration level but the results of DDF, Acidity and DDF are near to the acceptance

values. The induction period of the remaining samples are more than the acceptable limits.

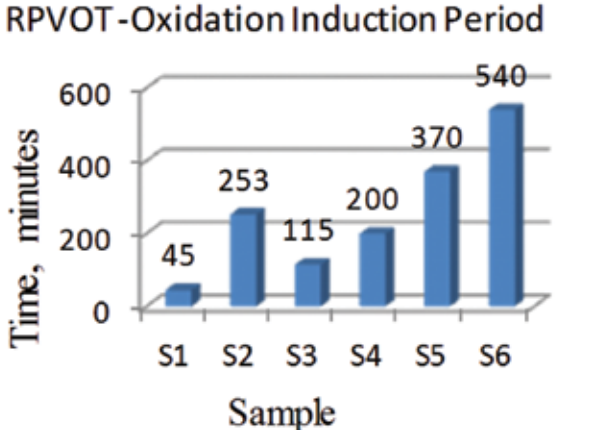

FIG 5: BAR CHART FOR RPVOT- INDUCTION PERIOD

5.3 Oxidation stability by small and rapid method

The small and rapid method was originally designed for aviation fuels, biofuels and middle distillates, where the oxidation stability of fuels sample are monitored on daily basis.

About 5-7ml oil sample is filled in the oil compartment and the equipment is hermetically sealed. The test compartment is filled with oxygen pressure to about 700 kPa (101.5 psi).

FIG 6: RECORDING BY RSSOT APPARATUS

When the test is started the temperature of the sample is elevated to 140^{O}C. At this point the oxygen is expanded to about 1000kPa (145.0 psi). The expanded pressure remains constant as long as the oil and along with additives has the ability to resist oxidation. Once the oxidation inhibitors have been consumed the oils begins to oxidize at a rapid rate.

Typical graph representation of measurement of induction process for mineral insulating oil by RSSOT is shown below

At this juncture the oxygen pressure drops from the elevated constant pressure. A 10% consumption of oxygen pressure considered to be the end point. The time taken for the oil to remain at plateau pressure to the end point is considered as the oxidation induction period (OIP). However these sample were experimented by RSSOT to understand the comparison of behaviour of uninhibited and uninhibited samples. (9-15).

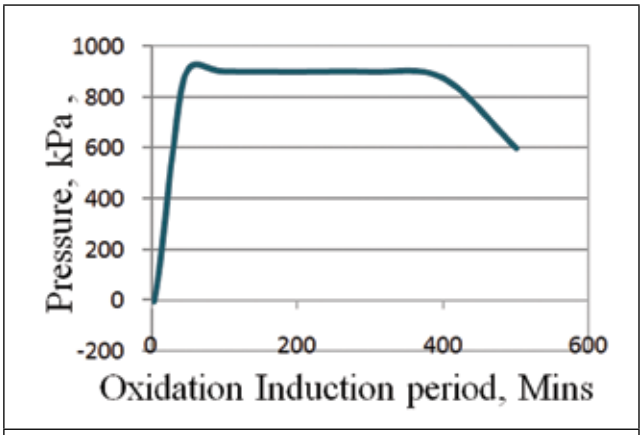

FIG 7: RSSOT GRAPH

TABLE 4

INDUCTION PERIOD OBTAINED BY RSSOT

SAMPLE CODE	TYPE OF OIL /	MINUTES
S1	uninhibited oils	35
S2		504
S3		159
S4		352
S5	inhibited oils	842
S6		908

The bar chart indicates the oxidation induction period (OIP) of same sample that were analysed by RPVOT method and zero air bubbling method.

The bar chart indicates the oxidation induction period (OIP) of same sample that were analysed by air bubbling method (IEC 61125 method C). The induction period for sample S1 is the least at 35 min. and it is also indicated in the zero air bubbling method where the results of DDF, acidity and is out of acceptable range. The induction

period of sample S3 is less than 195 min, (14-15) . Where as the zero air method indicates clear deterioration level but the results of DDF, Acidity and DDF are near to the acceptance values. The induction period of the remaining samples are relatively longer.

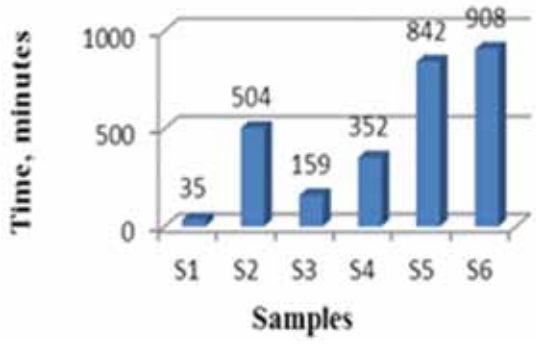

FIG 8: RSSOT RESULTS

6.0 MERITS AND DEMERITS OF OXIDATION STABILITY RAPID SMALL SCALE TEST

- Small sample volume: The rapid test method utilizes about 5-7ml of test sample, whereas the zero air bubbling method utilizes 270-360 ml of sample and RPVOT sample requires a minimum of 120 ml for analysis.
- Maximized user safety: The RSSOT equipment utilizes metal block fir maintaining the temperature and also utilizes the peltiar cooling technique for fast cooling. This mechanism enhances the safe working during the test period. Whereas the RPVOT method utilizes about 30- 40 liters of silicone oil as bath liquid. The use of high volume of oil as bath liquid are fire hazard. Hence it requires a monitoring technique until the test is completed.
- No sample preparation necessary: Sample preparation for the zero air bubbling system requires removal moisture by filtration of oil sample through G4 sintered glass. After filtration, the oil sample and distilled water are preweighed in 9-12 different tubes. The RPVOT method requires cleanliness of the vessel stock, filling of sample compartment of 90 psi oxygen pressure. Maintenance of leak proof system is slightly difficult, hence the test vessel requires as leak test procedure. Both the above methods require copper wire as catalyst in the ratio of 9.6 cm^2 and 56 cm^2 respectively. Where as the RSSOT method does not require catalyst preparation, just load the sample and adjust the initial pressurize.

6.0 CONCLUSION

Rapid small scale oxidation test (RSSOT) method has advantage of easy sample preparation, quantity of sample required is minimum, does not require copper catalyst for the complete analysis. Utilisation of minimum sample for the tests reduces problems of reclyling of used oil. The operational procedures involve easy steps and safe working methods reducing the risks of fire hazard and also delivers the results quickly. The results obtained by RSSOT method, for both uinhibited and inhibited mineral insulating oils indicate the same trend as that of the conventional methods viz, with zero air bubbling method and RPVOT method. Hence RSSOT method is suitable for laboratory study of oxidation stability of mineral insulating oils. The future work need to carried out on large scale evaluation of samples. The large scale evaluation will enable to fix the limiting parameters for RSSOT method.

7.0 ACKNOWLEDGEMENTS

Authors are thankful to Management of CPRI, Bengaluru and JSSRF, SJCE, Mysuru. Ms. Ann Pamla Cruze, would like to thank, Mr. V.V. Pattanshetti, Additional Director (Retd) and Mr. Nagaraja Rao, Joint Director (Retd), Dielectric Materials Division, CPRI, Bengaluru, for all the support to provide the laboratory facilities.

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