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Mineral insulating oils – Oxidation stability test method based on differential scanning calorimetry (DSC)

Huiles minérales isolantes – Méthode d'essai pour évaluer la stabilité d'oxydation fondée sur l'analyse calorimétrique différentielle par balayage

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MINERAL INSULATING OILS – OXIDATION STABILITY TEST METHOD BASED ON DIFFERENTIAL SCANNING CALORIMETRY (DSC)

FOREWORD

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IEC 62036, which is a technical report, has been prepared by IEC technical committee 10: Fluids for electrotechnical applications.

The text of this technical report is based on the following documents:

Enquiry draft	Report on voting
10/676/DTR	10/690/RVC

Full information on the voting for the approval of this technical report can be found in the report on voting indicated in the above table.

This publication has been drafted in accordance with the ISO/IEC Directives, Part 2.

The committee has decided that the contents of this publication will remain unchanged until the maintenance result date indicated on the IEC web site under "http://webstore.iec.ch" in the data related to the specific publication. At this date, the publication will be

- reconfirmed,
- withdrawn,
- replaced by a revised edition, or
- amended.

INTRODUCTION

The existing methods to assess oxidation stability of mineral insulating oil are very time consuming. A faster method is necessary for effective quality control and status monitoring. Differential scanning calorimetry (DSC) as a technique has been used for monitoring grease and lubricants oxidation stability. The use of DSC for evaluation of oil oxidation stability was originally suggested to IEC, TC 10 following publication of a literature review of DSC oxidation tests performed on petroleum products (10/367/INF April 1996). During IEC's TC 10 meeting in Geneva, 1998, it was decided to set up a working group for development of a standard based on DSC for rapid evaluation of mineral insulating oil oxidation stability.

MINERAL INSULATING OILS – OXIDATION STABILITY TEST METHOD BASED ON DIFFERENTIAL SCANNING CALORIMETRY (DSC)

1 Scope

The purpose of IEC 62036, which is a technical report, is to develop a rapid oxidation stability test method based on differential scanning calorimetry (DSC) to assess the oxidation stability of mineral insulating oils.

2 General remarks

The main function of insulating oil is insulation and cooling. The expected life span of transformer oil is 25 to 40 years, largely depending on operating temperature and electrical load. Specifications are prepared and used to fulfil all criteria required for proper functioning of the oil in service. Life expectancy from insulating oil has a large economic impact on the cost of operation of a unit.

The oxidation stability test is an important test as this will evaluate, to some extent, the life of the oil in service. Resistance of an oil oxidation is very much dependant on the refining process and type of crude oil. Both under-refined and over-refined oils may exhibit poor oxidation stability. The complex process of oxidation of in-service oils occurs slowly at the normal operating temperature of the transformer and is dependant on temperature, oxygen and catalyst. In the first stage of oil oxidation, radicals and peroxides are produced. These compounds are unstable and rapidly convert to volatile and soluble acids and finally producing insoluble material or sludge. All of these products have an adverse effect on electrical and physical properties of oil. The oil may reach a stage where it is not fit for its intended purpose.

To establish a long service life for the oil, an oxidation stability test is performed on the unused oil. There are several standard test methods for evaluation of the oxidation stability of transformer oil. The recommended international test method is IEC 61125. This test involves oxidizing the oil at 120 °C for 164 h and then measuring the acidity, sludge and dielectric dissipation factor (DDF). Other national test methods are based on the same principal and are time consuming. On delivery, it is required to test the oil for compliance with the specification. As this test is very time consuming, results are usually retrospective. Clearly, existing methods are time consuming and not very sensitive. Although there is no direct relation between the oil oxidation stability test and service life of the oil, oils that are very stable and resist oxidation are clearly preferred. Therefore, a fast method of determining the oxidation stability is needed for rapid evaluation of the oil and compliance to the specification.

In order to evaluate high pressure differential scanning calorimetry (PDSC) as a technique for testing oxidation stability of transformer oil and to establish a suitable method, transformer oil samples were analysed under varying conditions.

3 Effect of temperature on oxidation induction time

3.1 Isothermal

Six samples of transformer oil (A-F) were analysed using PDSC at different temperature programmes. Samples B and D were inhibited transformer oil, the remainder were uninhibited and sample F was a used oil. Oxygen at 300 psi was applied in each case and the sample weight was kept constant at 4 mg. The results are shown in Table 1. It was found that below 165 °C, no phase transition occurred in any of the six samples. Temperatures higher than expected, of up to 260 °C were required to give peaks in a reasonable time. At the lower

temperature, only sample D gave a peak at around 45 min. When this sample was run at 170 °C, the peak become sharper and clear and occurred at an onset of around 40 min. At 175 °C, the peak occurred at around 30 min and was sharper still. The same trend was observed in sample B, showing decreasing induction time with increasing temperature, but oxidation occurred after a slightly longer time. Sample B and D were inhibited oils, which showed a clear and sharp peak following the rapid oxidation and depletion of the inhibitor.

3.2 Temperature-programmed runs

The uninhibited oils, A, C, E and F showed no clearly defined peak in the thermograms of isothermal runs. Oxidation did not occur when the samples were run at a heating rate of 50 °C/min or 25 °C/min, or the curves were poorly defined. The samples were then run at a heating rate of 10 °C/min (TP 2) and more clearly defined exotherms were obtained. As with the inhibited oil samples, the uninhibited oils showed a broader, shallower peak with increasing heating rate, but the area under the peak remained the same. As the heating rate was increased from 2 °C to 5 °C, the oxidation induction time (OIT) decreased, but there was little change in the OIT between the heating rates of 5 °C and 10 °C. At a heating rate of 10 °C/min, all of the samples showed oxidation induction times between 16 min and 19 min and therefore could not be distinguished from one another. When the samples were run using a heating rate of 5 °C/min up to 180 °C, then 2 °C/min up to 210 °C (TP 3), there was a wider spread in the OITs obtained. This temperature programme was used because it was found that a slow heating rate was required to give clearly defined peaks for uninhibited oils, and oxidation usually occurred in the 180 °C – 210 °C range.

Oxidation of the inhibited oils B and D occurred at approximately the same time as it had done at 10 °C/min, but the uninhibited oils oxidized more rapidly. Samples E and C could not be distinguished, as they both had 0ITs of around 11 min and samples B and D were also very similar. The samples overall showed approximately the same ranking with the different temperature programmes. However, when the samples were run at 2 °C/min up to 180 °C, then 1 °C/min up to 210 °C (TP 4), the samples could be distinguished by their oxidation induction times. Again, the ranking was similar as with the other temperature programmes. This very slow rate of heating also clarified the peak obtained in the thermogram of sample F, which was a used oil and showed the most broad peak due to the complicated oxidation process in used oil. The used oil did not, however show the poorest oxidation stability.

4 Effect of sample size on oxidation induction time

Sample B (inhibited oil) and sample A (uninhibited oil) were analyzed by PDSC under 300 psi of oxygen, as above, using a temperature programme of 130 °C – 180 °C at 2 °C/min, 180 °C – 210 °C at 1 °C/min. Each sample was analyzed at weights of 1 mg, 4 mg and 10 mg. The oxidation induction time at the various sample sizes is given in Table 2.

4.1 Inhibited oil

The results showed that oxidation induction time increases with increasing sample size, in inhibited oil. This may be due to limited oxygen diffusion through the larger samples. The repeatability between triplicate determinations is good and is unaffected by sample weight.

4.2 Uninhibited oil

With uninhibited oil, however, there is little difference in oxidation induction time with sample size. The 10 mg sample showed slightly longer oxidation induction time, but this was within the margin of error for repeatability. Repeatability is also slightly poorer with the larger sample size and the peak is larger and more spread out, giving poorer resolution. If the sample size is very large, the accuracy is reduced, because the heat flow may be variable within the sample. Smaller sample sizes produce smaller peaks, better resolution and better accuracy. Therefore, the sample size should be as small as possible. A suitable sample size is normally 10 mg to 15 mg, however, much smaller sample sizes should be used with volatile products to minimize any decontamination of the DSC cell. A sensible sample size of 4 mg was chosen in this case, so as not to introduce sample handling difficulties.

5 Other factors effecting oxidation induction time

As well as heating rate and sample size, there are many other factors which may effect the results, such as purge gas, sample pan type, sample homogenity, particle size (if applicable) and computational effects. Sample pans used were aluminium, which were found to give repeatable results. The purge gas used was nitrogen, in a pure, dry form. This is suitable for temperature ranges between -100 °C and 400 °C. The rate of flow of 30 ml/min was found to be a little slow, since decomposition products would condense on the DSC cell, so this was increased to 60 ml/min; however, a flow rate above 60 ml/min produced turbulence and a noisy baseline. It was also found necessary to use a flow-through cover to allow the removal of decomposition products from the DSC cell; in addition, it was decided that local exhaust ventilation was required to remove the vaporized oil from the atmosphere.

6 Reliability of method

The high pressure DSC method for analyzing oxidation stability of transformer oils was found to show good repeatability between triplicate runs, however, some difficulty was encountered with the reproducibility of the technique. Results are shown in Table 3.

As can be seen from the results, the repeatability between triplicate determinations is good. When samples were run on the same day by the same operator, the standard deviation between OIT determinations was less than 0,5 min for the unused oils and only slightly higher for the used oil sample.

The results in Table 4 show that repeatability is generally good between samples run on the same instrument by the same operator but on different days. At TP3 (5 °C/min) this was true for all the samples except sample F, the used oil, which showed a larger discrepancy. At the slower temperature programme, this variation was slightly higher, up to 2 min, and 2,5 mins for the used oil. Isothermal runs of the inhibited samples, B and D showed variation of 0,6 min and 1,1 min, respectively, between runs on different days, ignoring the results on Day 1. On this particular day, the results of oxidation induction time were markedly different from the results on the other two days, and this was counted as an anomaly, which may have been due to deterioration of the samples themselves, which were left in laboratory light for some time. There were thought to be numerous reasons for the remaining variation. The main reason may have been the calculation of oxidation induction time, which was found to account for variation of up to 2 min. In the Pyris software, tangents to the onset curve and baseline are drawn with the mouse and extrapolated to the point at which the lines intersect. This depends on where the tangent to the curve is taken from and any changes in baseline heat flow or in the shape of the curve may result in a relatively large difference in calculated onset time. This is exacerbated by noisy baselines, which were common with the technique and may be due to changes in gas flow rate or pressure, the volatility of the samples, or interference from the glass woof plugs in the DSC cell cover. Generally, differential scanning calorimetry is a sensitive technique and variables such as gas flow rate and pressure, equilibration time and temperature and humidity of the room, should be kept constant.

7 Different instruments

Thirty-one samples of unused insulating oil consisting of 13 inhibited oils and 18 uninhibited oils were analyzed by PDSC by three different laboratories. Laboratory 1 used Perkin-Elmer DSC 7. Samples were analyzed at a heating rate of 130 °C to 260 °C at 5 °C/min, under 300 psi of oxygen. The second laboratory used TA Instruments heat flux type. Air was applied at 300 psi at a flow rate of 60 ml/min and the samples were analyzed from 100 °C to 350 °C at 20 °C/min. The samples were run in duplicate and the mean oxidation onset temperature calculated. At the third laboratory, samples were analyzed on a TA instrument, at a heating rate of 2 °C/min from 130 °C to 210 °C for the uninhibited oils and isothermally at 180 °C for the inhibited oils, under oxygen at 300 psi. Results are shown in Tables 5a and 5b.

Results from both Table 5a and 5b clearly indicate that the DSC results obtained at the three different laboratories show basically the same trend when the samples were analyzed under different conditions and using different instruments. Better correlation was obtained for laboratory 1 and 3. This correlation is better for uninhibited oils than for inhibited oils.

8 Interpretation of curves

Characterization of thermal events in the DSC trace is not easy. In many cases it was found that the particular shape of curves obtained was not reproducible. This may be due to changes in the sample itself, or operating variables such as heating rate, pan type or instrument used. For example, all of the thermograms obtained with the TA Instrument showed multiple peaks, compared to single peaks obtained with the Perkin Elmer instrument, for the same set of samples. This may have been due to impurities or reaction of different parts of molecules, but was more likely due to instrumental factors such as degree of thermal contact. It has so far been assumed that the exothermic peak obtained in the thermograms of the oils is representative of oxidation. This may not be the case and it may be due to some other exothermic reaction when the oil is subject to extreme conditions of heat and oxygen. Generally, melting, crystal transitions, vaporization and sublimation are observed as endothermic reactions, whereas curing, crystallization and decomposition are exothermic reactions.

9 Conclusion

High temperature differential scanning calorimetry (PDSC) provides an alternative method which is fast, simple and reliable. It was found that PDSC could be applied to the oxidation stability of uninhibited mineral insulating oil by measuring the onset time of the oxidation exotherm under high pressure and temperature when applying a slow thermal ramp. The sample size and heating rate effect the onset time and the technique was found to be sensitive to any change in cooling rate, gas flow rate or calibration variables. The method is capable of distinguishing inhibited oils from uninhibited oils. Repeatability of method is acceptable and if care is taken, reproducible results may be obtained and the onset time found to correlate to the induction period measured in the existing IEC 61125. However, the relationship between thermal onset time and other physical characteristics of the oil was poor. The type and manufacture of the DSC equipment has an influence on the results.

Table 1 – Oxidation induction time of oil samples at different temperature programmes

Temperature program	Oxidation induction time (OIT) in minutes					
	Sample A	Sample B	Sample C	Sample D	Sample E	Sample F
TP1 165 °C	ND	ND	ND	46,88	ND	ND
TP1 170 °C	ND	ND	ND	41,76	ND	ND
TP1 175 °C	ND	33,96	ND	30,52	ND	ND
TP1 180 °C	ND	22,37	ND	21,12	ND	ND
TP2	17,78	19,35	16,73	19,03	17,95	17,20
TP3	12,21	19,36	10,78	18,18	14,55	11,17
TP4	23,13	37,06	19,82	33,22	30,15	26,81

TP1 = isothermal at 165 °C, 170 °C, 175 °C and 180 °C

TP2 = 25 °C – 260 °C at 10 °C/min, hold for 10 min at 260 °C

TP3 = 130 °C – 180 °C at 5 °C/min, 180 °C -210 °C at 2 °C/min

TP4 = 130 °C – 180 °C at 2 °C/min, 180 °C -210 °C at 1 °C/min

ND = onset of peak is not clearly detectable in thermogram

OIT is given as an average of triplicate runs.

Table 2 – Oxidation induction time of oil samples at different sample weight

Sample weight mg	Oxidation induction time (OIT) in minutes					
	Sample A			Sample B		
1	24,32	24,11	24,16	30,95	31,58	30,63
4	24,21	24,11	24,12	35,00	35,74	35,07
10	24,18	25,77	26,93	40,61	40,31	40.44

Table 3 – Repeatability of oxidation induction time by PDSC

	Oxidation induction time (OIT) in minutes					
	Sample A	Sample B	Sample C	Sample D	Sample E	Sample F
Run 1	12,51	19,45	10,76	18,16	14,43	10,72
Run 2	12,44	19,34	10,68	18,24	14,74	11,92
Run 3	11,67	19,29	10,89	18,14	14,49	10,86
Average	12,21	19,36	10,78	18,18	14,55	11,17
Standard deviation	0,5	0,1	0,1	<0,1	0,2	0,7