Mineral oil lifetime estimation using activation energy

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Abstract—**Lifetime estimation of mineral oil is based on IEC 60216-1/2001, using accelerated thermal ageing at three temperatures), method which requires a long experimental time. In order to reduce the experimental times, this paper proposes a simpler method to draw the lifetime curve by determining an experimental point (carrying out only a thermal ageing at the highest temperature - which requires the least time) and curve slope (based on the activation energy of oxidation reaction). Assuming the volume resistivity and the loss factor as diagnostic factors, their variation curves with ageing time were drawn, and the lifetime values were calculated. Using differential calorimetry measurements (DSC curves) for four heating rates, the activation energy value Wa of oxidation reactions was obtained. Knowing the Wa value and the ageing time τ to achieve the end of life criterion for thermal ageing at the highest temperature (155 °C), the D3 lifetime value was determined and compared with D1 and D2 values obtained by accelerated thermal method at three temperatures. Finally is showed that, the differences between D3 and D1,2 values are relatively reduced and the method based on activation energy obtained by DSC, can be used to assess the lifetime of mineral oil.**

Keywords-mineral oil; lifetime; activation energy; thermal ageing (key words)

I. INTRODUCTION

The stronger thermal, electrical, mechanical etc. stresses whereat the insulation systems of in-service power transformers are subjected, lead to the continuously degradation and reduction of their lifetime. Nowadays, there are several power transformers put into operation for over 30 years and whose insulation systems can failed at any time [1]. The temporarily or the permanently accidental outage of a power transformer, could lead to major disturbances in users power supply, reducing its quality respectively. Therefore, power transformers users need to know in real time the condition of transformers, in order to take the best decisions regarding the predictive maintenance of equipments and also maintenance planning, repairing or replacing activities [2-3]. The most important parameter which permanently act on the insulation system components is the temperature. Thermal ageing of insulation systems from power transformers is connected to chemical reactions which are produced inside them, caused, mainly by oxidation and accelerated by temperature, oxygen and moisture. The temperature favors the development of oxidation reactions of hydrocarbons from oils by forming free radicals and hydroperoxides and finally oxides, acids and other oxidation products [4]. The oxidation contains three steps:

Initiation: $RH+O_2 \rightarrow RO_2\bullet$
Propagation: $RO_2\bullet + RH \rightarrow ROOH + R\bullet$
$R\bullet + O_2 \rightarrow RO_2\bullet$
Termination: $RO_2\bullet + R\bullet \rightarrow ROOR$

The oxidation rate and the concentration of transient products, depend on the chemical structure of the oil and the oxidation conditions, respectively, temperature, pressure, environment air contact. The lifetime of an insulation system is defined as the time interval under one or more stresses, wherefore, the value of a physical quantity which characterize the insulation operation, is modified below a limit value called end of life criterion. The choosing of end of life criterion is done based on active standards depending on the insulation and stress type. In order to assess the lifetime and the remaining lifetime of insulation systems accelerated thermal tests (in the laboratory) can be performed, according to IEC 60216-1/2001. This method is very time-consuming, especially in case of thermal ageing close to the operation temperature of oil [5]. Regarding the transformer oil, it can be considered, that thermal degradation is due of oxidation reactions whose rate v_R, depends on temperature according to an Arrhenius law:

$$v_R = v_0 \exp\left(-\frac{W_a}{RT}\right), \quad (1)$$

where W_a, is the activation energy of oil degradation reactions (thermo-oxidation reactions), v_0 - reaction constant, T - test temperature and R - general gas constant R = 8.314 J/molK. Choosing a certain property P of insulation, and assuming that P_0 is the value of property P, corresponding to the lifetime D (considering end of life criterion $P = P_0$), the following equation can be written:

$$\ln D(T) = a + \frac{b}{T}, \quad (2)$$

where a is a material constant depending on the limit value of property P (respectively, P_0) and the value of reaction constant v_0, and $b = W_a/R$ [6].

Knowing the lifetime curve $D(T)$, the lifetime assessment of an insulation at a given temperature T is possible. The experimental determination of insulation lifetime, means to draw the variation curves of chosen property P (rated to the initial value P_i) as a function of ageing time τ, in case of three values of ageing temperature $T_{1,2,3}$ and graphical estimation of intervals $\tau_{1,2,3}$, wherefore the values of selected lifetime criterion are achieved, respectively $(P_0/P_i)_{eol}$ (Fig. 1) [7]. Using the value pairs $(1/T_1, \ln\tau_1)$, $(1/T_2, \ln\tau_2)$ si $(1/T_3, \ln\tau_3)$, the lifetime curve can be drawn (Fig. 2). Computing the lifetime curve slope, the value of activation energy can be obtained ($W_a = bR$).

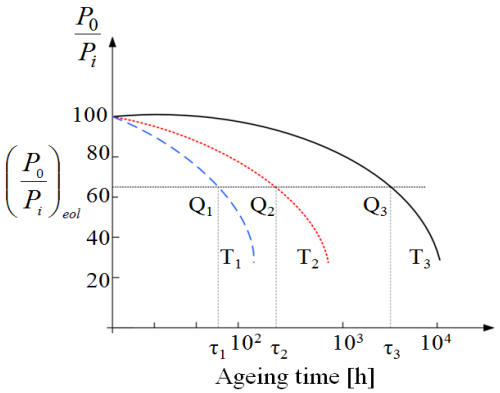

Figure 1. Accelerated thermal ageing curves [8].

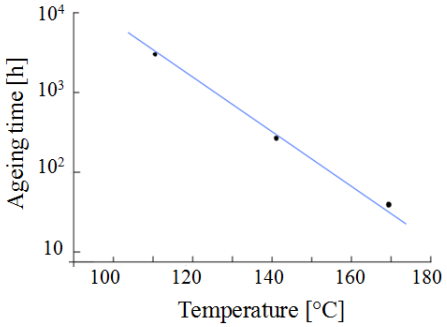

Fig. 2. The lifetime curve for semi-logarithmic coordinates

In this paper, the mineral oil lifetime, is determined using both accelerated thermal ageing method (at T_1 = 115 °C, T_2 = 135 °C and T_3 = 155 °C) as well as, using a faster method based on assessment of oxidation reactions activation energy by DSC and performing an accelerated test at a higher temperature (155 °C).

II. EXPERIMENTES

Two parallel experiments were performed using same transformer oil:

- One is the evaluation of the thermal lifetime based according to IEC 60216-1/2001 (Method M1). Accelerated ageing experiments were performed at three different temperatures (i.e. T_1 = 115 °C, T_2 = 135 °C si T_3 = 155 °C) and for ageing times ranged between 500 and 5000 h;

- Second (proposed in this paper) is based on a evaluation of W_a and subsequent lifetime evaluation (Method M2).

The volume resistivity and the loss factor were used as diagnostic factors in order to assess the ageing condition of the mineral oil samples. The volume resistivity has been calculated using the absorption currents values measured at 60 seconds after voltage applying (according to IEC 60247). The absorption currents were measured using a Keithley 6517 electrometer [5], applying a DC voltage U_0 = 300 V, for 2 h. Using a dielectric NOVOCONTROL spectrometer [8], the loss factor values were determined for the electric field frequency f = 0,1 mHz.

DSC (Differential Scanning Calorimetry) measurements were performed in non-isothermal mode (temperature ramp with constant heating rate) on a Setaram 131 EVO (Setaram Instrumentation, France) apparatus, in the following conditions: sample weight, 3.91 ± 0.7 mg, air flow, 50 mL/ min, aluminum pans of 100 µl capacity (sealed), temperature range, 30 - 310 °C, heating rate, 2, 4, 6 or 10 °C /min. Because the oil was fairly volatile and evaporated before oxidation, the sample containing pans were sealed using the Setaram device. A volume of around 70 µL of air was present in each sealed pan enabling the oxidation process in static atmosphere. An example of a DSC curve is shown in Fig. 3. Data processing was made using the Calisto Data Processing (CDP) software of Setaram. The oxidation onset temperature (OOT) was calculated, according to ASTM E2009-02 [9] as the intersection point of the recorded baseline and the slope of the oxidation exotherm, using the specific CDP function. The $T_{0.6}$ parameter was calculated as the temperature at the 0.6 of the height of the baseline substracted oxidation peak (Fig. 3). The thermal effect (ΔH_{ox}) and the peak temperature of exotherm oxidation peak (T_m) were calculated using the CDP function *Integration*. Tangential sigmoid mode has been chosen to draw the baseline of the integral.

The activation energy of oil oxidation has been evaluated from DSC measurements, using the onset of the low temperature oxidation peak (at 170 °C, Fig. 3). The values of the $T_{0.6}$, or heating rate (β) were plotted as a function of temperature according to the isoconversional methods listed in Table 1. Similar calculations were performed for OOT . In (3)-(6), T_f represents the temperature at a fixed amount transformed (in this case $T_{0.6}$), R is the general gas constant and W_a is the activation energy and C_1 - C_4 are constants.

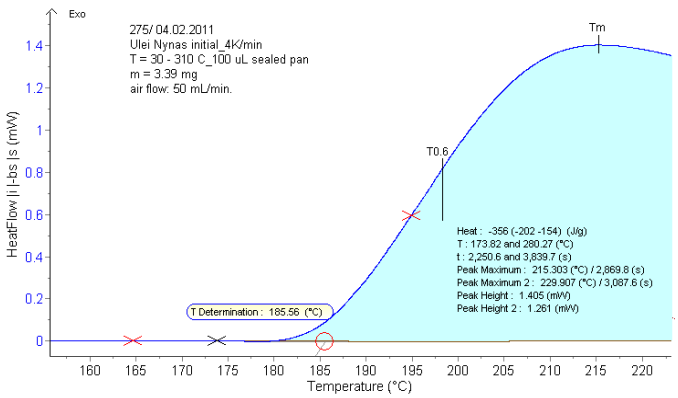

Fig. 3 - Example of a DSC curve of the studied oil (heating rate 4 K/min.) and determination of the kinetic parameters of oxidation

TABLE I. ISOCONVERSIONAL METHODS RECOMANDED IN LITERATURE FOR ACTIVATION ENERGY EVALUATION

Equation (no.)	W_a calculation	Reference
$\ln\frac{\beta}{T_f^2} = -\frac{E_a}{RT_f} + C_1$ (3)	Plotting $ln\frac{\beta}{T_f^2} = f(1/T_f)$ is obtained a straight line with the slope - W_a/R	[10,11]
$\ln\beta = -1{,}0518\cdot\frac{E_a}{RT_f} + C_2$ (4)	Plotting $ln\,\beta = f(1/T_f)$ is obtained a straight line with the slope -(W_a/R) 1.0518	[11,12]
$\ln\frac{\beta}{T_f} = -\frac{E_a}{RT_f} + C_3$ (5)	Plotting $ln\frac{\beta}{T_f} = f(1/T_f)$ is obtained a straight line with the slope - W_a/R	[11,13]
$\ln\frac{\beta}{T_f^{1.8}} = -\frac{E_a}{RT_f} + C_4$ (6)	Plotting $ln\frac{\beta}{T_f^{1.8}} = f(1/T_f)$ is obtained a straight line with the slope - W_a/R	[11]

The value of W_a for the oxidation process, has been also evaluated using the ASTM E698 recommended method [22], which requires a plot of lnβ vs1/T_m. The plots corresponding to above mentioned equations, are straight lines, the corresponding slopes being equal or proportional (in the case of Ozawa's method) to - W_a/R. The mean value of the activation energy $W_{a,a}$ (used in further lifetime estimations) was calculated as the arithmetic average of the W_a values .

III. RESULTS

In Figure 4, the variation curves of volume resistivity ρ_v (diagnostic factor) as a function of ageing time for three ageing temperatures $T_{1,2,3}$ (115, 135 and 155 °C), are presented. It can be seen that, the values of ρ_v decrease with thermal ageing time and the higher the ageing temperature, the more important the decrease of resistivity (due to the degradation processes activated by temperature and the increase of charge carriers concentration inside the samples). Assuming as end of life criterion the volume resistivity value $\rho_v = 1.5\cdot10^{11}$ Ωm, the coordinates of the points $Q_{1,2,3}$, respectively Q_1(155 °C, 350 h), Q_2(135 °C, 1600 h) and Q_3(115 °C, 6700 h) were obtained. Based on (2), the lifetime curve parameters b = 12255,23 K^{-1}, a = -22.78 and the value of activation energy W_{a1} = 101,83 kJ/mol were calculated. Thus, the lifetime value of oil was calculated assuming the operation temperature T = 80 °C, respectively $D_1 = 1.53.10^5$ h.

In Fig. 5, the variation curves of loss factor tgδ (measured at f = 1 mHz) as a function of ageing time for the same temperatures $T_{1,2,3}$, are presented. It can be observed that, the loss factor values increase with ageing times and temperatures. This is due, to the by-products, ions and molions which appear as a result of thermo oxidation reactions, intensifying the electric polarization and conduction phenomena. Assuming as end of life criterion the value tgδ = 50, the coordinates of $Q_{1,2,3}$

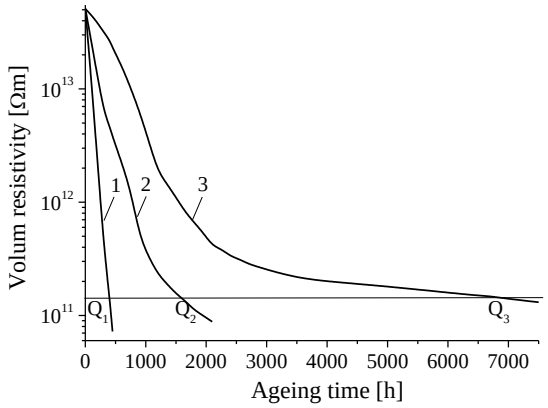

Fig. 4. Variation of volume resistivity as a function of ageing time at: T_1 = 155 °C (1), T_2 = 135 °C (2), T_3 = 115 °C (3).

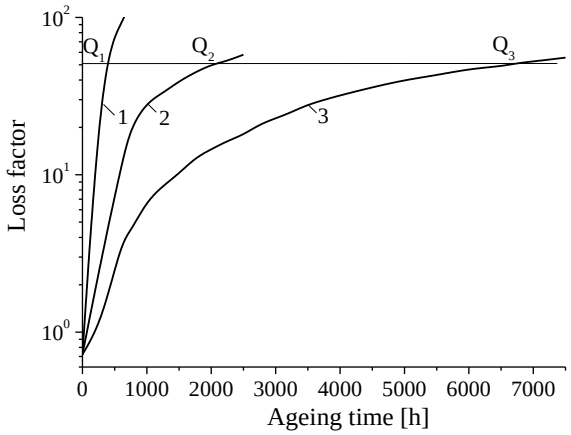

Fig. 5. Variation of dielectric loss factor as a function of ageing time at: T_1 = 155 °C (1), T_2 = 135 °C (2), T_3 = 115 °C (3) (f = 1mHz).

points, respectively Q_1(155 °C, 350 h), Q_2(135 °C, 1600 h) and Q_3(115 °C, 6700 h) have been obtained. Based on (2), the lifetime curve parameters b = 12260 K^{-1}, a = -22.76 and then the value of activation energy W_{a2} = 101,90 kJ/mol were calculated. Thus, from (2) the lifetime value of has been calculated assuming the operation temperature T = 80 °C, respectively $D_1 = 1.58.10^5$ h.

By analyzing the values of activation energy obtained based on both diagnostic factors (volume resistivity and loss factor), it can be seen that these values are approximately equal (the differences between these values are less than 3.3 %). Thus, it can be noted that, either diagnostic factors can be used in order to assess the mineral oil condition. Unfortunately, the accelerated thermal ageing method is very time-consuming especially for thermal ageing close to the operation temperature (approximately one year for temperature T = 115 °C).

The kinetic parameters of the oil oxidation process calculated from DSC curves are shown in Table 2. The parameters of the linear fitting of the plots mentioned in Table 1 as well as the values of the activation energies calculated from $T_{0.6}$ are presented in Table 3. It can be seen that there is a good fitting on different linear relationships and the resulted W_a values are close enough. The average value of activation energies $W_{a,a}$ has been taken for further lifetime evaluations.

It should be noted that the activation energy was also evaluated from the curve $\ln(\beta/OOT^2) = f(1/OOT)$; the average

value (obtained by Kissinger, Osawa, Boswell and Starink methods) was 139 kJ/mol. Another method for W_a evaluation [14] has been also applied, leading to a value of 73 kJ/mol (Table 3). This method is based on the linear relationship $ln\beta = f(1/T_m)$, where T_m is the peak temperature. The different values of the activation energies obtained from different temperature parameters can be explained by the autocatalytic character of the oxidation process. Hence, the activation energy should decrease as the oxidation advances.

The activation energy calculated from DSC data falls close to that found by electrical measurements if $T_{0.6}$ is used as temperature parameter. The lifetime criteria used for electrical ageing assume a certain oxidation degree related to the deterioration of the oil properties up to a limit level. Therefore, if OOT is taken, for example, as temperature parameter, there is no oxidation or no significant oxidation hence the oxidation state of the material is not similar to that considered in the electrical ageing and the evaluated lifetime is significantly different to that from electrical ageing. In such a case, the $T_{0.6}$ appears to be more suitable to be used for activation energy calculation and for further lifetime evaluation according to the procedure proposed in this work.

TABLE II. KINETIC PARAMETERS OF THE LOW TEMPERATURE OXIDATION PROCESS CALCULATED FROM THE NON-ISOTHERMAL DSC CURVES

β (K/min.)	OOT (°C)	$T_{0.6}$ (°C)	T_m (°C)	ΔHox (J/g)
2	177.6	186.4	195.3	-281
			212.6	-109
4	185.6	197.4	214.6	-202
			230.1	-154
6	190.5	204.5	222.7	-166
			265.0	-161
8	196.4	214.0	241.3	-188
			276.6	-96

TABLE III. FITTING PARAMETERS OF THE LINEAR RELATIONSHIPS ($Y = M + NX$) CORRESPONDING TO DIFFERENT METHODS AND THE ACTIVATION ENERGY

Temp. parameter	Method	Correlation	M	N	W_a (kJ/ mol)	$W_{a,a}$ (kJ/ mol)
$T_{0.6}$	Kissinger	0.9997	14.81	-12096	100.5	102.4
	Ozawa	0.99978	29.17	-13080	103.3	
	Bosswell	0.99986	22.01	-12569	104.4	
	Starink	0.99971	16.23	-12210	100.5	
T_m	ASTM E698	0.9962	19.45	-8795	73	73

Comparing the activation energy values experimentally obtained by Method 1 (W_{a1} = 101,83 kJ/mol and W_{a2} = 101,90 kJ/mol) with the value (W_{a3} = 102.4 kJ/mol) obtained by DSC (Method 2), it can be noted that, the lower differences are registered for activation energy value obtained using the $T_{0.6}$ parameter (Table 3). Taking into account the W_{a3} activation energy value and the results corresponding to accelerated thermal ageing at 155 °C, the parameter a = - 22.76 and b = 12323.6 K^{-1} of lifetime curve can be calculated. In case of operation at the constant temperature T = 80 °C, the lifetime value $D_3 = 1.86 \times 10^5$ h can be obtained, close to the D_1 and D_2 lifetimes, estimated using the former method.

IV. CONCLUSIONS

To assess the lifetime D for mineral oil by accelerated thermal ageing method, the either of two diagnostic factors from volume resistivity and loss factor can be used.

Accelerated thermal ageing standard method, requires long times especially in case of ageing temperature values close to the operation temperature values of mineral oil.

The assessment of activation energy by DSC method, allowed the reduction of test time. The error of this method is below than 20 %.

The use of the activation energy calculated from a DSC parameter related to equivalent oxidation extent as in the case of electrical parameters is required. $T_{0.6}$ appears adequate to be used for W_a calculations and for further lifetime evaluations.

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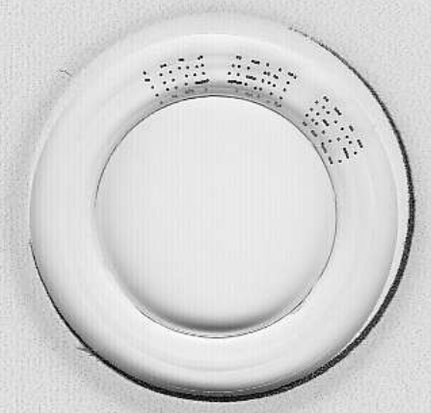

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