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ACTIVATION ENERGY OF TRANSFORMER OILS

ENERGIA AKTYWACJI OLEJÓW TRANSFORMATOROWYCH

Abstract: The power transformers are the key components of power grid from the reliability point of view. Due to operation conditions, aging of particular parts of power transformers appears and this fact also causes changes of the important electrical and mechanical properties. Transformer working life is given by a working life of its insulating system. The insulating system of these devices is inseparably composed of the solid (based on cellulose) and oil insulation. Liquid part fulfils besides the insulation also cooling function and the analysis of this part of insulating system during the laboratory thermal aging became the main aim of our experiment. Activation energy was chosen as the main parameter corresponding to the actual condition of insulating oil. Two groups of insulating oils were examined. Three kinds of mineral petroleum-based oils are in the first one (common commercial products – Technol, ITO 100, BTSi); the second group contains three oils based on synthetic esters (Dibutyl phthalate – dibutyl ester of phthalic acid, Dioctyladipate – di(2-ethylhexyl) ester of adipic acid, Diisobutyl adipate – bis(2-methylpropyl) ester of adipic acid). The activation energy was measured by thermogravimetry analysis. Thermal aging process has been still processing due to extensiveness of this project. Meanwhile, the activation energy was analyzed on the samples in virgin state and after 1000, 2000 and 3000 hours of thermal aging at the temperature of 90 °C.

1. Introduction

Power transformers are the key components of the whole power grid in light of reliability. Operation conditions cause aging of particular parts of power transformers, which influences their important electrical and mechanical properties. Transformer service life is given by a working life of its insulating system composed of the solid (based on cellulose) and oil insulation.

Nowadays, the attention is given mainly to application possibilities of ecological materials. This trend is observed also in problems of oil filled transformers, where substitution of the petroleum-based oils by more ecological insulating liquids is studied.

For reasons given, the main objective of presented experiment is to compare the properties of three commonly used mineral transformer oils (Technol, ITO 100 a BTSi) with three synthetic liquids (DBP, DOA a DIBA) based on synthetic esters. Behaviour of activation energy along accelerated thermal aging (oils were exposed for 3000 hours at the temperature of 90°C) was evaluated for both oil groups.

2. Activation energy

Since the activation energy has been chosen as the main evaluating parameter, it is necessary to begin by specifying of some facts related to this term.

Activation energy is defined as the minimum energy necessary for a specific chemical reaction to occur. It is usually denoted by E_a and is given in units **kJ/mol**. Figure 1 illustrates the activation energy nature.

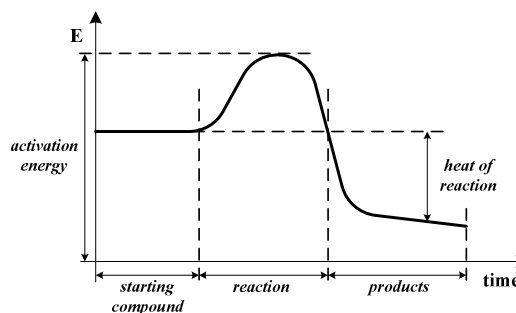


Fig. 1. The nature of activation energy

Activation energy is the decisive factor in electrical technology diagnostics affecting the lifetime of all electrical insulating materials. The higher the activation energy of the material is, the better is the resistance of this material to chemical reactions that cause degradation processes in its inner structure. This is applied also on insulating systems of power transformers (mineral oil and paper). When these components are combined they provide much better insulating properties than either of the materials does individually [1]. The problem with using these materials as insulation in electrical de-

vices is that they are subjected to aging and decomposition over the operation time. Aging process is accelerated mostly by excessive temperature and moisture presence. Presence of aluminium or copper and mainly oxygen are the other factors accelerating the degradation of transformer insulating system. The oxygen together with temperature also represents the decisive reaction (thermal oxidative reaction) for degradation of organic based materials. [2, 3]. The activation energy reflects very well all these degradation processes and its behaviour in dependence on operation time is very desired value.

There are several methods how to measure the activation energy in practice, however many of them are very time consuming. We prefer the determination by thermogravimetry analysis. Next section deals with this method considering it is not very common.

3. Decomposition kinetics by thermogravimetry

According to Mackenzie [4], thermogravimetry is a technique in which the mass of a substance is measured as a function of temperature whilst the substance is subjected to a controlled temperature programme.

Obtained curves (expressing the sample mass dependence on temperature) called thermograms are used as the basic data for activation energy calculation. Figure 2 shows thermograms of all tested oils (see section 4.1 for exact specification) after 1000 hours of aging at the temperature of 90 °C and heating rate of 2°C/min.

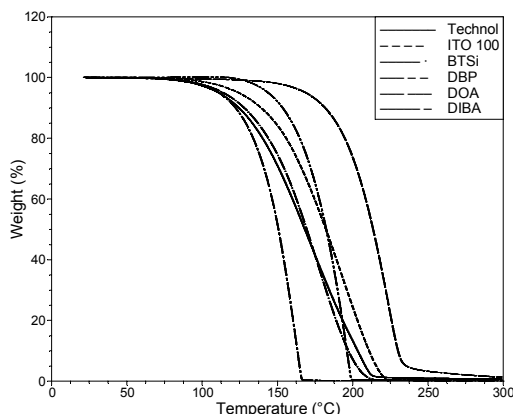


Fig. 2. Thermogravimetry of all tested oils after 1000 hours of aging (heating rate 2°C/min)

As obvious, total thermal decomposition of tested oils occurs during the thermogravimetry

analysis (sample mass decreasing down to 0% of original mass is observed). Figure 2 also shows that decomposition reaction has just one step and thermal decomposition of all synthetic oils is more intensive compared to mineral oils. Thermal decomposition of material is required for activation energy calculation from thermogravimetry curves. This decomposition is needed to repeat at several different heating rates. Four rates of heating are optimum to use. [5]. It results in common thermogram, containing all thermogravimetry curves of given material for different heating rates. Common thermogram of BTSi oil obtained for heating rates of 2, 4, 6 and 8 °C/min is illustrated as an example in Figure 3.

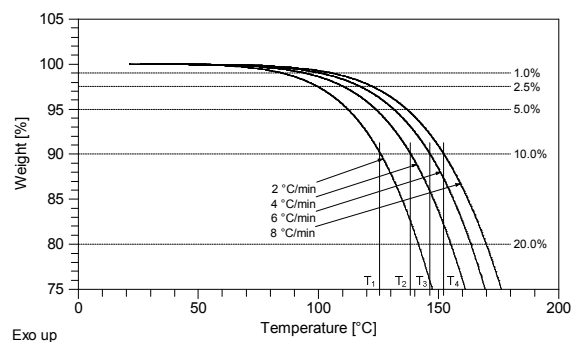


Fig. 3. BTSi oil - common thermogram

We can notice shift of individual thermograms due to increasing heating rate. Just this shift stands in the basis of activation energy calculation. Firstly different conversion levels were chosen on the common thermogram (on which the activation energy was analyzed), e.g. 1; 2,5; 5; 10 and 20 % (see Figure 3). Option of more conversion levels is necessary for verification of reaction mechanism nature. If calculated values of activation energy are similar for all chosen levels, it means the reaction mechanism is the same within the whole decomposition.

In case it is not, it is necessary to choose the conversion level (or reaction), which is the most characteristic for decomposition for final evaluation. E. g. if we evaluated the activation energy for 1 % conversion without further analysis, resulting value would be influenced e.g. by moisture vaporization from the sample. This reaction is typical for the temperature range from 100 to 120°C and it is responsible for primary decrease of thermogravimetry curve in many cases.

We obtain four absolute temperatures ($T_1 - T_4$) at constant conversion from each thermogravimetry curves in Figure 3 (10% conversion level is analysed).

The activation energy is then determined from so called Arrhenius plot (plot of the logarithm of heating rate versus the reciprocal of the temperature - $1000/T_{1-4}$) for each conversion level [6]. Arrhenius plot of BTSi oil is demonstrated in Figure 4. Activation energy is calculated from the slope of the lines.

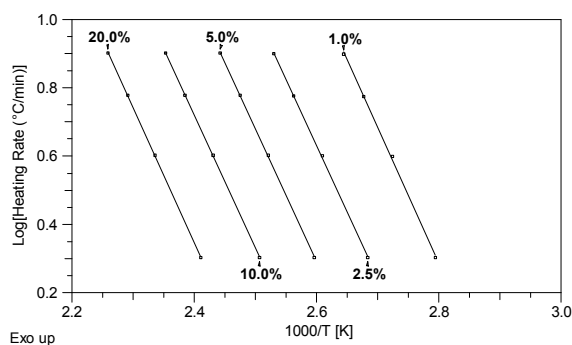


Fig. 4. BTSi oil - Log Heating Rate Plot (Arrhenius plot)

Arrhenius plot also helps to control the reaction mechanism. If the particular specimen decomposition mechanism were the same at all conversion levels (1 – 20 %), the lines would all have the same slope [6].

Calculation of activation energy from the slope in Figure 4 follows using the method of Flynn and Wall [7]:

$$E_a = -\frac{R}{b} \left[\frac{d \log \beta}{d(1/T)} \right], \quad (1)$$

where

- E_a is activation energy (J/mol),
- R is gas constant (8,314 J/mol K),
- T is temperature at constant conversion (K),
- β is heating rate ($^{\circ}\text{C}/\text{min}$),
- b is constant (0,457) see [5].

Further details for calculation may be found in ASTM E 1641 standard [5].

So calculated activation energy can be subsequently used for construction of material life-time plot and for calculation of the rest of the operation time of material.

There is indisputable advantage of described technique that even with the associated calculations, the total time to evaluate a material is less than one day.

4. Experimental

4.1 Samples specification

Two groups of insulating oils were chosen for the purpose of our experiment (see Table 1).

Tab. 1: Oil samples

Petroleum based oils	Synthetic oils
Technol	DBP (dibutyl phthalate)
ITO 100	DOA (dioctyladipate)
BTSi	DIBA (diisobutyl adipate)

Three kinds of mineral petroleum-based oils are in the first one (common commercial products); the second group contains three oils based on synthetic esters. Specification of synthetic oils is as follows:

Dibutylfthalate (DBP) – dibutyl ester of phthalic acid – it is colourless or slightly yellow viscous liquid, stable at ordinary physico-chemical conditions. This substance decomposes and toxic combustion products release after the boiling point (340°C) exceeding and at burning process as well. DBP is suitable to products for industrial purpose only.

Dioktyladipate (DOA) – di(2-ethylhexyl) ester of adipic acid – it is colourless or slightly yellow viscous liquid and it isn't classified as a dangerous substance. DOA is considered to be biodegradable substance without any negative effects on environment.

Diisobutyladipate (DIBA) – bis(2-methylpropyl) ester of adipic acid – it is also colourless or slightly yellow substance without any negative effects on environment. It is stable at ordinary physico-chemical conditions and it isn't classified as a dangerous substance.

4.2 Aging process

The selected oils were exposed to thermal aging in closed vessels at the temperature of 90°C for 3000 hours. Activation energy was analyzed according to ASTM E 1641 standard in following time intervals: virgin state, 1000, 2000 and 3000 hours of thermal aging.

4.3 Thermogravimetry

Data was collected on Simultaneous thermal analyzer SDT Q600 from TA Instruments. Quite small samples (approx. 18 – 21 mg) and aluminium cups were used because of quick

heat transfer. Oil samples were tested from ambient to 300°C, at different heating rates of 2, 4, 6 and 8°C/min. All analyses were provided under air atmosphere (100 ml/min). The calorimeter was calibrated for temperature and heat flow by using sapphire and zinc.

5. Results and discussion

Activation energy was analyzed for 1; 2,5; 5; 10 and 20% conversion of all tested oils in virgin state and after 1000, 2000 and 3000 hours of thermal exposition.

It was necessary to choose the optimum conversion level for activation energy calculation before the final data evaluation. As the example of such optimization see Table 2, that summarizes the activation energy values of tested oils in virgin state and in all monitored conversion levels.

Tab. 2: Influence of conversion level on activation energy – oils in virgin state

Conver. level	Activation energy [kJ/mol]					
	Techn.	ITO 100	BTSi	DIBA	DOA	DBP
1 %	73,90	38,90	67,70	81,10	223,40	99,50
2,5 %	69,10	43,00	67,30	76,60	129,50	90,30
5 %	67,60	46,70	67,30	75,00	107,80	87,00
10 %	66,90	50,50	67,40	73,80	99,10	84,00
20 %	67,10	55,70	67,90	72,60	96,10	83,50

As said before, as long as only one chemical reaction is dominant during the decomposition, activation energy is then very similar within all conversion levels. This condition is fully satisfied only in BTSi oil, in which there is no difference what conversion level will be chosen for activation energy evaluation. Technol, ITO 100, DIBA, DBP and DOA oils have different values of activation energy mainly at lower conversion levels (1 a 2,5 %), which can refer e.g. to water vaporization. It wouldn't be suitable to consider these levels in order to describe the main reaction mechanism. Since the maximum differences in activation energy are observed in DOA oil, its Arrhenius plot is presented in Figure 5.

As obvious, 10 % conversion level of DOA oil seems to be the best level for its evaluation. Since the same situation is observed also in the rest of tested oils, this conversion level was chosen as optimal for activation energy calculation.

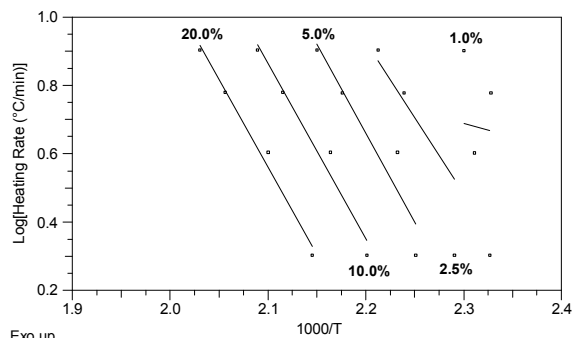


Fig. 5. DOA Arrhenius plot – virgin state

Final results are presented in Table 3. Figure 6 then provides view of activation energy behaviour along the aging process of tested oils.

Tab. 3: The results for 10 % of conversion

Oil	10 % of conversion			
	Virgin state	1000 hours	2000 hours	3000 hours
Technol	66,9	66	65,6	67
ITO 100	50,5	74,7	72,9	76,4
BTSi	67,4	68	65,6	66,7
DIBA	73,8	72	76,4	77,6
DOA	99,1	102,4	87,7	87,4
DBP	84	87,5	83	76,9

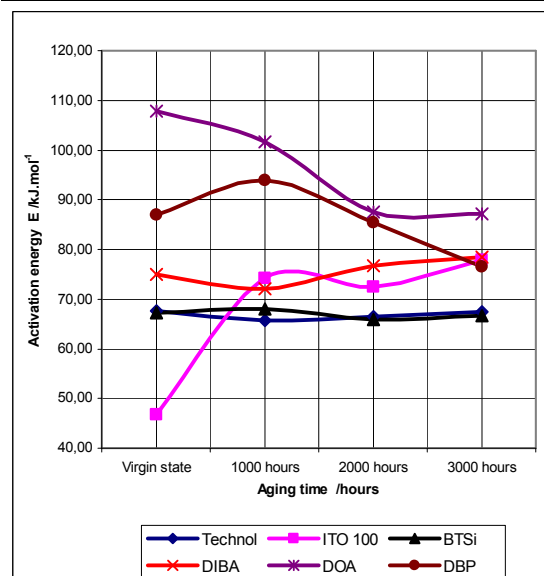


Fig. 6. Activation energy of tested oils for 10 % conversion level vs. aging time

Obtained results demonstrate higher activation energy of synthetic DOA and DBP oils. However this value has tendency to decrease within the aging process. Their instability in the first phases of thermal aging can be caused by lower oxidative stability, which was proved by FT-IR analysis [8]. Mineral oils (except ITO 100 oil) together with synthetic DIBA oil show the higher stability of activation energy, even

though its absolute value is generally lower than value of synthetic oils.

The highest activation energy at all aging levels was observed on DOA oil. This oil shows also the best thermal resistance of all tested oils (see TG curve in Figure 2). Activation energy of DBP oil decreases rapidly along the aging. Activation energy behaviour of DIBA oil is very similar to mineral oils.

6. Conclusion

Experimental results demonstrate the expressive differences among individual oils. Activation energy is only one of the main parameters deciding on application possibilities of these materials. It is necessary to consider also electrical parameters of synthetic oils (such as loss factor, permittivity, polarization indexes, volume resistivity etc.) for complete estimation of the applicability of these oils. Electrical parameters have been also monitored within this project. Results are presented e. g. in [9, 10].

7. Acknowledgment

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8. References

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