STUDY OF SOME INSULATING OILS AGING BY THERMAL CYCLING

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Abstract - The By gravimetric measurements and coupled thermal analysis techniques (DTG+TG+DTA) the aging of different sorts of insulating oil was studied by thermal cycling between -40^{0}C and 85^{0}C. The experimental results showed that, during the thermal cycling of the investigated mineral oils, their composition changes due to the volatilization of the volatile fractions (mass losses between 3.9% and 5.8%), unlike the investigated vegetable oil that showed a mass increase of approx. 0.66%. It has also been found that the mineral oils can be ensure a safe operation, without significant changes up to a maximum of 100^{0}C, as long as investigating vegetable oil can be used without degradation risk up to 200^{0}C.

Keywords: electro insulating oils, aging, thermal cycling, thermo oxidation, volatilization.

1. INTRODUCTION

In the context of sustainable development, the secure supply of electricity with minimum environmental impact and at reasonable costs is a priority issue. The secure supply of electricity at reasonable costs is given primarily by the cost of resources and by the safe and sustainable operation of electric equipment and facilities.

In order to ensure an adequate thermal transfer and an appropriate insulation in the transformers of the facilities for transport, distribution and use of electricity several billion litters of insulating oil are used [1, 2]. Traditionally, these plants use mineral origin oil; although it has adequate functional characteristics [3, 4], its main drawback is that it shows a very low biodegradability [5, 6], its use being a major environmental risk [7]. In this context, a significant attention is given worldwide for obtaining insulating oils from plant resources (renewable) and for their characterization [1-6, 8-11].

During operation, as a results of the contact with various materials (copper, steel, cotton, paper, etc.) and of electrical and thermal stresses, insulating oils undergo a degradation process [3, 4, 8, 9, 12-14], hereinafter "aging", which limits the safe operation period.

From thermal point of view, in electrical transformers the insulating oils undergo successive heating and cooling cycles - depending on ambient temperature and transformer's load.

Given these considerations, the aim of this paper is to study the behaviour of some insulating oils exposed to accelerated aging by thermal cycling.

2. EXPERIMENTS

Three sorts of electro insulating oils were subject to thermal cycling in a thermo-climatic room (type VC 4018, VÖTSCH-Industrietechnik GmbH), according with the temperature diagram given in fig. 1.

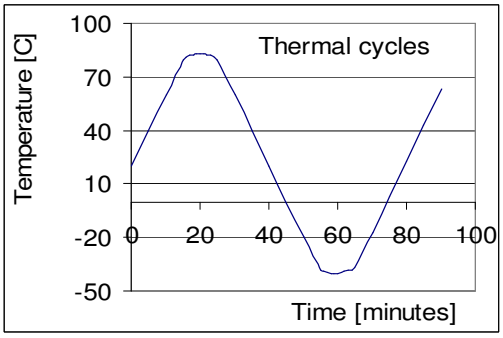


Fig. 1. Thermal treatment profile of applied cycles (thermo cycles)

By performing 917 thermal cycles between –40^{0}C and 85^{0}C, several parameters were determined for the commercial sorts of Nynas oils [15] and MOL TO-30 oils [16], as well as for an experimental model of electro insulating oil (bio_Exp. model) developed within a research contract [11] by the team. Thus, there were determined the mass loss (by gravimetric measurements - on a HR-type analytical balance 200 - A & D Instruments Ltd.) and the parameters characterizing the thermo oxidation (by coupled thermal analysis techniques TG-DTA-DTG). These oil samples were exposed in a thermal room in open Berzelius beakers (thus ensuring unlimited contact with atmospheric oxygen inside the thermal room). There have also been drawn TG-DTA-DTG thermograms for an oil sample recovered after 34 years of use from a 1.5MVA transformer, which originally was charged with TR30 oil produced in Romania [17].

The thermal analysis of oil samples was performed with a simultaneous TG/DTG+DTA analyzer produced by Netzsch - Germany, in dynamic synthetic air atmosphere (gas flow rate of 30 cm^3/min), under non-isothermal linear regime, at heating rate of 10 K min^{-1}. Measurements were made in the range room temperature (RT) to 500^0 C and into Pt-Rh crucibles. The results of measurements were processed and graphically represented using the dedicated Proteus Software, from Netzsch - Germany.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The results of the gravimetric measurements and the variation of samples' mass over the thermal cycling are shown in fig. 2.

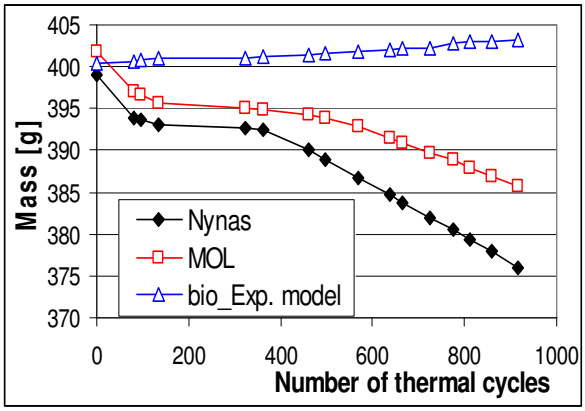
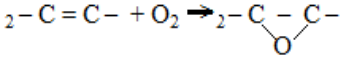


Fig. 2. Variation of samples' mass over the thermal cycling

By analyzing data in fig. 2, it is found that, over the first 80 thermal cycles, due to the evaporation of volatile components in the samples, the investigated mineral oils show a mass loss as follows: of 5.126 g (approx. 1.28%) for Nynas and 4.785 g (approx. 1.19%) for MOL. After the evaporation of volatile components, the mass of mineral oil samples remain fairly stable (between 95 and 362 cycles). After 362 thermal cycles, the samples' mass show a linear decreasing trend until the end of the cycling process (cycle 917), reaching in the end to the total mass loss of 23.041g (5.7737%) for Nynas and 16.025g (3.9881%) for MOL, respectively. This behaviour suggests that, within the first 362 thermal cycles, decomposition processes in volatile fractions are initiated for some constituents from the composition of these oils. In the case of the experimental model of biodegradable vegetable oil developed by the authors, it appears that, unlike other vegetable oils, the sample exposed to thermal cycling do not show mass losses; on the contrary, even a slight mass increase was noted, with a total of 2.2662 g, i.e. 0.6646% over the 917 thermal cycles applied. This mass increase can be explained by the adsorption of the volatile fractions removed from the mineral oils (the samples were exposed to thermal cycling in open beakers, located in the same enclosure) and / or by the retention of atmospheric oxygen by the oxidation of the double bonds of the vegetable oil's fatty acids:



This explanation is also supported by the results reported in [18, 19].

Based on the data in fig. 1, the specific mass losses due to thermal cycling of the investigated oils were calculated. The variation of specific weight losses, expressed as percents per cycle, with the applied thermal cycles is shown in fig. 3.

The TG – DTA and DTG thermograms registered for Nynas sample before exposing the oil to thermal cycling is shown in fig. 4, while fig. 5 shows the thermograms registered after 917 thermal cycles.

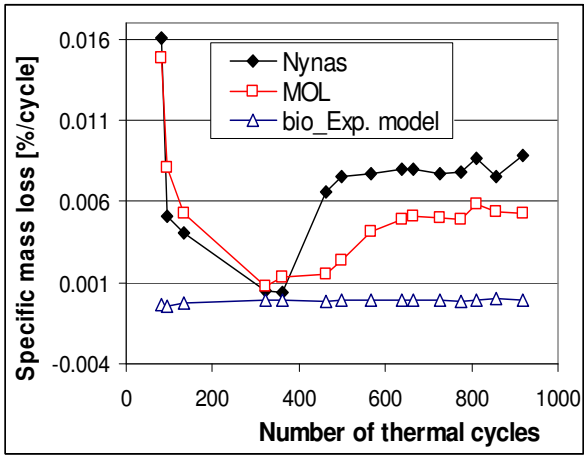


Fig. 3. The variation of specific mass losses over the thermal cycling

Analyzing fig. 4, it results that the progressive warming of the oil sample to about 90^0C triggers a first endothermic process with mass loss that has the maximum velocity at 211.9^0C, immediately followed by a second endothermic process for which the mass loss has maximum velocity at 274^0C. During these two processes, 96.67% of the samples' mass is volatilized. The rest of sample undergoes three successive exothermic processes, beginning on 294.9^0C (with maximum velocities registered at 294.4^0C, 307.9^0C and 320.4^0C respectively); these processes are probably of oxidation, without a noticeable change in the sample's mass. In the end, at about 440^0C, a final exothermic process with mass loss is triggered, being followed by a second exothermal process with 2.34% mass loss (from the initial mass of the sample), having the maximum velocity at 512.3^0C; this is a combustion process with formation of gaseous products - the solid residue remaining in the crucible at 575^0C being of 0.98% of the initial mass of the sample.

The analysis of fig. 5 shows that the thermal behaviour of Nynas oil after undergoing 917 thermal cycles (as shown by Fig. 1) is similar to the initial one (Fig. 4); the difference consists in the increase by 10^0C of the temperature where the volatilization begins (the volatile fractions left during thermal cycling), in the systematic decreasing of the temperatures characteristic to the thermo oxidation processes, in the disappearance of the fraction having the endothermic minimum to 274^0C and of the fractions registering the exothermic peak to 294.4^0C and to 307.9^0C and in the decreasing of the residue at 575^0C from 0.98% to 0.62%.

TG-DTA and DTG thermograms registered for MOL TO 30 sample before being exposed to thermal cycling is shown in fig. 6, while fig. 7 shows the thermograms after 917 thermal cycles have been applied.

The comparative analysis of fig. 4 and fig. 6 shows that the initial samples of Nynas and MOL TO 30 oils show similar behaviour. The difference consists in the fact that both the starting temperature of the first endothermic volatilization process and the characteristic exothermic processes (for thermal oxidation) are higher, namely the volatilization begins at approx. 110^0C (compared to about 90^0C for Nynas).

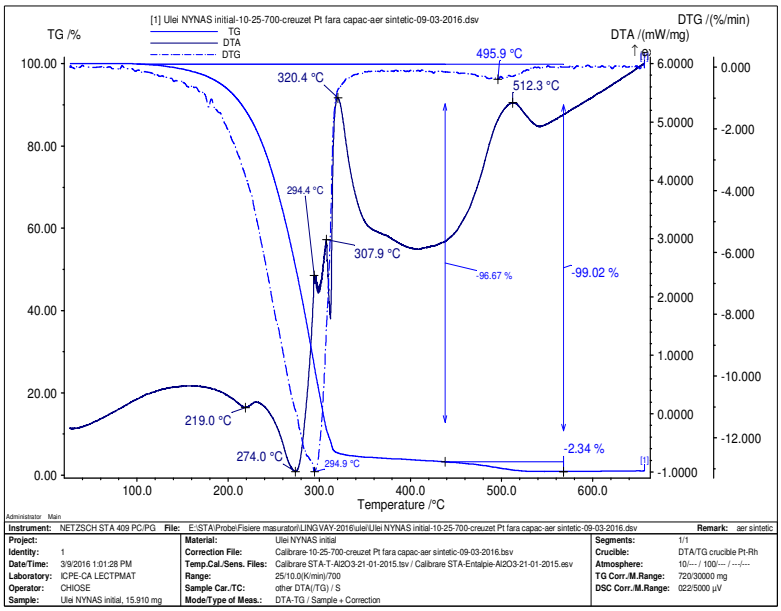


Fig. 4. TG – DTA and DTG thermograms registered for Nynas sample before cycling

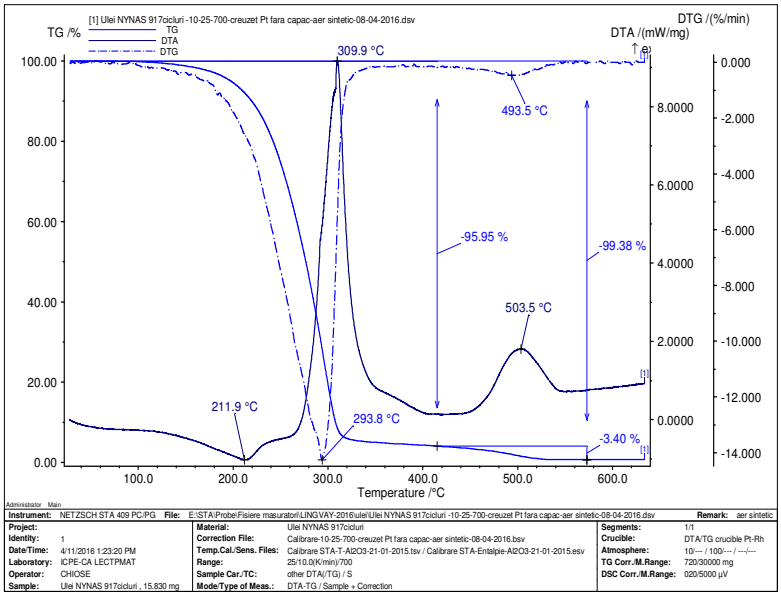


Fig. 5. TG – DTA and DTG thermograms registered for Nynas sample after 917 cycles (Fig. 1)

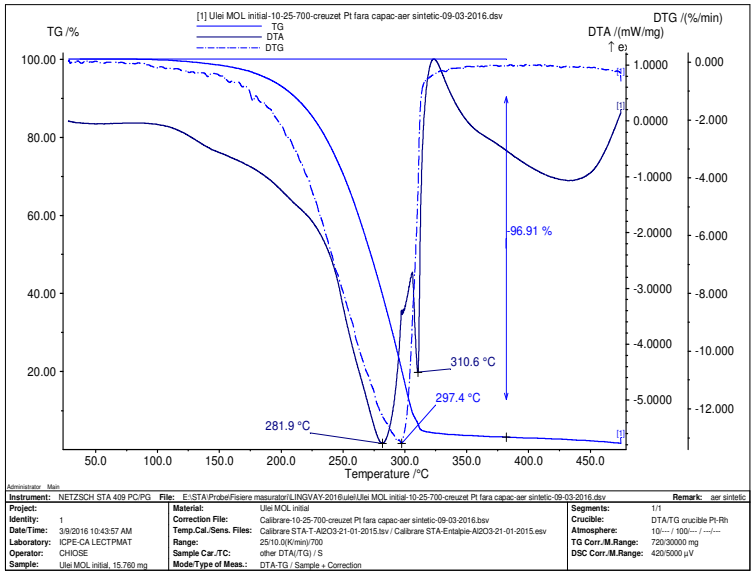


Fig. 6. TG – DTA and DTG thermograms registered for MOL TO 30 oil sample before thermal cycling

The comparative analysis of fig. 6 and fig. 7 reveals that following the thermal cycling MOL TO 30 undergoes an aging process similar to the one identified for the Nynas investigated oil.

The thermograms obtained for the oil recovered from a 1.5MVA transformer after 34 years of use are shown in fig. 8, while fig. 9 shows the thermograms for MOL TO 30 oil after 363 thermal cycles.

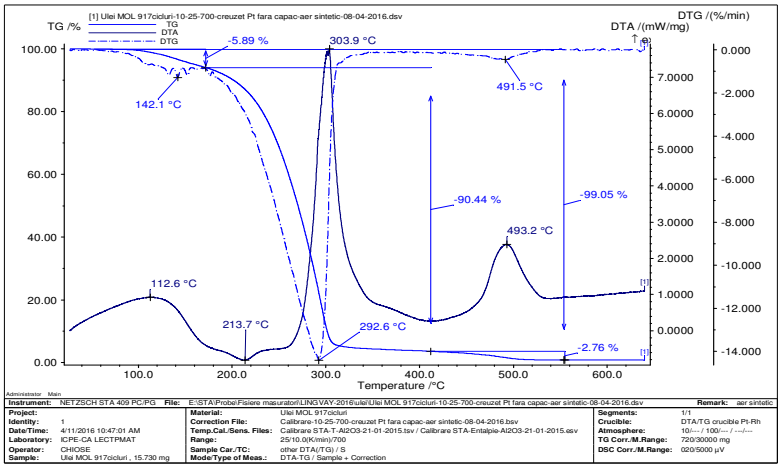


Fig. 7. TG – DTA and DTG thermograms registered for MOL TO 30 oil sample after 917 thermal cycles (Fig. 1)

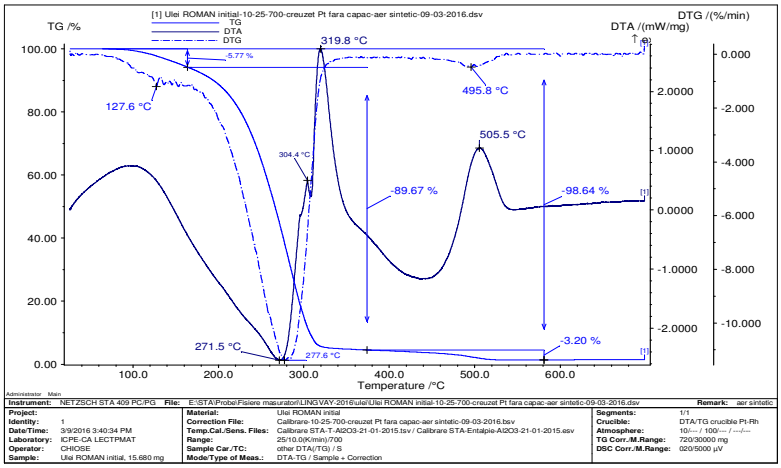


Fig. 8. TG – DTA and DTG thermograms for the Romanian oil sample TR30 recovered after 34 years of use

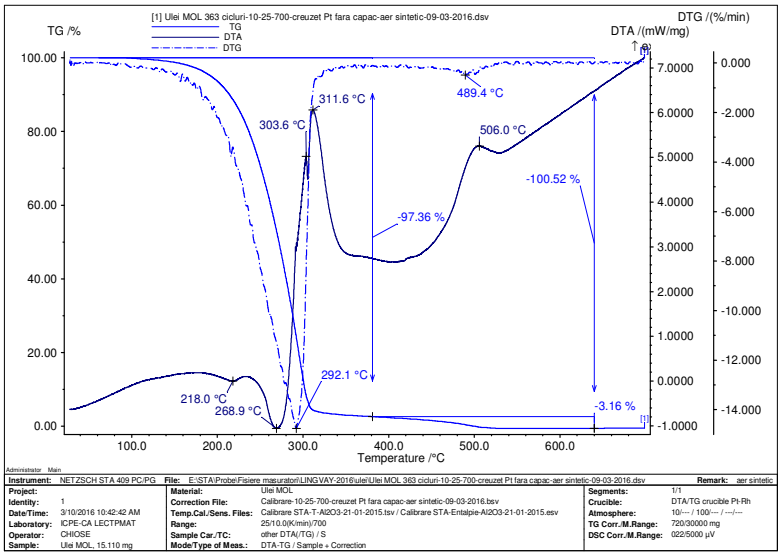


Fig. 9. TG – DTA and DTG thermograms for MOL TO 30 oil sample after 363thermal cycles

The comparative analysis of fig. 8 and fig. 9 reveals a very good similarity between the two oils (registered differences are very low), this fact suggests that the application of 363 thermal cycles as shown in Figure 1 corresponds to the aging obtained during 34 years of operation (in the operating conditions specific to the 1.5MVA transformer of which the oil was sampled).

The thermograms obtained for the experimental model of biodegradable vegetable oil developed by authors before applying thermal cycling are shown in fig. 10, while fig. 11 shows the results after 917 thermal cycles.

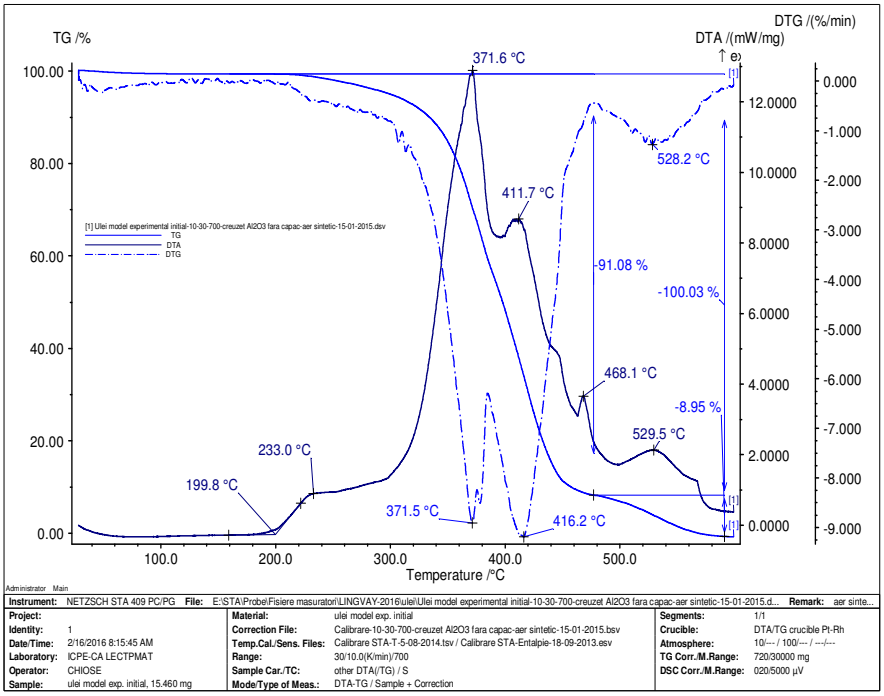


Fig. 10. TG – DTA and DTG thermograms for the sample of experimental model of oil before thermal cycling

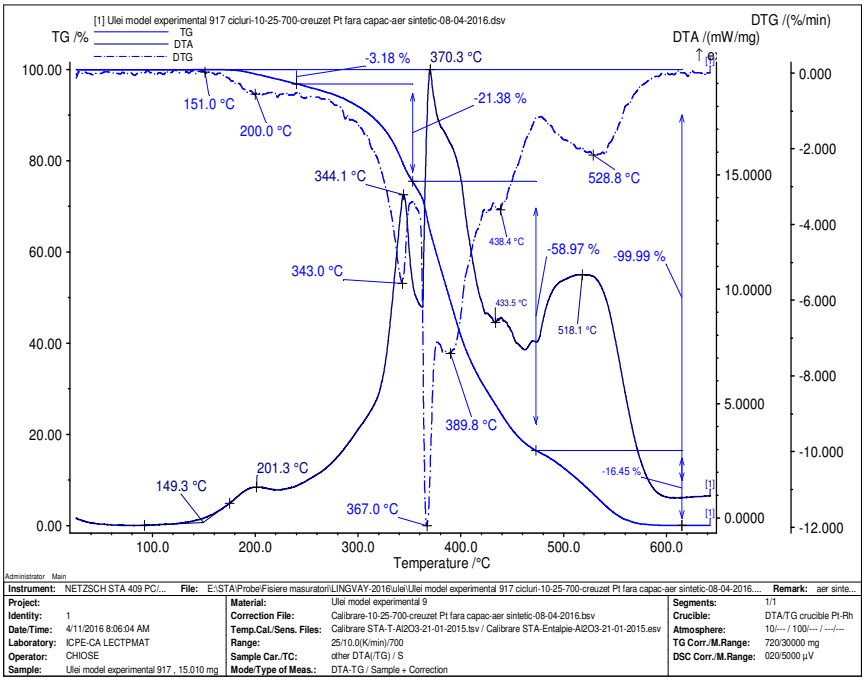


Fig. 11. TG – DTA and DTG thermograms for the sample of experimental model of oil after applying 917 thermal cycles (Fig. 1)

The analysis of fig. 10 reveals that during the progressive warming of the experimental electro insulating vegetable oil developed within [11], before the application of thermal cycles, the first transformation process starts at 199.8^{0}C; this is an exothermal process with the maximum velocity at 233^{0}C, when the oil starts to lose mass (3.18% up to 250^{0}C) as a result of the volatile products formation. To about 250^{0}C several successive processes are triggered - exothermal oxidation processes with formation of gaseous products with maximum velocities registered at 371.6^{0}C, 411.7^{0}C, 468.1^{0}C and 529.5^{0}C which lead to the total weight loss of the sample (0% residue at 580^{0}C). After applying 917 thermal cycles (fig. 1) behaviour of the sample is similar to the original sample, the differences consisting in lowering the characteristic temperatures with about 10 - 30^{0}C. These findings indicate that the maximum temperature of use / exploitation of this oil is of at least 200^{0}C, comparing to about 100^{0}C for the investigated mineral oils.

4. CONCLUSION

By gravimetric measurements and coupled thermal analysis techniques (TG+DTG+DTA) the aging of some sorts of electro insulating oils have been studied by thermal cycling between -40^0C and 85^0C. Data processing and analysis revealed that:

- during the thermal cycling the composition of mineral oils is changing as a result of the volatilization of volatile fractions, the total mass loss after 917 thermal cycles being in the range of 3.9% to 5.8%, depending on the commercial type of oil;
- the aging of the mineral oils due to thermal cycling increases their thermal oxidation capacity, and decreases the thermal stability;
- the investigated experimental model of vegetable oil do not show mass losses by volatilization during the thermal cycling - a mass increase of about 0.66% was found which could be due to the alkylation of the double bonds –C=C– from the structure of the fatty acids from the investigated vegetable oil;
- the mineral oils can be safely operated, without any significant change up to100^0C, unlike the investigated vegetable oil that can be used without risk of degradation up to 200^0C;
- for the case of the investigated mineral oils, by applying 363 thermal successive cycles by modifying the temperature between -40^0C and 85^0C equivalents to an exploitation of 34 years in a 1.5MVA transformer.

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