Study Regarding the Bahaviour of an Insulating Vegetable Oil Exposed to Accelerated Thermal Aging

PETRU BUDRUGEAC[1], IOSIF LINGVAY[1], ALEXANDRA PICA[2], BEATRICE GABRIELA SBARCEA[1]*

[1]National Institute for Research and Development in Electrical Engineering INCDIE ICPE-CA Bucharest, 313, Splaiul Unirii, 060042, Bucharest, Romania

[2]Research Institute for Advanced Coatings, Bucharest, 313 Splaiul Unirii, 060042, Bucharest, Romania

The simultaneous thermal analysis method (thermogravimetry/derivative thermogravimetry + differential thermal analysis (TG/DTG+DTA) and determination of iodine index have been used for characterization of an experimental vegetable insulating oil exposed to thermal cyclic and isothermal accelerated aging in pure state and in contact with red copper. The results obtained by thermal analyses show that three main successive processes of thermo-oxidation occur at progressive heating of initial (un-aged) and thermal aged oil samples. The accelerated thermal aging determines the change of composition and thermal properties of oil, which involves the formation of sites with an oxidative reactivity greater than those from initial (un-aged) oil. It has been put in evidence the catalytic role of red copper in the process of oil oxidation. The change of composition of oil as result of thermal aging also results from the decrease of iodine index. The general mechanism of auto-oxidation of vegetable oils gives a qualitative explanation of obtained results.

Keywords: vegetable oil for electrical insulation, thermal (TG, DTG+DTA) analysis, aging, iodine index of oil, red copper catalyst

Electrical insulating oils are widely used in electrical equipment and electroenergetic components such transformers, capacitors, measuring installations, the neutral treatments, etc. [1-6]. Traditionally, mineral oils with appropriate electrical properties and relatively low cost are used [3]. However, the use of such oil presents a number of limitations such as: relatively low ignition point (cca 130^{0}C), soil and water pollution in case of accidental leaks or spillages [7], low biodegradability [6]. In this context, a significant attention is given worldwide for obtaining insulating oils from plant resources (renewable) and for their characterization [3, 6-14].

In a previous paper [6], the characterization by thermal analysis techniques (thermogravimetry (TG), derivative thermogravimetry (DTG) and differential thermal analysis (DTA)) of some sorts of mineral and vegetable oils of electrotechnic using was presented. It was shown that the vegetable oils exhibit a thermal stability greater than mineral oils. Based of these results, an experimental model of electro insulating oil (bio-Exp model) was developed within a research contract by the team [15]. The corrosiveness and thermal stability of this oil as well as of other four commercial electroinsulating oils –all in contact with copper and carbon steel - have been studied through gravimetric determination, XRF analysis and dynamic viscosity measurements [13]. The aim of this paper is the application of coupled thermal analysis method (TG, DTG+DTA) for studying the behavior of *bio-Exp.oil* exposed to accelerated aging.

Experimental part

The *bio-Exp.oil* preparation was described elsewhere [15]. It was the subject to accelerated thermal aging in a thermo-climatic room (type VC 4018, Votsch - Industrietechnik in the following conditions: [16] either by performing 363 and 917 thermal cycles between 40 and 80^{o}C or by isothermal (thermal) aging at 110 ± 3^{o}C for 768 h.

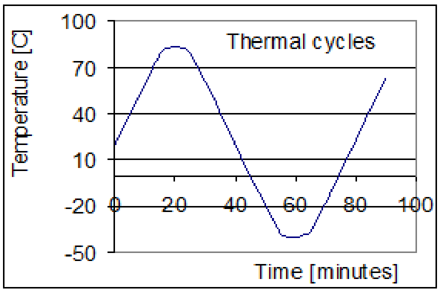


Fig.1. Thermal treatment profile of applied cycles (thermo cycles) [16]

To put in evidence the effect copper on the thermal stability of oil, it was also performed the thermal ageing (110^{o}C; 768h) of *Bio-Exp. oil sample* (≈ 200g) in which was introduced a red copper foil of 4 dm^2 surface area and Φ=30μm thickness. The initial (un-aged) oil and aged samples of oil were characterized by coupled thermal analysis (TG/DTG+DTA) and by determination of iodine index.

The thermal analyses of oil samples was performed with a simultaneous TG/ DTG+DTA analyzer produced by Netzsch-Germany, in synthetic air atmosphere (gas – flow rate of 30 cm^3/min), at heating rate of 10 K min^{-1}. Measurements were made in the temperature range 20-630^{o}C. The mass of each sample was around 15 mg. The results of measurements were processed and graphically represented using the dedicated Proteus Software, from Netzsch-Germany.

The iodine index (the mass of iodine in grams that is consumed by 100 grams of oil) was determined by HANUS method [17].

Results and discussions

TG, DTG and DTA curved registered for initial un-aged and thermal aged soil samples are shown in figures 2-6. The inspection of these figures shows that at progressive heating of all investigated samples these are three main successive processes noted in figures 2-6 by I, II, III.

* email: gabriela.sbarcea@icpe-ca.ro

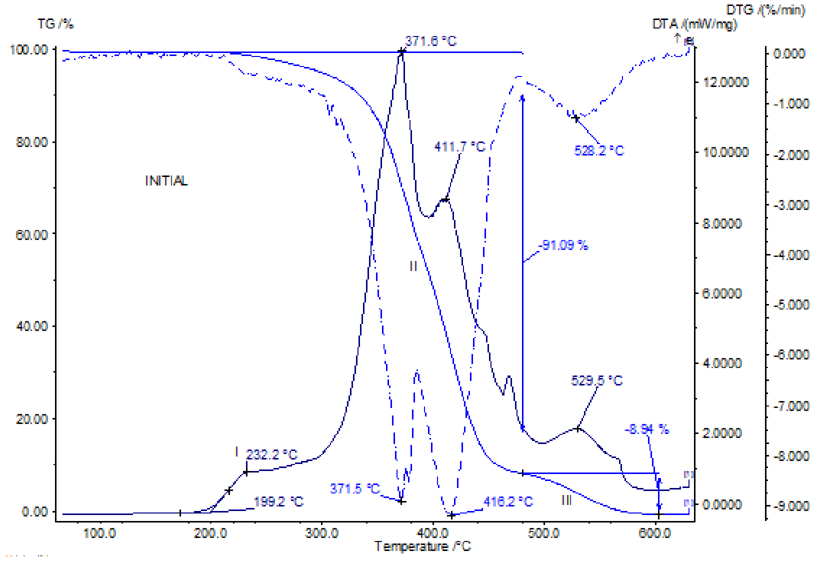


Fig.2 TG, DTG and DTA curves registred for unaged oil

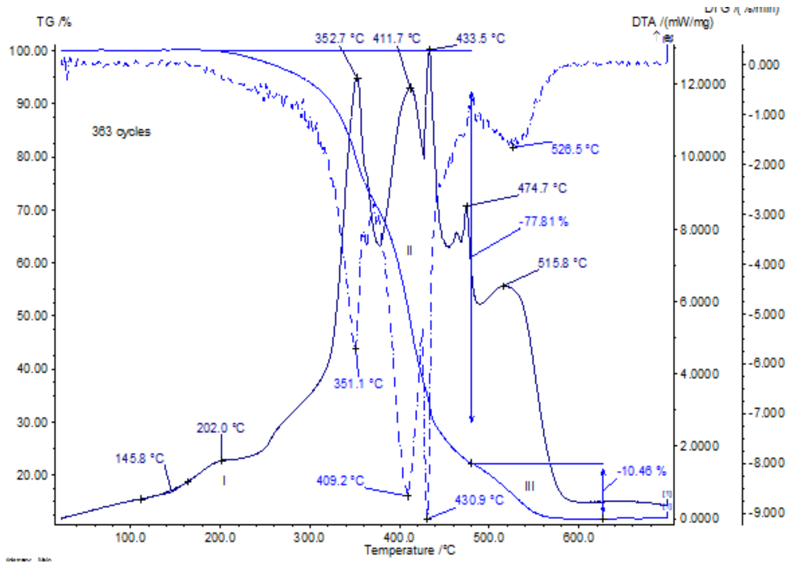


Fig.3 TG, DTG and DTA curves registred for oil sample after 363 cycles

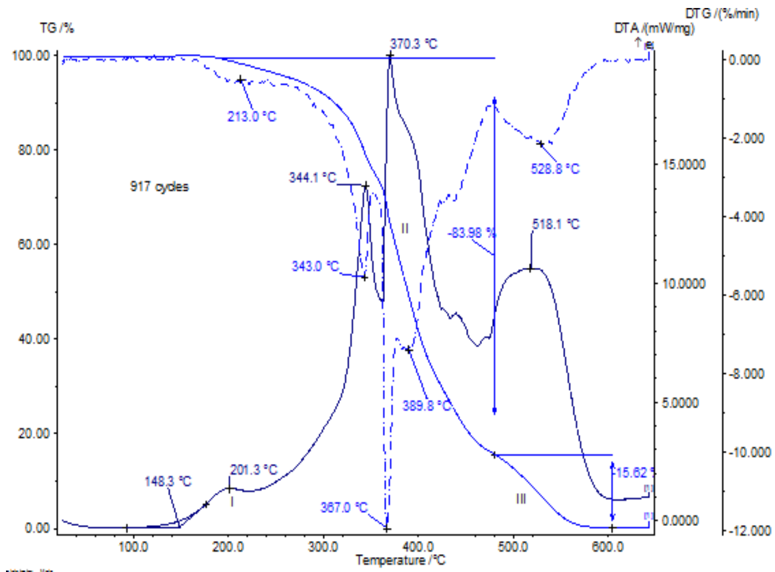


Fig.4 TG, DTG and DTA curves registred for oil sample after 917 cycles

The process I is characterized by an exothermic DTA peak and consists in *addition* of oxygen to the unsaturated chain of the fatly acid from glycerides. In this process, O_2 inserts into C-H bonds adjacent to double bounds within the unsaturated fatty acids (see scheme 1).

Figures 7 and 8 show the values of onset temperature (T_{onset}) of process I and maximum temperature (T_{max}) corresponding to DTA peak characteristic for this process. The inspection of these figures shows that: (a) the thermal cycling and isothermal aging determine the decrease of both T_{onset} and T_{max} and (b) for the same duration of isothermal aging (768 h), the values of T_{onset} and T_{max} for oil in contact with red copper are lower than those corresponding to oil in pure state.

Both these statements indicate that the accelerated thermal aging determinates the change of physical-chemistry properties of oil, which also involves the formation of sites with an oxidative reactivity greater than

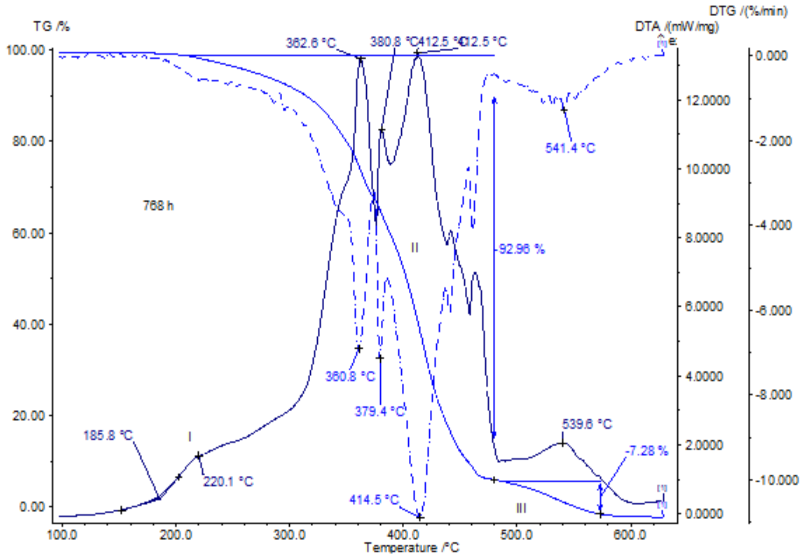


Fig.5. TG, DTG and DTA curves registred for oil sample after 768 h of isothermal aging at 110°C

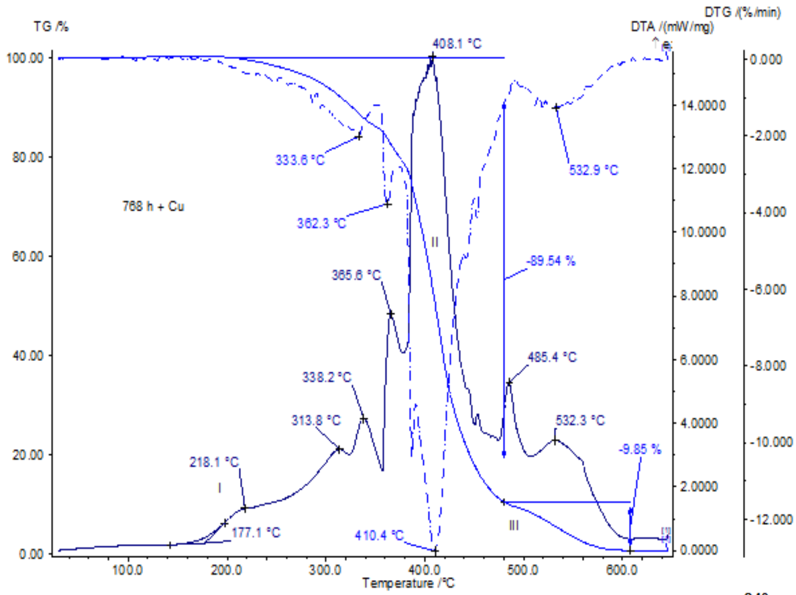
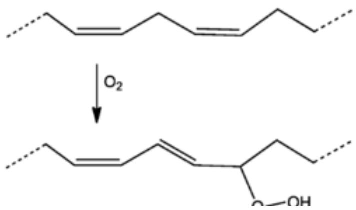


Fig.6. TG, DTG and DTA curves registred for oil sample in contact with red copper after 768 h of isothermal aging at 110°C



Scheme 1. The formation of hydro peroxide in the first stage of oxidation of dienes containing fatty acid derivative

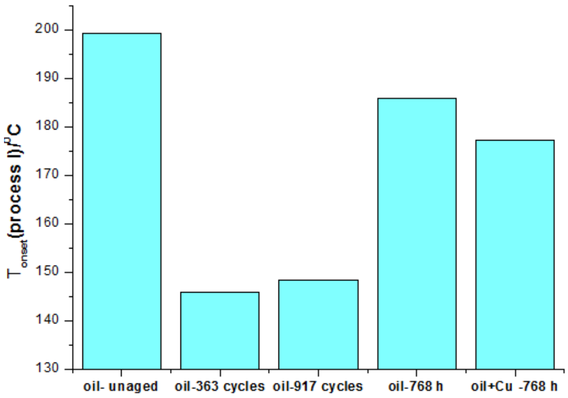


Fig.7. Onset temperatures for process I of oxidation with formation of solid compounds

those from initial (un-aged) oil. The results for oil in contact with copper foil suggest that red copper exhibit a catalytic activity in the oxidation of oil during the aging.

The change of structure as result of thermal aging was evidenced also from the TG, DTG and DTA curves

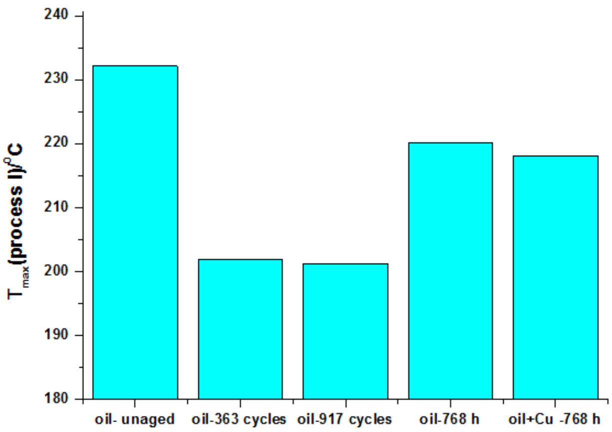


Fig.8. Temperatures corresponding to maximum of DTA peak characteristic for process I with formation of solid compounds

corresponding to processes II and III, which consist in the oxidation and / or decomposition of the compounds resulted in process I. These last two processes occur with formation of volatile compounds. For all investigated oils, the process II is characterized by several DTG and DTA peaks. The number of these peaks is greater for aged samples and the corresponding characteristic temperatures depend on the kind of thermal aging and the duration of aging.

The change of structure as result of thermal aging is also evidenced from the values of iodine index, which are shown in figure 9.

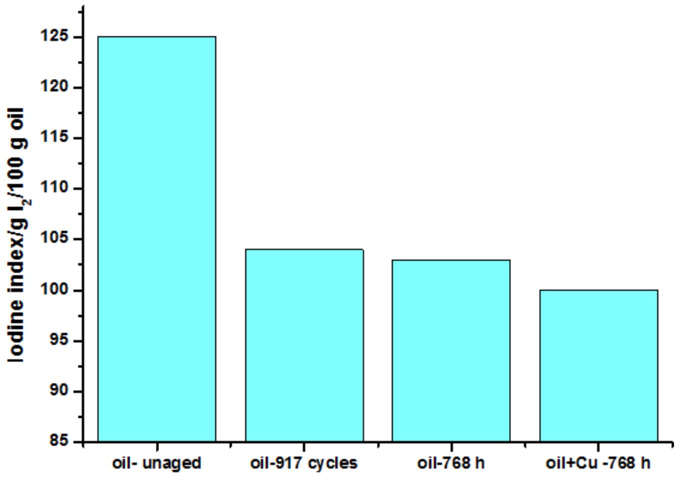
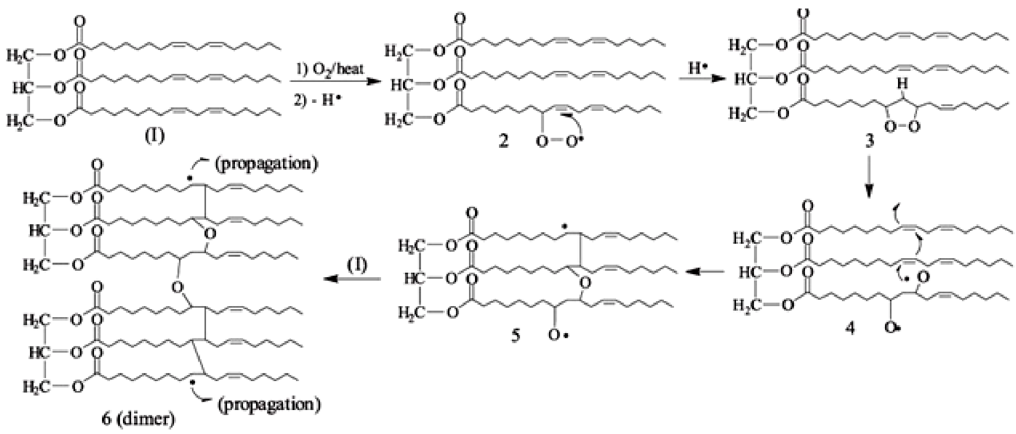


Fig.9. Iodine index for un-aged and thermal aged sample of oil



Scheme 2 Mechanism of auto-oxidation of vegetable oils [19]

The thermal aged samples exhibit practically the same iodine index that is substantially lower that the iodine index of initial (un-aged) oil, suggesting that the thermal aging determines the increase of saturation degree of oil. This result and those presented in figures 7 and 8 could be explained by the mechanism of oxidation of vegetable oils developed by Gomez et at [18] (scheme 2), according to which the oxidation pathway starts by the formation of hydroperoxides and peroxide radicals in allylic or bis-allylic sites (species 2 in scheme 2) [19,20].

Transformation of the peroxide radicals generally involves competitive reactions such as formation of cyclic peroxides (species 3 in scheme 2), isomerization of double bonds or even formation of dimers, oligomers, and polymers (species 6, scheme 2). This mechanism of auto-oxidation is also valid for oils that contain groups providing from fatty acids with a single double bound. According to these mechanism, the number of double bounds decrease by auto-oxidation (reactions 3→4→5 in scheme 2). This explains the decreasing of iodine index by thermal aging. On the other hand the auto-oxidation determines the increasing of number of carbon atoms with a high degree of substitution, which exhibit a high auto-oxidative reactivity.

Conclusions

The results obtained by thermal cyclic and isothermal accelerated aging of an experimental vegetable insulating oil in pure state and in contact with red copper show that three main successive processes occur. The first process consists in the formation of solid hydroperoxides, while the second and third processes consist in thermo-oxidations with formation of volatile compounds. The thermal parameters of entire process depend on the kind and duration of aging. The parameters of the first process indicate that the thermal stability decreases by thermal aging and the red copper has a catalytic role in the oxidation of oil.

The change of composition of oil as results of thermal aging is also supported by results obtained at determination of iodine index, according to which the degree of unsaturation of pure initial (un-aged oil) is greater that those corresponding to thermal aged samples. The obtained results were explained by the general mechanism of auto-oxidation of vegetable oils.

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