Studies on the Influence of Copper and Insulation Paper on the Accelerated Thermal Ageing of Some Insulating Fluids

IOSIF LINGVAY[1], GABRIELA OPRINA[1]*, VALERICA STANOI[2], ALEXANDRA PICA[3], LIVIA CARMEN UNGUREANU[2], FLORENTINA SERBAN[3]

[1]National Institute for Research and Development in Electrical Engineering INCDIE ICPE-CA Bucharest, 313 Splaiul Unirii, 030138, Bucharest, Romania

[2]National Institute for Research, Development and Testing in Electrical Engineering, 118A Decebal Blvd.,200746, Craiova, Romania

[3]Research Institute for Advanced Coatings, Bucharest, 313 Splaiul Unirii, 030138, Bucharest, Romania

The behaviour of some insulating fluids in contact with copper foil and / or insulation paper under thermal stress (110±3^{0}C for 1000 hours), in a closed system (the access of atmospheric oxygen being limited), has been studied by determining the changes in viscosity and concentration of CO_2 and CO. The experimental data revealed that, following the applied heat treatment, the change in viscosity of the esters-based insulating fluids (both synthetic and vegetable) is approximately 7 times lower than in the case of the investigated mineral oils. It has also been found that, following the thermal ageing, the gas content of the mineral oils is substantially higher than in the esters-based oils (8 times higher for CO_2 and 4 times higher for CO, respectively). The experimental results indicate superior values for the thermal stability and compatibility with the insulation paper of ester-based insulating fluids.

Keywords: transformer oil, mineral oil, ester oil, thermal ageing, insulation paper

The reliability of electrical systems is a complex issue, of significant practical importance.

Durability and safe operation of electrical equipment is largely determined by the ageing of the materials (functional characteristics degradation) used to achieve them. This is due to the fact that, during operation, the materials are exposed to a series of stress factors, which determine the modification of their characteristics.

Power transformers are complex electrical equipment, their construction implying both metallic materials (steel - shaft / casing, Fe-Si alloy - core, copper - windings etc.) and minerals (insulation paper, transformer oil, insulating bases etc.). During exploitation, these materials are simultaneously exposed to electrical, thermal, mechanical, chemical stress, which induces the deterioration of their functional characteristics, leading in some extreme cases to equipment damage (along with the associated direct and indirect implications - interruption of electricity supply, explosions / fires, property damage, environmental pollution etc.).

Traditionally, within the electrical transformers, in order to simultaneously ensure the heat transfer from winding to environment in the case of appropriate insulation (homogenization of electrical fields), mineral oils are used as insulation fluids [1-3].

Although the mineral insulating oils have a high quality to price ratio, they also present a series of disadvantages such as: low biodegradability [4,5], due to their sulphur content they corrode the metallic parts (particularly copper) and the corrosion products (sulphides) significantly reduce the transformer insulation [6-11], relatively low fire point (below 150^{0}C), degrades the insulation paper with furans and gas formation [12-14], relatively low thermal stability [3, 15-19] etc.

Under practical operating conditions, the insulating oils (in contact with insulation paper, copper, steel, paints used to protect the inner part of the transformer tank etc.) are exposed to thermal and electrical stress. Under the concerted action of these stress factors, a series of chemical processes take place, degrading both the oils and the materials they are in contact with.

The ageing of insulating oils is determined by the dissolved oxygen content of the oil due to thermo-oxidative processes [10, 15, 18, 19], followed by the formation of a series of gaseous degradation products such as CO, CO_2, CH_4, C_2H_4, C_2H_6 etc., which leads to an increase in oil viscosity. The gas content of the insulating oils represents a good indicator of the oil ageing degree. Recent studies have shown that the thermo-oxidative processes of oils are favoured by the presence of copper in the system [8,10].

The *aim of this paper* is to study the influence of copper and / or insulation paper on the thermo-oxidative degradation processes of some insulating oils.

Experimental part

Three types of mineral origin transformer oil were investigated: a sort of predominantly vegetable oil, a synthetic ester-based oil and an experimental 100% vegetable oil (*demonstrator model*). The investigated oil sorts are summarized in table 1.

Table 1
INVESTIGATED OILS

Sample code	Oil type	Oil origin
Oil1 (O1)	Mineral	MOL TO-30.01R [20]
Oil2 (O2)	Predominantly vegetable ester	Biotemp® [21]
Oil3 (O3)	Synthetic ester	LUMINOL [22]
Oil4 (O4)	Vegetable ester with 0.5% antioxidant	MF-UPMEE;P1MF [23]
Oil5 (O5)	Mineral	Nynas [24]

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

Samples of approximately 200 g of insulating oil (Table 1) have been placed in Erlenmeyer flasks with ground slide and ground-glass stopper, along with a copper foil of 1.2 dm^2 [25] and/or about 1 dm^2 of Kraft insulation paper (22HCC type manufactured by Weidmann, in line with IEC 60641-1/2007) and were exposed to thermal ageing by storage at 110±3^{0}C for 1000 h in a drying chamber, XL 980 type France Etuve.

Before and after the heat treatment, the dynamic viscosity of the investigated oils was determined using Brookfield method, with a VM2 viscometer from Sheen Instruments. Periodically, during the heat treatment, 4-5 mL: oil samples have been used to determine the CO and CO_2 content by a CLARUS 600 gas chromatograph manufactured by Perkin Elmer (US).

Results and discussions

The values of dynamic viscosity (*DV*), before and after 1000 hours of heat treatment at 110±3^{0}C, are shown in table 2.

The analysis of the data shown in table 2 revealed that, during the applied heat treatment, the viscosity of the investigated oils changes depending on the type and nature of the oil.

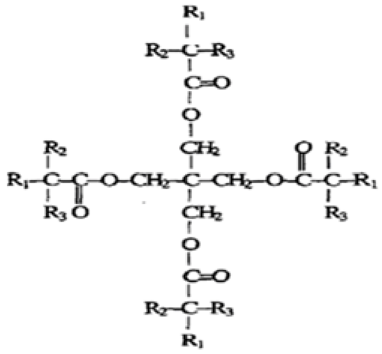
Table 2
VISCOSITY OF INVESTIGATED OILS

Oil sample	Dynamic viscosity at 25ºC [cP]		
	Initial	After heat treatment	Δ_{DV}[%]
O1	26	29	11.5
O1+Cu		30	15.4
O1+paper		34	30.8
O1+Cu+paper		35	34.6
O2	72	74	2.8
O2+Cu		78	5.5
O2+paper		76	1.4
O2+Cu+ paper		79	5.6
O3	56	57	1.8
O3+Cu		59	3.6
O3+ paper		58	1.8
O3+Cu+ paper		60	3.6
O4	70	71	-1.4
O4+Cu		73	-4.3
O4+ paper		72	-2.9
O4+Cu+ paper		74	-5.7
O5	28	32	14.3
O5+Cu		34	21.4
O5+ paper		39	39.3
O5+Cu+ paper		41	46.4

Following the thermo-oxidative processes, in the mineral oils case, the viscosity increases from 11.5 to 14.3% for the simple oil sample. When the oils are in contact with copper foil, a higher viscosity modification is registered, ranging between 15.4 and 21.4%; this may be explained by the catalytic activity of the Cu_2O film that have been formed [6, 8, 10]. A even higher increase in viscosity is registered when oils are in contact with insulation paper - an increase of 30.8% and 39.3% respectively. These high increases are probably due to two parallel and/or successive processes, whose results are cumulative, i.e. the oil thermo-oxidation process and the chemical processes between the hot oil and the insulation paper (degradation processes of paper and oil). The highest increases (34.6% and 46.4% respectively) were registered for the oil samples Oil1 and Oil5 when being in simultaneous contact with insulation paper and copper foil; this finding suggests that, within the system, several complex processes with synergic effects take place.

In the case of the mixture Oil2 (vegetable oil with a small addition of mineral oil), the increases in viscosity are significantly lower than in the case of traditional mineral oils (Oil1 and Oil5) - of only 2.8% in the case of simple oil, of 5.5% in the case of oil in contact with copper foil, of 1.4% in the case of oil with insulation paper and of 5.6% in the case of the complex system Oil2+Cu+insulation paper. It is also found that, in the case of Oil2+insulation paper, the viscosity increase is significantly low (lower than in the case of simple Oil2), suggesting that the esterified cellulose formed by the reactions between the vegetable ester component of Oil2 and insulation paper [11] inhibits the thermo-oxidative processes that take place inside the simple oil.

The lowest increases in viscosity were registered in the case of synthetic ester Oil3, indicating that the organic radicals R from the ester structure [1, 31]



Scheme 1

are acyclic, without double bonds and consequently stable, hard to be oxidized. However, the catalytic effect of the copper foil is also registered in this case, indicated by the higher increase in viscosity - of 3.6% in the case of synthetic ester O3 and of 1.8% in the case of simple oil O3. For O3, as expected, the contact with the insulation paper does not influence the thermo-oxidative processes of the oil.

A special behaviour was registered in the case of oil Oil4 – vegetable oil with 0.5% antioxidant addition [23] – whose viscosity decreases as a result of the heat treatment. These decreases in viscosity are likely due to the thermal oxidation of the double bonds –C=C– with peroxide groups formation, which are subsequently converted to an –OH group, the end product having a lower viscosity. For this case, also, the copper presence catalyzes the process and the decrease is much greater.

The relatively small changes in viscosity during the thermal ageing of the ester-based insulating fluids in simultaneous contact with copper and insulation paper – of maximum 5.7% in relation to over 35% in the mineral oils case-suggests they ensure a high stability of the magnetic nano-powders suspension when they are used in insulating ferrofluids [26-28].

Measuring the gas content evolution (mainly CO_2 and CO) formed during the oil use is an indirect method to asses the aging of both insulating oils and insulation paper [29, 30]. The experimental results obtained from the measurements of CO_2 and CO content (end products of the complex thermo-oxidative processes) are shown in figures 1-10.

The analysis of figures 1-10 revealed that, during the applied heat treatment, the CO_2 and CO content of the oils under investigation changes with the type and nature of the oil.

By analyzing figure 1 and figure 5 it results that the initial content of CO_2 and CO for the mineral oils Oil1 and Oil5 is zero and that, during the heat treatment, the content

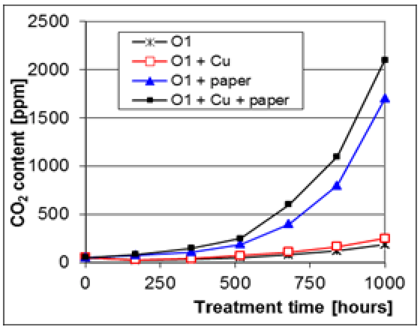


Fig. 1. CO_2 content evolution during the heat treatment for O1

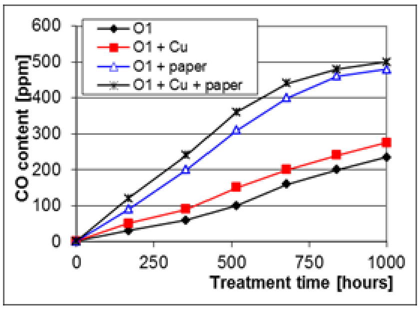


Fig 2. CO content evolution during the heat treatment for Oil1

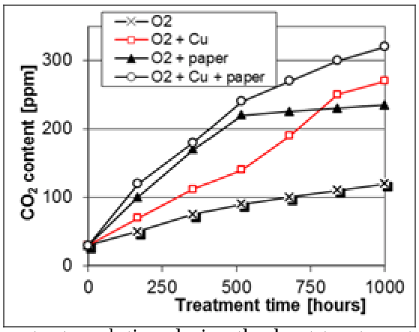


Fig 3. CO_2 content evolution during the heat treatment for Oil2

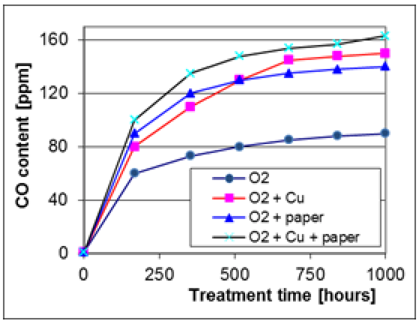


Fig. 4. CO content evolution during the heat treatment for Oil2

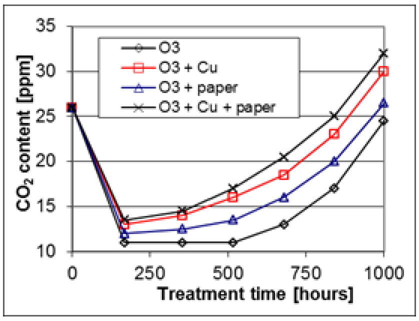


Fig 5. CO_2 content evolution during the heat treatment for Oil3

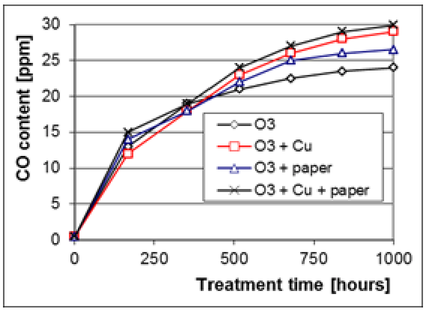


Fig 6. CO content evolution during the heat treatment for Oil3

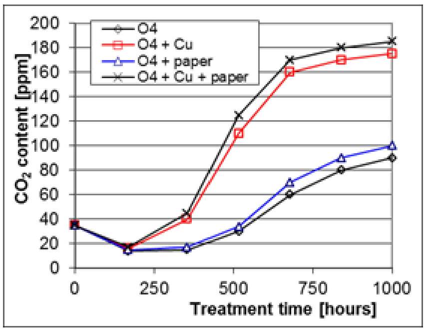


Fig 7. CO_2 content evolution during the heat treatment for Oil4

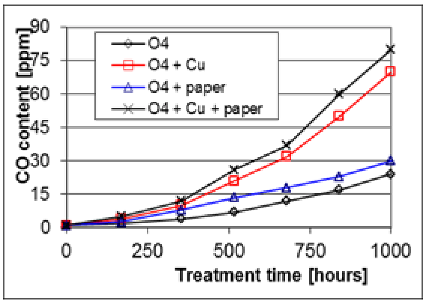


Fig 8. CO content evolution during the heat treatment for Oil4

systematically increases, after a monotonically increasing function, being (both for Oil1 and Oil5) as follows: simple oil < oil + copper < oil + insulation paper < oil + copper + insulation paper; thus, the content reaches 2100 ppm CO_2 and 500 ppm CO in Oil1 and 2500 ppm CO_2 and 680 ppm CO in Oil5. This order indicates that the thermo-oxidative processes in the mineral oils are accelerated by the presence of the copper foil and particularly by the insulation paper. Figure 2 and figure 10 reveal that CO content in oils Oil1 and Oil5 increases linearly in the first approx. 700 hours of heat treatment, whereupon, for concentrations greater than 400 ppm, it tends to limit asymptotic; this finding suggests a change in the mechanism and kinetics of the degradation processes.

In the synthetic ester-based oils case (e.g. Oil3 in fig. 5) and in the vegetable oil case (e.g. Oil2 in fig. 3 and Oil4 in fig. 7) it is found that they have an initial CO_2 content (between 25 and 35 ppm, varying with the ester origin); except Oil2 case, this content drops significantly (below 15 ppm) in the first 168 hours of heat treatment. This finding suggests that esters, unlike mineral oils, have a high ability to absorb CO_2 (probably from the air that comes into contact with during technological processing) and, at the beginning of the heat treatment, the removal / release of dissolved CO_2 occurs.

This phenomenon is not noticed in the case of Oil2 (fig. 3), that contains also a mineral oil fraction, which starts the process of CO_2 formation; thus, in the first stage of the heat treatment, the CO_2 amount formed is higher than the initial content absorbed in oil.

Figure 3 and figure 7 show that CO_2 formation processes into ester-based oils have a tendency to limit after reaching certain limit concentrations of CO_2, being registered higher values for O2 (up to approximately 300 ppm) and significantly lower values for O4 (below 180 ppm). For the synthetic ester O3 case (fig. 5), the CO_2 concentrations are considerably lower (up to 32 ppm) and do not appear a limitation tendency – probably, in this case, during the 1000

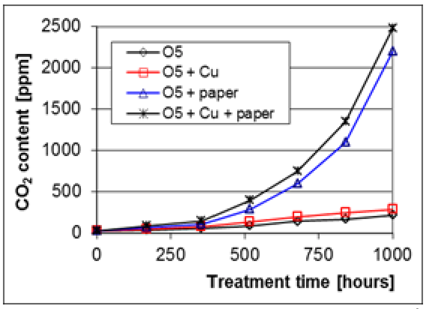


Fig 9. CO_2 content evolution during the heat treatment for Oil5

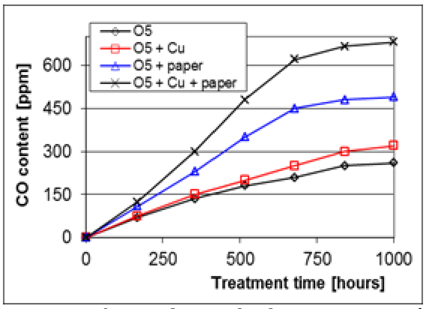


Fig.10. CO content evolution during the heat treatment for Oil5

h of heat treatment the concentrations have not reached the minimum values at which the CO_2 formation processes are limited).

Figures 4, 6 and 8 show that, for the ester-based oils, the concentration of the CO formed during the thermal stress is linearly increasing in the first approximately 700 hours of heat treatment, whereupon it tends to limit asymptotic to a limit value of up to 30 ppm in the case of synthetic ester O3, of up to 58 ppm in the natural ester O4 and up to 160 ppm for the predominantly vegetal Oil2. This trend could be explained by the reduction of the dissolved oxygen content from the oil exposed to thermal stress [31]. It is also found that the presence of the insulation paper in oil has an insignificant influence on CO formation, indicating a good stability of the paper under thermal stress in ester-based oils. It is noticed that the CO quantities formed are systematically higher in the copper presence than in its absence, suggesting [6, 8, 10] that in ester-based oils, the CuO film formed on the copper foil surface is catalyzing the CO formation processes.

By performing a comparative analysis of the results shown in Table 2 and in Figures 1-10, it was found that the thermal stability of the ester-based insulating fluids is significantly higher than that of mineral-based insulating fluids – inclusively in practical operation (in contact with copper foil and insulation paper); this finding is in good agreement with previously reported results [32].

Considering that the insulating vegetable oils present a high thermal stability and a good compatibility with the insulation paper, that they have a high biodegradation rate and are made using renewable resources through environmental-friendly technologies, it is recommended to replace the mineral-based insulating oil from transformers with vegetable oil in order to ensure the sustainable development. In this context, a continuous information and environmental education at users regarding the insulating fluids is necessary [33, 34], as well as a reconsideration of the regulations and laws concerning the environmental protection.

Conclusions

By determining the changes in viscosity and the CO_2 and CO content, the behaviour under thermal stress (110±3^{0}C for 1000 hours) of some insulating fluids in contact with copper foil and / or insulation paper have been studied. Processing the experimental data for the five types of investigated oils revealed that:

-as a result of the applied heat treatment, the modification in viscosity of the ester-based insulating fluids (synthetic and vegetable as well) is approximately 7 times higher than in the case of mineral oils;

-in similar experimental conditions, the CO_2 content as a result of the applied heat treatment is 8 times higher in the case of mineral oils than in the case of ester-based oils;

-in similar experimental conditions, the CO content as a result of the applied heat treatment is 4 times higher in the case of mineral oils than in the case of ester-based oils;

-the CO_2 content of the mineral oils (under thermal stress) in contact with insulation paper is substantially higher in the absence of the paper (of 9 times in oil Oil1 case and of 11 times in oil Oil5 case), in contrast to the ester-based oils, where the increases were less than 10% (except in Oil2 case, when the insulation paper presence doubled the CO_2 content).

These experimental findings lead to the following conclusions:

- the physico-chemical changes due to thermal stress are substantially lower in the case of ester-based insulation oils than in the case of mineral oils or mineral oils; thus, the thermal stability of mineral oils is inferior to that of the ester-based oils;

- the physico-chemical stability of the insulation paper exposed to thermal and chemical stress in ester-based insulating fluids is superior to mineral oils, so the ageing process of the paper in contact with ester-based oils is substantially slower than in the case of mineral oils.

Based on these findings and conclusions, it is recommended to replace the mineral oils from electric equipment with insulating fluids based on natural esters that are environmental friendly and that ensure a superior stability and durability of the insulation systems.

Acknowledgment: This work was financially supported by the UEFISCDI of Romania, under the scientific Programme PN II – Contract 100/2014 - UPMEE.

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Manuscript received: 1.02.2017