Thermochemical Stability of Some Transformer Oils- Flammable Gas Formation Due to the Thermal Aging

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The amounts of flammable gases formed in some transformer oils during the long-term storage (1000 hours) at 110 ± 3°C in closed containers (limited access to atmospheric oxygen) were determined qualitatively and quantitatively by gas chromatography technique. The comparative experimental results showed that when two types of mineral oils, one synthetic oil and two types of vegetable oils are in simultaneously contact with copper and insulating paper, the total amount of flammable gases formed by thermal aging is about 40 times higher in the mineral oils than in the ester based oils. It has also been established that the electrical-use copper foil catalyses the formation processes of the flammable gases, the maximum effect being for the mineral oils (an increase of 8 times of ethane and 25 times for methane gases). It has further been observed that the contact with the insulating paper during the thermal treatment of the ester based oils does not influence the formation of flammable gases, compared with the mineral oils where the amount of the formed gases is doubled.

Keywords: transformer oil, mineral oil, synthetic esters, natural esters, flammable gases

The safety in exploitation of the equipments and installations related to the transportation and distribution of electrical energy represents a complex problem with a great practical importance. The duration and reliability of the electrical equipment subjected to voltage is determined mainly by the aging of the insulating systems under the action of stressors. During the operation, the materials corresponding to the insulating systems are exposed simultaneously to the stress factors (electrical, thermal, chemical and mechanical etc.) that degrade their functional characteristics resulting the weathering of insulation.

The electrical insulating fluids are commonly used in electrical transformers, power cables (the ones with oil/paper mixed insulation), capacitors, etc. In these applications the electro-insulating fluid is exposed to the electrical stress generated by the operating voltage. It is noticed that in the case of deforming regimes (primarily due to the reactive character of some consumers), transient generators and harmonics [1-4], the effects of the electrical stress are intensified. Under the action of the voltage applied to the electrically insulating fluid, polarization phenomena occur and due to the dielectric losses (given by the permittivity of the fluid and by the frequency of the applied voltage), the heat is released and the fluid is heated. On the other hand, in the case of cables and transformers, both losses by joule and pellicular effect contribute to the heating of the insulating fluid due to the current circulated through conductors. The heating effect is more pronounced in the case of the deforming regimes (with a high content of harmonic currents) generated by nonlinear consumers [5, 6]. In this case the dielectric losses and those due to the film effect are higher and they increase at increasing frequency / increasing order of harmonics. It is found that electrical stress acting on the electro-insulating fluid generates thermal stress under some conditions.

The mineral oils made from crude oil by distillation are traditionally used as electrical-insulating fluid in electrical equipments, having in their composition paraffins, isoparaffins, napthenes - isoparaffins and other components [7, 8]. Although the mineral oils have a good performance / cost ratio, they present a number of drawbacks such as: relatively low flammability (about 135°C [8, 9]) – high fire risk, ability to degrade cellulose-based insulation (electro-insulating paper) with the formation of toxic products (as furans) [10-13]; they are hardly biodegradable [14,15] and because of their sulphur content they are corrosive to copper, the corrosion products affecting the electrical-use copper foil catalyses the formation processes of the flammable gases, the maximum effect being for the mineral oils (an increase of 8 times of ethane and 25 times for methane gases). Worldwide, there are sustained concerns for the development and experimentation of electrical insulating fluids, [7-10, 14, 15, 20-22] in order to eliminate these disadvantages and to produce of environmentally friendly oils, suitable for the application. When the electro-insulating fluids are in contact with the materials from the construction of the transformers (copper for electrical purpose, insulating paper, etc.), as well as with the gases absorbed by the contact with the atmospheric air (oxygen, nitrogen, carbon dioxide), a series of chemical processes take place under the influence of the thermal stress. The most important are: the decomposition with formation of volatile products (gases) [24-28], thermo-oxidation (in closed systems, limited by the available oxygen [29-31]) and cellulose degradation (at electro-insulating paper) [10 - 13, 32], with implications upon operational safety and transformers lifetime [11, 12, 33-42].

It was supposed that the electrical stress acts on electro-insulating fluids in exploitation and, as a result of the collision of the fast electrons e– fast with an organic compound Rx-Ry from the fluid composition [24], the activated compounds Rx-Ry* are formed (1):

\[ e^{-\text{fast}} + Rx-Ry \rightarrow e^{-\text{slow}} + Rx-Ry^* \]  (1)

The deactivation of the activated molecule/compound R_x-R_y^* takes place (2) by emission of the light energy h\nu in UV spectra (Corona effect) [24].
The free radicals formed in equation (3) are usually short life radical [24] and they recombine, generating different products that cannot be found in the initial oil composition. A part of these products, as hydrogen, methane, ethylene, ethane, are gaseous and easily flammable [43], with major implications on safety in exploitation of the transformers [9]. Under the action of the thermal stress, the degradation processes of the cellulose from electro insulating paper are accelerated and, besides furfurals and water [11, 12, 32], flammable gases can also be formed (eq. 4).

In equation (4), 5HMF is 5-(hydroxymethyl)-2-furaldehyde, 2FOL is furfuryl alcohol and 2FAL is furfural. In the presence of oxygen, formic anhydride resulting from the decomposition of 5HMF generates formic acid, which, can be decomposed into CO and water (in excess of oxygen), CO and water or CO₂ and H₂ [43], depending on the exploitation conditions of the transformer.

It is noted that both cellulose degradation processes and other chemical processes that take place in the presence of electro-insulating fluids are influenced by the mechanical stress, respectively by the transformer core vibrations (due to the alternating magnetic field). The processes are accelerated by stirring and, therefore, as a result of the concentrated and synergistic of electrical, thermal and mechanical stress factors on the electrical insulating fluids, the gas emissions are considerable. Some gases can exceed even 3 times the volume of the oil [43] leading to an increased risk of explosions and fires [9, 43].

Taking into account these considerations, the aim of the present work is the comparative study of the flammable gas formation due to the thermal aging of different types of electro-insulating fluids (mineral oils and esters containing oils). Also, the influence of the electrical-use copper and electrical-insulating paper on the formation of gases was investigated.

**Experimental part**

For quantitative and qualitative determination of the flammable gases formation during the thermal aging of some electrical insulating fluids, 200 g of oil sample was introduced in Erlenmeyer flasks. Five types of oil were investigated comparatively (table 1): two mineral oils [44-48], a predominantly vegetable ester oil [45], a synthetic ester [46] and a vegetable ester oil with a high oleic acid content (dehydrated and with 0.5% antioxidant added [47]).

Four similar samples were prepared for each type of investigated oil (table 1), namely the pure oil, oil with approx. 100 cm² copper foil added (36±4μm thickness), oil with approx. 100 cm² Kraft insulating paper added (type 22HCC paper manufactured by Weidmann), and oil with both 100 cm² copper foil and 100 cm² insulating paper. The prepared samples were sealed in order to limit the atmospheric oxygen and were exposed to thermal aging at 110±3°C for 1000 h in a XL 980 type oven. The composition of the flammable gases (H₂, CH₄, C₂H₄ and C₂H₆) formed inside the investigated oils was determined before and during the thermal treatment using a Perkin Elmer 600 CLARUS (USA) type chromatograph.

**Results and discussions**

Figure 1 shows the evolution in time of each flammable gas content for a mineral oil (Oil 1) during the thermal aging and figure 2 presents the total amount of flammable gases.

It is noted from figure 1 that the amount of H₂ formed in Oil 1 in the absence of copper and paper has a limitation tendency to a value of 7.5 ppm H₂, after 500 h of thermal treatment. Also, it is observed that up to 500 h the content of CH₄ increases up to 10 ppm, followed by a limitation tendency. The content of C₂H₄ increases relatively slowly to 8 ppm (at 500 h) followed by an exponential increase up to 50 ppm for 1000 h of aging. After an initiation period of 500 h, the content of C₂H₆ increases exponentially up to 10 ppm in 1000 h. These results indicate that in the absence of copper and paper, the Oil 1 has the tendency to decompose as a consequence of the applied thermal treatment by breaking of C-C and C-H bonds and simultaneous formation of H₂, CH₄, C₂H₂ and C₂H₆. With the exception of C₂H₄ release, these processes accelerate significantly after approx. 500 h of aging. This behavior suggests that the formation of the flammable gases was accelerated autocatalytically.

The substantial acceleration of C₂H₆ after reaching the concentration of 4 ppm H₂ and 10 ppm CH₄, as well as the trend that limits these values, suggest that, over these concentrations, the secondary addition reaction of H₂ to C₂H₂ is predominant, leading to the formation of C₂H₆. The development of this process is also supported by the content of H₂ that presents an identical evolution in time (limited to about 7.5 ppm) in Oil 1 samples both in contact with copper and in contact with insulating paper.

By analyzing figure 1 and figure 2, a substantial intensification of the flammable gas formation in the case of Oil 1 sample in contact with Cu foil is noted. This result is explained by the catalytic activity of Cu and/or Cu₂O film.
formed by the reduction of the initial oxygen content in oil [20-22, 31, 43, 49-52]. However, an inhibition of flammable gas formation in contact with the insulating paper was observed, except for C2H4. This suggests that in the case of Oil 1, the insulating paper captures the chemical species that maintain the formation processes of flammable gases.

Figure 3 shows the evolution in time for content of each flammable gas in the second mineral oil (Oil 5) during thermal aging and figure 4 presents the evolution in time of the total content of the flammable gases.

By comparing figure 3 with figure 1, it is found that the two mineral oils behave similarly, with significant differences for the samples that are in contact with the insulating paper at which the formation of CH4 is about 4 times more intense in Oil 5 than in Oil 1. This determination suggests that in Oil 5 the formation process of SHMF and formic aldehyde (equation 4) is more intensive, which is also supported by the results of the comparative determinations of furan compounds [10] in such oils. For both investigated mineral oils, there is a pronounced catalytic effect of copper on the formation process of CH4 and C2H6. Thus, after 1000 h of treatment at 110°C in the presence of copper, there is an increase in C2H6 and CH4 amounts of about 8 times and 30 times, respectively, as compared with the samples of oils without copper. Under the simulation of operating conditions (simultaneous contact with both copper and insulating paper), the total gas emissions in Oil 5 were up to 15%, higher than in Oil 1.

A similar behavior of Oil 1 and Oil 5 in contact with copper was found, situation in which this increase being primarily due to gas releases after the contact with cellulose; the total amount of released gas in Oil 5 sample is approx. 15 times higher than in the case of Oil 1.

The evolutions in time of each flammable gas content for vegetable ester based oil Oil2 during thermal aging are represented in figure 5 and the evolution in time of the total amount of flammable gases is shown in figure 6.

Figure 6 shows that the formation of C2H6 is predominant during thermal aging of Oil 2. The catalytic effect of Cu upon the formation of CH4 and C2H6 is less pronounced than in the cases of mineral oils (fig. 1 and fig. 3). In the presence of copper, the emissions of CH4 increase about 2 times (as compared with 30 times for Oil 1 and Oil 5) and those of C2H6 increase with only approx. 30% (in comparison with 8 times for mineral oils). The trend of the curves in figure 6 and figure 7 suggests that the formation of gases in Oil 2 is the result of autocatalytic processes with an initiation period of approx. 700 h at 110°C.

From figure 6 it is found that at thermal aging of Oil 2 in contact with copper, after 1000 h of exposure the total amount of released gases is about 40% higher than in the absence of copper. Also, it is observed that in the presence of electro-insulating paper the amount of released gases is 30% higher than in the absence of it. By comparing these values with those from figure 2 and figure 4 it is noted that
both the influence of copper and influence of paper on the formation processes of flammable gases in Oil 2 is insignificant as compared with Oil 1 and Oil 5. Making a comparison of figure 6 with figures 2 and 4, it is observed that under the operating conditions (oil in contact with both copper and insulating paper), the total amount of flammable gases is more than 5 times less in Oil 2 than for mineral oils.

The evolution in time of each flammable gas for synthetic ester based oil Oil 3 during thermal aging is presented in figure 7 and the evolution in time of the total flammable gas content is shown in figure 8.

By analyzing figure 7, it is noticed that the formation of H₂ as a result of the thermal treatment applied to synthetic ester Oil 3 is predominant after an autocatalytic process, with an initiation period of about 700 h at the applied temperature (110°C). Also, it is observed that the process of H₂ formation is not remarkably influenced by copper or insulating paper. The presence of Cu foil during thermal treatment accelerates the processes of CH₄ and C₂H₄ formation (about twice) and does not influence the formation of C₂H₆. Moreover, the presence of insulating paper inhibits the formation processes of C₂H₄ (its amount formed after 1000 aging hours in contact with the paper is about 3 times lower than in the absence of it).

By comparing the data in figure 8 with those in figures 6, 4 and 2, it is found that after 1000 h of thermal treatment at 110°C of the synthetic ester Oil 3 in contact with both copper and insulating paper, the total amount of the formed flammable gases is about 7 times less than in Oil 2, about 37 times lower than in Oil 1 and about 41 times lower than in Oil 5.

The evolutions in time during the thermal aging of each flammable gas content for the sample with high oleic acid content, Oil 4, are presented in figure 9 and the evolution in time of the total flammable gas content is presented in figure 10.

From the data presented above in figure 9, it is found that the evolutions of the flammable gas formation during thermal aging of Oil 4 are similar with those reported in the case of Oil 3 (fig. 7). By comparison the figure 10 with figure 8 and figure 6 it is observed that after 1000 h of thermal treatment applied in conditions similar to those in operation (simultaneous contact with copper and insulating paper) the total amount of flammable gases formed in Oil 4 is about 40% higher than in synthetic ester Oil 3 and more than 4 times less than in the predominantly vegetable oil, Oil 2.

The risk of explosion of the transformer tank and the occurrence of devastating fires in the electric transformers are primarily determined by the formation of flammable gases as a result of aging [9, 43] under the synergic action of thermal and electrical stressors. Considering that under
specific operation conditions the transformer oils are in simultaneous contact with both electro-insulating paper and electrical-use copper, table 2 presents comparatively the total amount of flammable gases formed in the investigated oils after 1000 h of aging at 110 ± 3°C, in order to compare the risk of explosion and devastating fires (fig. 11 [53]) with all the environmental consequences [54-57].

By analyzing the data in table 2 it is observed that the both Oil 3 and Oil 4 are more safety in exploitation compared with the mineral oils (Oil 1 and Oil 5). Thus, it is noted that Oil 5 presents a substantially higher risk of explosion and fire than Oil 3 (up to 38 times) and Oil 4 (up to 24 times). The experimental data regarding the total amount of flammable gases formed by the thermal aging of the investigated transformer oils (figs. 4, 6, 8 and 10) indicate that the safety in operation of the transformers using synthetic oils (Oil 3) or vegetable esters (Oil 4) is over 5 times higher than in the case of Oil 2 and approx. 40 times higher than in the case of mineral oils (Oil 1 and Oil 5). All the natural esters (vegetable oils) are obtained from renewable resources by environment-friendly technologies, they are not toxic and biodegrade rapidly under natural conditions [14,15], do not form copper sulfide during exploitation [18-22], do not degrade / stabilize the insulating paper [10-13] and have a high flammability point [9, 29-31]. Taking these results into consideration, we can state that the traditional mineral oils can be replaced by natural esters (vegetable oils) for sustainable development and environmental protection. In this context, it is considered necessary that, through sustained environmental education [58-60], the manufacturers and the users of electrical equipments should stop the use of the traditional mineral oils in the favour of vegetable ones.

### Conclusions

The flammable gases formed by thermal aging of the transformer oils were determined quantitatively and qualitatively by gas chromatography after long-term storage (1000 h) at 110 ± 3°C in closed vessels (restricted to atmospheric oxygen) of five transformer oils. By comparing the results obtained for two mineral oils and for three ester based oils (one synthetic and two vegetal oils), the main conclusions are related to their behaviour in contact with copper foil and/or electrical insulating paper.

The total amount of gases formed if the oil is in contact with copper is about 10 times higher in mineral oils and about 2 times higher in ester oils than in the absence of copper. This suggests that during the thermal treatment, the metallic copper stimulates/catalyzes the processes of flammable gas formation. The catalytic effect of copper is more pronounced in CH₄ and C₂H₆ formation processes inside the mineral oils (the gas amount increases 8 times for C₂H₆ and 25 times for CH₄). The contact with insulating paper during the thermal treatment of ester based oils does not influence the formation of flammable gases, unlike mineral oil, Oil 5, in which the amount of gas formed is twice in the presence of paper. Under operating conditions (i.e. oil in simultaneous contact with copper and insulation paper), the total amount of flammable gases formed by
thermal aging is approx. 40 times higher in mineral oils than in ester based oils.

Based on the obtained experimental results, it is found that the risk of explosions and fires in a mineral transformer oil is more than 40 times higher than in the case of using ester based oil (synthetic or natural / vegetal).

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References

4. MATEI G., LINGVAY D., SPAFIU RC., TUDOSIE L.M., Electrotechnica, Electronica, Automatica, 61, no. 4, 2016, p. 52
5. DORIAN M., MITULET A., LINGVAY M., Electrotechnica, Electronica, Automatica, 61, no. 2, 2013, p. 58
7. OOMMEN T.V., Electrical Insulation Magazine, 1, no. 1, 2002, p. 6
8. LINGVAY I., BUDRUGEAC P., UDREA O., RADU E., MARINESCU M., Electrotechnica, Electronica, Automatica, 63, no. 1, 2015, p. 64
14. RADU E., UDREA O., MITREA S., PATROI D., LINGVAY I., Electrotechnica, Electronica, Automatica, 63, no. 4, 2015, p. 84
15. RADU E., UDREA O., LINGVAY M., SZATMARI I., LINGVAY I., Journal of Sustainable Energy, 6, no. 2, 2015, p. 52
17. MAINA R., TUMIATTI V., IEEE Transactions Dielectrics and Electrical Insulation, 16, no. 6, 2009, p. 1655
55. STERE E.A., POPA I., Electrotehnica, Electronica, Automatica (EEA), 65, no. 1, 2017, p. 102
56. NEAMTU, S., BORS, A.M., STEFAN, S., Rev. Chim. (Bucharest), 58, no. 9, 2007, p. 938
57. STERE E.A., POPA I., Electrotehnica, Electronica, Automatica (EEA), 65, no. 2, 2017, p. 163
59. OLLERER K., Calitatea Vietii, 23, no. 1, 2012, p. 25
60. OLLERER K., Journal of Integrative Environmental Sciences, 12, no. 3, 2015, p. 205

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