Studies on the Behavior Some Paints in Electro-insulating Fluid Based on Vegetable Esters

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For the purpose of using three different types of painting materials for the inner protection of the transformer vats, their behavior was studied under actual conditions of operation in the transformer (thermal stress in electro-insulating fluid based on the natural ester in contact with copper for electro-technical use and electro-insulating paper). By comparing determination of the content in furans products (HPLC technique) and gases formed (by gas-chromatography) in the electro-insulating fluid (natural ester with high oleic content) thermally aged at 130 °C to 1000 hours in closed glass vessels, it have been found that the presence the investigated painting materials lead to a change in the mechanism and kinetics of the thermo-oxidation processes. These changes are supported by oxygen dissolved in oil, what leads to decrease both to gases formation CO_2, CO, H_2, CH_4, C_2H_4 and C_2H_6) and furans products (5-HMF, 2-FOL, 2 -FAL and 2-ACF). The painting materials investigated during the heat treatment applied did not suffer any remarkable structural changes affecting their functionality in the electro-insulating fluid based on vegetable esters.

Keywords: painting materials, vegetable ester, transformer, thermal ageing, furfurals, oil gassing

With a view to sustainable development, the continued and secure supply of electric energy EE for human activities (both industrial and domestic) is a top priority. Continuous supply and at EE qualitative parameters imposed are determined by the safety in operation of the installations and equipment related to the EE production, transport and distribution systems. A series of electrical equipment from EE systems such as transformers, reactors, etc. uses electro-insulating fluids (*transformer oil*). The safety and durability of this equipment is caused by the degradation (ageing) of insulation systems due to the complex processes of interaction between the components of the vats (carbon steel protected by painting layers), electro-insulating fluid, electro insulating paper, copper conductors, etc.

Under the practical conditions of operation, under the synergic action of thermal and electric stress, complex interactions between the components of the system leads to a series of processes such as: degradation of electro-insulating paper [1-11], corrosion of metal components, especially copper, with the formation of the products of corrosion that substantially reduces the insulation resistance and dielectric rigidity of the electro-insulating fluid [12-19], the formation of furans products (toxic products determined and monitored by various techniques) [3, 8, 20-23], formation of the inert gases such as CO_2 as well as flammable as H_2, CH_4, C_2H_4, C_2H_6 etc. [24-34].

Several studies [2, 4, 13, 15, 17, 19, 30, 33] have highlighted that the copper components of the transformer after thermal oxidation form Cu_2O films with catalytic effect [35, 36] on the processes formation the gases by decomposing the electro-insulating fluid.

As a result of these processes, in extreme situations occurs explosions and incineration of electro-insulating fluid equipment [37-39] with serious consequences for the population [40, 41] by the pollution of the environment [42, 43] (soil, surface waters, groundwater, the air with gaseous harmful emissions, particulate matter and smoke etc.) and EE supply disruptions (consumers remain unpowered until remediation) as well as urban utilities subterranean distribution networks (underground power cables, PVC pipes, PE and corrosion protection of steel pipes are degraded [44-50].

These risks can be substantially reduced by providing adequate information and education [51-53] to high-risk equipment managers in exploitation and mobilizing them to implement the latest technical solutions developed in the field [8, 19, 39].

Electro-insulating fluids based on mineral oils [54] are traditionally used in electrical equipment, which, although having adequate dielectric and thermal performance at a relatively low price, presents a number of drawbacks to electro-insulating fluids based on vegetable esters (recently developed and tested [55-68]) such as: relatively low flammability point (up to 135 °C) - high fire risk [39], degradation of cellulose from electro-insulating paper with furans formation, very low biodegradability [69].

The painting materials used in the internal coating of the electric equipment housing/vats with electro-insulating fluid are exposed to degradation due to thermal stress and contact with the electro-insulating fluid and a dissolved gases therein.

Degradation/exfoliation of paint layers show a high risk to the safety of the equipment. The products of the degradation processes lead to decrease of the functional characteristics of the dielectric fluid. Due to their resistivity [70] much different from that of the electro-insulating fluid, the pieces of degraded paint, detached from the painted surfaces migrate through the electro-insulating fluid to the transformer coils where it produces the partial increase of

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the discharge, what leads the extreme to transformer failure. The degradation/ageing of painting materials under the influence of environmental factors (humidity, temperature, presence of oxygen, etc.) occurs through complex thermo-oxidation processes [71-77].

On the other hand, as in the case of magnetic nanoparticles [78, 79] (iron oxides), under the influence of thermal stress, the components of paints, mainly pigments (usually metallic oxides) can initiate/favour degradation processes of the electro-insulating fluid with the formation of gaseous products and/or furans products.

In view of these considerations, the purpose of the work is to study the behaviour of some painting materials exposed to specific thermal stresses in electric transformers, respectively in electro-insulating fluid based on natural esters in contact with electro-insulating paper and copper for electro-technical use.

Experimental part

In order to evaluate the compatibility of some painting materials (table 1) with electro-insulating fluid, 90 ± 10 μm sheets have been made by applying the paint to a teflon plate and the foils detachment after curing the material.

In order to evaluate the influence of the dyeing material (used for dyeing the transformer vats) on the complex processes occurs in the electro-insulating fluid in the transformer (obtained from a sunflower oil with high oleic content, having the density d_{20° = 0.925 kg/L *MF-UPMEE* [83]) the paint films have been exposed to aging by thermal storage in oil at 130 ± 3 °C.

Thermal treatment was carried out in a France Etuve type XL 980 thermostatic oven in closed containers (with limited access to atmospheric oxygen).

For comparison in parallel and under the same conditions have been thermally treated:

A. - 300 mL oil;
B. - 300 mL oil + 1 dm^2 paper + 1 dm^2 copper foil;
C. - 300 mL oil + 1 dm^2 paint film (PS-1 ÷ PS-3);
D. - 300 mL oil + 1 dm^2 paint film (PS-1 ÷ PS-3) + 1 dm^2 paper + 1 dm^2 copper film.

The Kraft electro-insulating paper used was Weidmann type 22 HCC, and the 30 μm thick copper film corresponds to [84].

Prior to and during the heat treatment, oil samples were extracted from each vessel and the content in CO_2, CO, H_2, CH_4, C_2H_4 and C_2H_6 have been determined by gas-chromatography (with a Perkin Elmer 600 Clarus gas-chromatograph, USA) and by liquid- chromatography (HPLC equipment 1100, produced by Shimadzu Corporation Kioto Japan) was determined the content of furans compounds.

Prior to the start of heat treatment and after 500 or 1000 hours of exposure, the image of the paint samples was visually analyzed (photographic catches).

Results and discussions

Pictures of the paint film samples before and after the thermal treatment applied are shown in figure 1.

Analyzing Figure 1 it is observed that after the thermal treatment in oil with copper foil and electro-insulating paper (similar to the conditions of transformers operation) the appearance of the ***PS-2*** and ***PS-3*** paint films has not changed, and ***PS-1*** has a slight color change tendency. No staining of the films during the applied thermal treatments was found in any of the paint types investigated.

The results of the liquid chromatographic determinations, respectively, of the contents of ***5-HMF***, ***2-FOL***, ***2-FAL*** and ***2-ACF*** in the oil samples exposed to closed containers (limited oxygen atmospheric access) at 130 °C (with and without contact with paints investigated and/or copper film and electro-insulating paper) are shown in figures 2-5.

Analyzing figure 2 it is noted that the ***5-HMF*** content of the oil samples with paint film, after 1000 h of thermal storage is lower than the reference (pure oil and oil with electro-insulating paper and copper film). It is noted that in the case of ***PS-1*** and ***PS-2*** in the first 500 h of treatment,

Table 1
INVESTIGATED PAINTING MATERIALS

Sample Cod	Commercial cod	Composition	Solvent
PS-1	AquaCover 200 [80]	Epoxy, polyamine hardener	Water
PS-2	Sigmaprime 200 [81]	Pure epoxy - bicomponent	Thinner 91-92
PS-3	Phenguard 930 [82]	Bicomponent, epoxy-novolac	Thinner 91-92

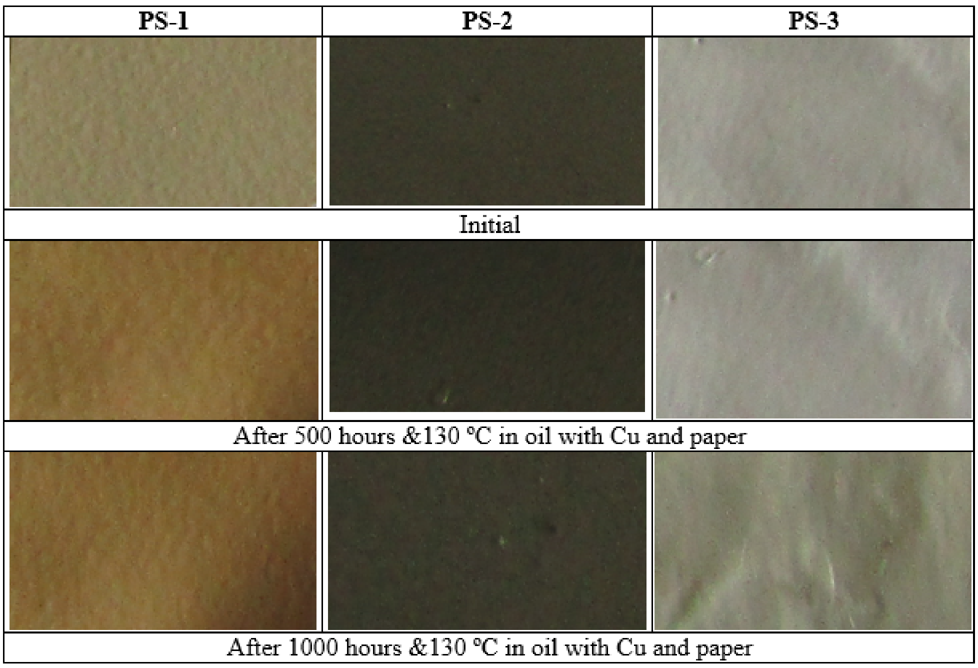

Fig.1. 1. Image of painting samples before and after applied thermal treatments in oil

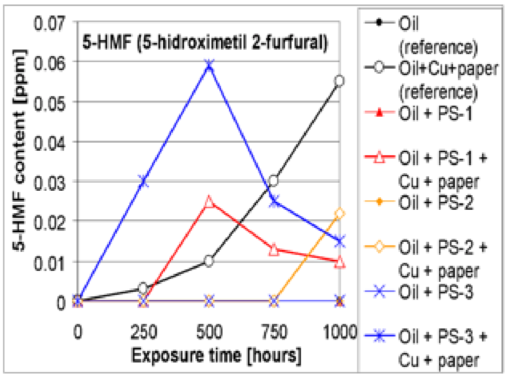

Fig.2. 5-HMF content evolution in the investigated oil samples

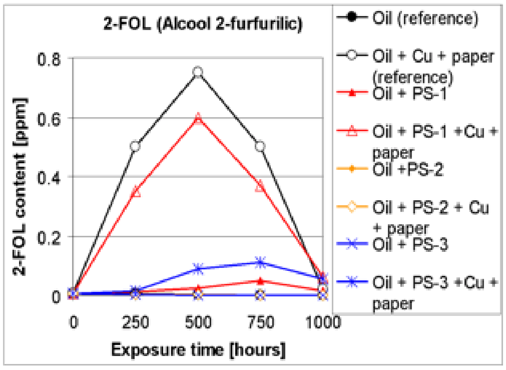

Fig.3. 2-FOL content evolution in the investigated oil samples

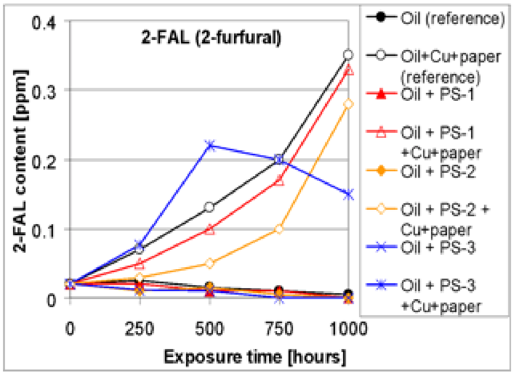

Fig.4. 2-FAL content evolution in the investigated oil samples

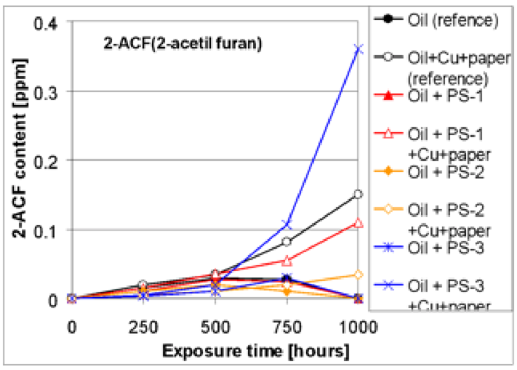

Fig.5. 2-ACF content evolution in the investigated oil samples

the exceedance of the reference values is recorded but only in the presence of copper and paper. It is noted that in all cases the presence of copper and paper leads to the formation of ***5-HMF*** much more intense than in the absence of these. It is also, noted that in the presence of ***PS-2***, ***5-HMF*** formation is insignificant, respectively null in pure oil, and in the presence of Cu and paper, ***5-HMF*** formation begins after 70 h of treatment reaching 0.02 ppm at 1000 h.

Analyzing figure 3, it is noted that 2-FOL formation is significantly increased in the first 500 h of thermal treatment reaching 0.75 ppm in the presence of Cu and paper (and 0.6 ppm at PS-1, Cu + paper), after which in all samples 2-FOL formation decreases below 0.08 ppm.

In figure 4 it is noted that 2-FAL formation is more intense only in the presence of copper and paper - the maximum value of 0.3 ppm being recorded in the oil + Cu + paper reference.

In figure 5 it is noted that the content of 2-ACF in all oil samples slowly increases during the first 500 h of thermal treatment, then in the samples without Cu and paper, it decreases (reaching 0 ppm per 1000 h) and in the samples with Cu and paper growth is pronounced (especially at PS-3 and less at PS-1). It is noted that, at over 500 h of treatment, the 2-ACF content into the oil with Cu and paper, exceeds the value recorded for the reference.

As can be seen from (fig. 2-5) the evolution of the furans products formation is different, situation in which - for the comparison of the compatibility of the investigated coating materials with the electro-insulating vegetable oil - it is considered adequate to analyze the evolution of the total furans content of the oil samples (fig.6).

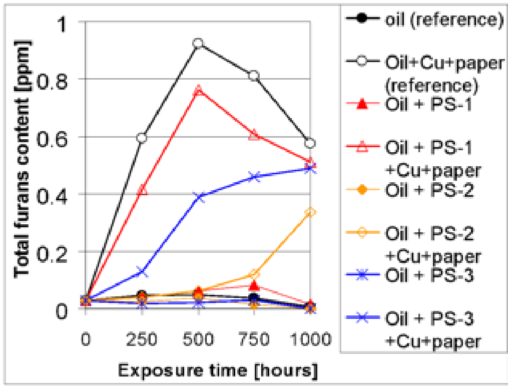

Fig.6. Total furans content evolution of investigated oil samples

Analyzing figure 6, it is noted that, after 1000 h of thermal treatment at 130 °C, the highest total content (approx. 0.6 ppm) in furans products was recorded in the sample case of oil + Cu + paper (no painting material) - values close to the reference value about 0.5 ppm) being obtained in the presence of ***PS-1*** and ***PS-3*** and a much lower value for ***PS-2*** (0.33 ppm). For samples of oil without Cu and paper, the content in furans products is insignificant - below 0.05 ppm.

The total content of furans products of all oil samples is systematically lower in the presence of paint films. This finding indicates that all three painting materials investigated are compatible with the electro-insulating fluid based on vegetable ester and that the formation of furans products is mainly determined by the presence of electro-insulating paper (cellulose) in the system. In figure 6 it is noted that the behavior of the ternary complex oil/ paint/ cellulose/Cu system is determined by the quality (type) of the paint material.

Thus, in the first 500 h of thermal treatment at 130 °C, the presence of ***PS-1*** leads to a significant increase in the furans content (up to about 0.75 ppm), after which, the content decreases at approx. 0.5 ppm at 1000 h of treatment.

In the presence of ***PS-2*** the increase of furans concentration in the oil is much slower, respectively at 750 h of treatment reaches only 0.12 ppm after which, an acceleration of the process is recorded and at 1000 hours it reaches 0.33 ppm. In the presence of ***PS-3*** there was a relatively rapid increase (up to 0.4 ppm furans products) in the first 500 h and at the continuation of thermal treatment

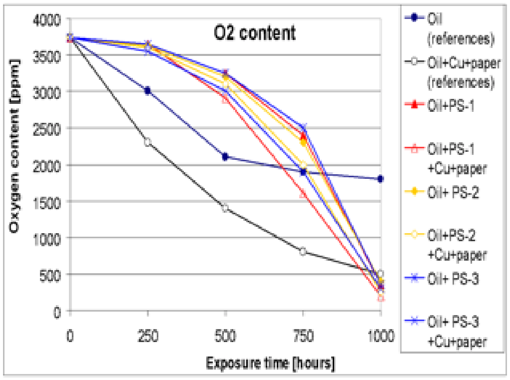

Fig.7. Oxygen content evolution of oil samples

it's recording a limitation trend reaching up to 0.5 ppm at 1000 h. All these observations and findings indicate that the presence of the investigated coating materials inhibits the formation of furans products.

The complex processes what occurs in the ternary complex oil/paint/cellulose/Cu system, in addition to the furans products formation, are accompanied by variations in the oil-dissolved gases content. Thermal treatment done in closed glass vessels (under conditions of limiting access to atmospheric oxygen in the system), following the thermo-oxidative processes of system components, the dissolved oxygen content in oil, decreases - as illustrated in figure 7.

Analyzing figure 7 it is found that in the absence of paint films (references) the decrease in dissolved oxygen content in the oil is exponential in contrast to the paint film samples when the decrease is polynomial.

This finding indicates that in the presence of the investigated paint materials, the mechanism and the kinetics of oxygen consuming processes change. It is also found that 1000 hours of thermal treatment at 130 °C in the presence of investigated paint materials dissolved oxygen in the initial oil (3740 ppm) is almost entirely consumed, respectively drops below 350 ppm. These finding suggest that dissolved oxygen in the oil is preferentially consumed by the investigated paint materials and thus inhibits the thermo-oxidation processes for Cu, oil and paper.

Under the action of thermal stress in the ternary complex oil/paint/cellulose/Cu system, in addition to the oxygen-consuming thermo-oxidation processes, occur a series of complex gases-forming processes such as CO_2 and CO (oxidation of organic components H_2, CH_4, C_2H_4, C_2H_6 etc. [24-34]. The results obtained by gas-chromatography on the investigated oils, respectively the evolution during the thermal treatment at 130°C of total content in în CO_2, CO, H_2, CH_4, C_2H_4 and C_2H_6 - are presented synthetically in figure 8.

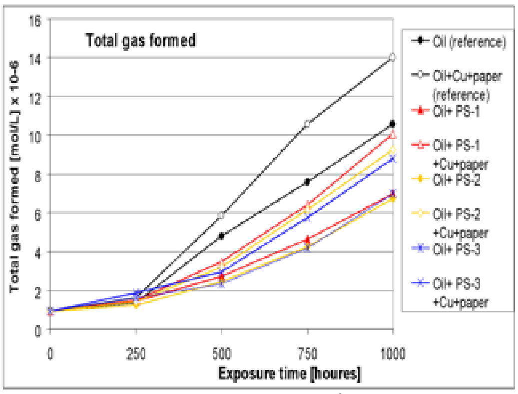

Fig.8. Total content evolution in gases formed in the oil samples

In figure 8 it is noted that in all cases the total gases content is higher in the thermally treated oil samples in contact with Cu and electro-insulating paper.

It is also, found that in all cases the presence of the investigated paint materials leads to the decrease of the total volume of formed gases. This finding, correlated with the observations in figure 6 and 7, suggests that at thermal stress of 130 °C, both furans formation and gases formation processes are largely determined by the oxygen dissolved in oil.

Conclusions

The behavior of three different commercial types of painting materials exposed to thermal stress at 130 °C under the specific conditions of electric transformers, respectively in electro-insulating fluid (based on vegetable oil) in the presence of Cu and electro-insulating paper, was investigated both by HPLC and gas chromatography technics and by observations comparative visuals (compared to reference systems).

After the comparative processing of the experimental data obtained, it was found that in the investigated coating materials presence, in thermal treated vegetable oil, both the formation of furans products (***5-HMF, 2-FOL, 2-FAL*** and ***2-ACF***) and of the gases (CO_2, CO, H_2, CH_4, C_2H_4 and C_2H_6) is inhibited.

It is also, been found that the presence of paint materials in vegetable oil/copper film/cellulose (electro-insulating paper) system changes the mechanism and kinetics of the thermo-oxidation processes with the participation of the dissolved oxygen in the system.

Visual observations have highlighted the fact that during the thermal treatments applied to the investigated coating materials, they did not suffer change - the only remarkable change consisting of a slight tendency to change color to ***PS-1***. In view of the above, it is considered that the investigated painting materials - from the point of view of the formation of furans and gases at temperatures up to 130 °C - are compatible with the natural ester-based electro-insulating fluid in the electrical applications (transformers) and can be used for the inner painting of electrical equipments with vegetable oil.

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