Comparative Studies on the Behaviour of Copper in Various Electrically Insulating Fluids

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This paper presents an exhaustive study regarding the behaviour of copper in various insulating fluids when exposed to 110^{0}C for 1000 hours in closed systems, with no access to atmospheric oxygen. Following the analysis carried out, it was found that the variation of oxygen concentration in the investigated oil samples, during the thermal treatment, may be best described using an exponential decrease versus time. Moreover, from the gas chromatography determinations with respect to the evolution of the CO and CO2 content in the oils during the thermal treatment one found out that these fit very well the Richards model, which corroborated with all the other analysis confirms the fact that the copper films undergo consistent morphological changes only when exposed to mineral oils, so that it is of paramount importance that, taking into account this aggressive character, the equipment placed in direct contact with these oils should be carefully inspected on a periodical basis. This behaviour is thought to be a direct consequence of the sulphur compounds contents for these oils, the secondary oxidation products of these compounds increasing their corrosive aggressiveness.

Keywords: copper corrosion, electrically insulating oils, carbon monoxide evolution, carbon dioxide evolution, Richards model

In the perspective of the sustainable development, the problem of safety in operation of electrical equipment, including those using electrically insulating fluids (oils), is of great complexity and importance.

The durability in operation of the electrical installations under voltage is determined, primarily, by the aging of the insulation systems that during operation, are exposed simultaneously to electrical, thermal, chemical stress, etc. [1].

The electrical insulating fluids used in electrical equipment (transformers, condensers, etc.) interact during operation with both atmospheric oxygen (thermal degradation processes [2 - 9]) and materials they are in contact with (copper, paper insulation and/or cotton etc.) that can corrode /degrade [8-11]. Various studies have highlighted that the corrosive aggressiveness of the electro-insulating mineral oils is due to their sulphur content [9-17]. The copper corrosion products, whether they dissolve in oil or form oil dispersed solids (sulphides) and /or deposit on paper or cotton insulations, reduce drastically the dielectric rigidity of the insulation system [9-20], which can lead to the damage of the transformer [21].

The electrical insulating fluids used in electrical equipments are traditionally based on mineral oils which, although they have a relatively low cost and proper performance (dielectric characteristics, fluidity), have the disadvantage of an appreciable sulphur content which makes them corrosive and difficult to biodegrade. On the other hand, in the case of some incidents (transformer damages), large amounts of mineral oil spread or ignite with a major negative impact on the environment [40, 41] by pollution with persistent organic pollutants [42, 43].

Various comparative studies have been reported to replace the mineral oils with synthetic esters based oils or with natural esters (vegetable oils) [2 - 7, 9 - 11, 22 - 27]. From these studies, as well as from [28-31], it results that the use of the vegetable oils (with or without antioxidant additives [28]) as an insulating fluid has a number of advantages as compared with mineral oils: higher thermo-oxidative stability, flammability point that is higher with about 100°C, rapid biodegradability, non-toxic-their production and use has no negative impact on the environment, etc.

The behaviour of copper in the insulating fluids is determined by a series of factors such as: temperature - thermal regime, sulphur and oxygen content of the fluid, etc.

From recent studies concerning the corrosion of copper and the influence of copper on the thermal stability of various electrically insulating fluids subjected to thermal aging by storage for 700 hat 110°C in open vessels (unlimited access to atmospheric oxygen), made by coupled techniques of thermal analysis (TG, DTA, DTG), XRF, SEM microscopy coupled with EDAX and gravimetric determinations [9, 10] it resulted, that the rate of the copper corrosion is largely determined by the sulphur content of the investigated oil and that the thermal stability of the investigated oils is significantly reduced in the presence of copper - which is probably due to the catalytic activity of the Cu_2O film which is able to form on the metal surface [32, 33]. Similar results have been also observed on electro-insulating fluids aged by repeated thermal cycles (917 cycles) between -40^{0}C and 80^{0}C [6, 11, 26].

In this context, the purpose of the present paper is to study the behaviour of copper in various insulating fluids, exposed at 110^{0}C for 1000 h in closed vessels (with no access to atmospheric oxygen).

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Experimental part

The behaviour of cooper in various electrically insulating fluids exposed to accelerated aging (110°C for 1000 h in closed vessels - without access to atmospheric oxygen) was studied experimentally.

The electro-insulating fluids were of 4 commercial types and a new/experimental product, 100% vegetable oil developed for electrical applications [34], respectively:

- sample O 1 - MOL TO30, mineral oil [35];
- sample O 2 - BIOTEMP, biodegradable oil (especially based on vegetable esters) [36];
- sample O3 - LUMINOL TRi, synthetic esters bases oil [37];
- sample O4 - P1MF-new product, 100% vegetable esters based oil [34];
- sample O5 - NYNAS-NytroTaurus, Standard-grade, mineral oil [38]

About 200 grams of investigated oil sample were placed in a Erlenmeyer flask with a ground glass joint and a glass stopper together with an electrolytic copper foil of 36 ± 4μm thickness and a surface area of 120 cm^2 and were subjected to thermal aging by storage at 110 ± 3°C for 1000 h, in a France Etuve XL 980 oven.

Before thermal storage and during the thermal treatment, in the oil samples investigated with a gas chromatograph Perkin Elmer type Clarus 600, both the content of oxygen and CO and CO$_2$ was determined. The initial sulphur content of the oil samples has also been determined by XRF technique with a Bruker - Germany (type TIGER S8).

The copper foil surface morphology (both initially and after exposure to investigated oils), was analyzed by SEM microscopy using INCA Energy 250 energy dispersive spectrometer (EDS) - Oxford Instruments belonging Auriga (Zeiss) field emission scanning electron microscope (FESEM) and by interferometric microscopy (with a WYKO NT1100h type device and related processing software produced by VEECO).

The copper foils were weighed before and after exposure with an analytical scale type AW220 from SHIMADZU Corporation (Japan). Degreasing and washing of the copper foils exposed to the thermal treatment in oil was performed with acetone, and drying was done at ambient temperature.

Results and discussions

The results of the XRF determinations indicated that the O1 and O5 mineral oil types contain 0.02% and 0.03% sulphur respectively For O2, O3 and O4 samples, the presence of sulphur was not distinguished because the content was below the detection limit of the equipment.

The representative SEM images of the initial copper foil (before exposure to thermal treatment in the investigated oils) are shown in figure 1. In figure 2, figure 3 and figure 4 the images of copper foils exposed to thermal treatment in O1, O4 and O5 oils respectively are presented. The

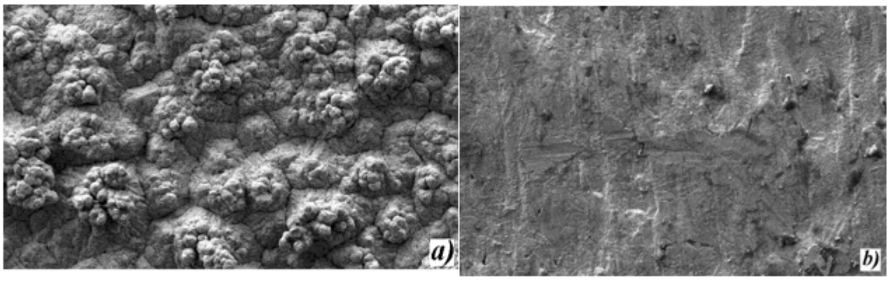


Fig. 1. Representative SEM x5000 images for the initial cooper foil: a) -matte side; b) - glossy side

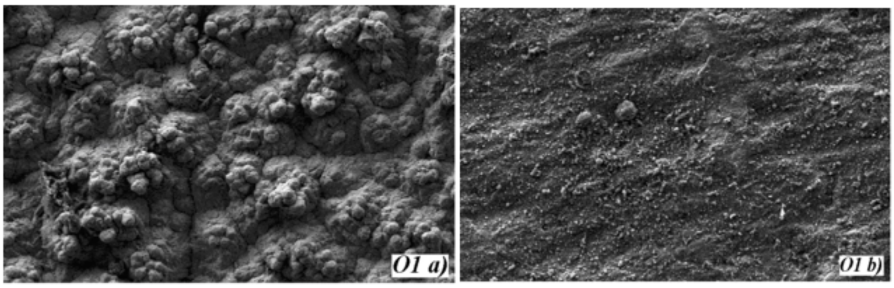


Fig. 2. Representative SEM x5000 images for the cooper foil exposed to the thermal treatment in O1: O1 a) - matte side; b) - glossy side

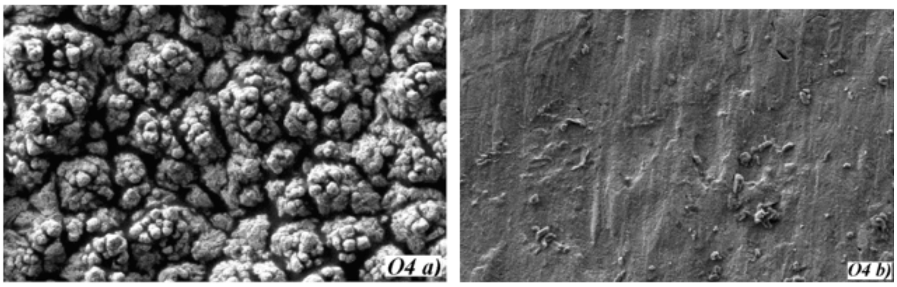


Fig. 3. Representative SEM x5000 images for the cooper foil exposed to the thermal treatment in O4: O4 a)-matte side; b) - glossy side

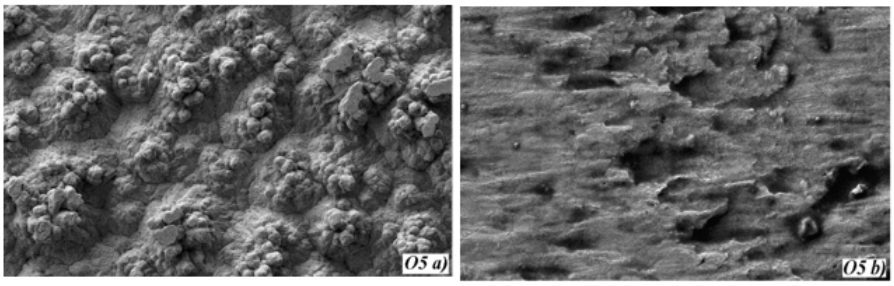


Fig. 4. Representative SEM x5000 images for the cooper foil exposed to the thermal treatment in O5: O5 a) - matte side; b) -glossy side

appearance of copper foils exposed to the thermal treatment in O2, O3 and O4 does not present morphological changes from the initial appearance (fig.1).

By comparative analyses of images presented in figure 1 with those in figure 2, figure 3 and figure 4 it is observed that during the thermal treatment of the copper foil, only the films exposed in mineral oils O1 and O5 suffer significant changes in morphology. Correlating this observation with the result of the XRF determinations concerning the sulphur content of the investigated oils, it is confirmed that the corrosive aggressiveness of the oils is determined by their sulphur content.

The results of the energy dispersive spectrometer (EDS) carried out in 10 points (catches) on each side of the copper foil, initially and after exposure to 1000 hours at 110°C in the investigated oils are summarized in table 1.

The analysis of the data in table 1 shows that the superficial layer (up to a depth of 0.5-0.9μm) of the initial copper foil does not contain sulphur in detectable amounts, but it contains 0.56% weight oxygen on the matte side and 0.49% weight oxygen on the glossy side (probably superficial oxide film as a result of the contact with air).

After an exposure for 1000 h at 110°C in the investigated oils, the surface of the copper foil changes and in all cases increases the oxygen content, and in the O1 and O5 mineral oils, sulphur products are formed (copper sulphide) - which are partially deposited on copper (more on the matte side) and partially dispersed in oil (with colour change to black and sludge formation, as reported for thermally treated oils [9-11, 26, 39]).

The aspect of the oil samples with copper foil is shown in figure 5, before and after exposure 1000 h at 110°C in closed vessels.

The results of the gravimetric determinations, respectively the initial and final mass of copper foils exposed in the investigated oils, are presented in table 2.

By analyzing data from table 2 it is found that the mass of the copper foils decreases in O1 and O5 mineral oils when exposed to the thermal treatment, which can be explained by the formation of copper sulphide that remains on the surface of the foil in small amount (table 1) and the most (black powder) is dispersed in oil (fig. 5), resulting in a decrease in the weight of the copper foil. Taking into account the sulphur content of O1 and O5, 0.02% and 0.03% respectively, considering the overall copper dissolution reaction (1):

$$Cu + S \rightarrow CuS \quad (1)$$

and performing a stoichiometric calculation for 200 g of oil samples, it is found that, during the applied thermal treatment, all the sulphur content of O1 and O2 was converted practically into copper sulphide.

The results of gas chromatographic determinations concerning the evolution during the thermal treatment of the dissolved oxygen content in the investigated oil with and without copper contact are shown in figure 6.

By analyzing figure 6 it is found that in all investigated oil samples, during the thermal treatment, the oxygen concentration decreases exponentially over time. The analytical equations describing the decrease in time t of the oxygen concentration C (t) [ppm] in the investigated oils obtained from figure 6 have the following form:

$$C_{(t)O_i} = a_i e^{-b_i t} \quad (2)$$

in which $C_{(tT)Qi}$ represents the evolution of the oxygen concentration in *i*, eg. $C_{(t)O1}$ in O1 and similarly $C_{(t)O2}$ in O2, $C_{(t)O3}$ in O3 etc.

From table 3 it can be observed that all the oil samples subjected to the evaluation show a time evolution of the oxygen concentration that can be modelled by a kinetic equation of the equation 2 type, the correlation coefficients of these equations being higher than 0.98 regardless of the tested sample or of the contact medium, with or without copper.

Table 1
THE RESULTS OF EDS DETERMINATIONS

Sample Cu foil		Average content [%]			
		Matte side		Glossy side	
		oxygen	sulphur	oxygen	sulphur
Initial (blank)		0.56	-	0.49	-
Exposed in :	O 1	3.26	1.49	1.67	0.79
	O 2	0.76	-	0.68	-
	O 3	2.96	-	1.31	-
	O 4	0.65	-	0.56	-
	O 5	4.55	1.66	4.02	0.92

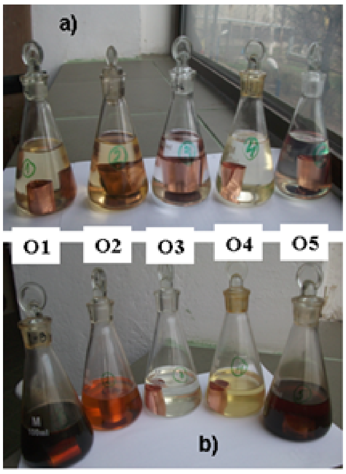


Fig. 5. The appearance of oil samples with copper foil, a) before and b) after exposure to thermal treatment

Table 2
THE EVOLUTION OF THE GAS CONTENT IN OIL 3

Oil sample	The mass of the cooper foil[g]		Δm
	Initial	After 1000 hours to110^{0}C	[g]
O 1	4.4812	4.4017	–0.0795
O 2	4.5841	4.5860	0.0019
O 3	4.3539	4.3578	0.0039
O 4	4.5370	4.5395	0.0025
O 5	4.4515	4.3361	–0.1154

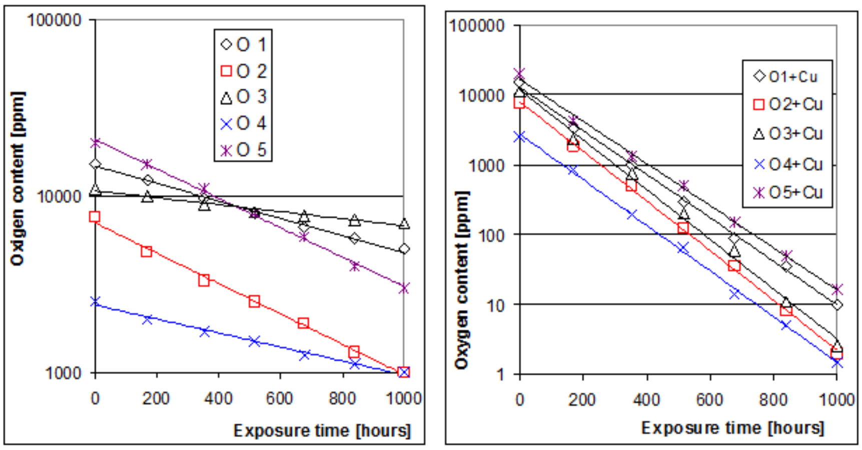


Fig. 6. Evolution of the dissolved oxygen content in the investigated oils with and without copper contact

Table 3
THE VALUES a_i AND b_i FOR O1 – O5

Oil sample	Without cooper			In contact with cooper		
	$a_i \cdot 10^{-4}$	$b_i \cdot 10^3$	Correlation coefficient, r	$a_i \cdot 10^{-4}$	$b_i \cdot 10^3$	Correlation coefficient, r
O 1	1.464	1.1	0.997	1.274	7.2	0.999
O 2	0.709	2.0	0.998	0.798	8.2	0.997
O 3	1.068	0.5	0.986	1.170	8.2	0.997
O 4	0.240	0.9	0.995	0.278	7.5	0.999
O 5	2.078	1.9	0.999	1.669	6.9	0.999

By analyzing figure 6 it is found that during the applied thermal treatment, the oxygen in the oils in contact with copper is consumed almost entirely and in the absence of copper the oxygen is consumed only partially. This ascertainment can be explained by the fact that the oxygen consumption can be both due to both some oxidation processes of the investigated oils with the formation of peroxide products [2, 6, 9, 31] and / or CO_2 and CO and due to the oxidation processes of the cooper foil by the reactions:

$$4Cu + O_2 \rightarrow 2\,Cu_2O \quad (3)$$

$$2\,Cu_2O + O_2 \rightarrow 4\,CuO \quad (4)$$

The colour of the copper foils did not change during the thermal treatment in the investigated oils, suggesting that the probability of the process (4) is small. The formation of the superficial oxide film on the copper foil is supported by the increase in oxygen content of the Cu film surface (table 1) and by the increase of the mass of cooper foils immersed in the O2, O3 and O4 samples (table 3) during the thermal treatment.

The results of gas chromatographic determinations on the evolution of the CO and CO2 content in the investigated oils during the thermal treatment were processed by modelling with both a predefined relation f_1 (x) (5) in MATLAB and a relation f_2 (x) - Richards model (6):

$$f_1(x) = \alpha \cdot exp(\beta \cdot x) + \gamma \cdot exp(\delta \cdot x) \quad (5)$$

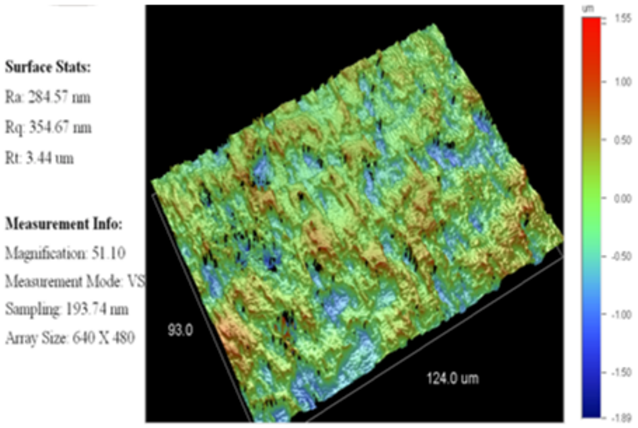
$$f_2(x) = \frac{a}{(1+exp(b-c \cdot x))^{(1/d)}} \quad (6)$$

Table 4
THE MODELLING OF THE EVOLUTION OF CO FORMATION IN THE INVESTIGATED OILS

Sample		*$f_1(x)$ – MATLAB predefined function*					*$f_2(x)$ – model Richards*				
		α	β	γ	δ	Err	a	b	c	d	Err
O 1	Without Cu	$-2.39 \cdot 10^6$	$2.8 \cdot 10^{-4}$	$24 \cdot 10^5$	$2.9 \cdot 10^{-4}$	371	302.83	0.601	$32 \cdot 10^{-4}$	0.284	137
	With Cu	$-1.16 \cdot 10^6$	$39 \cdot 10^{-4}$	$116 \cdot 10^5$	$40 \cdot 10^{-4}$	1425	342.6	-7.177	$27 \cdot 10^{-4}$	$2.3 \cdot 10^{-4}$	233.7
O 2	Without Cu	70.22	$2 \cdot 10^{-4}$	-69.16	$-90 \cdot 10^{-4}$	6.41	83.2	33	0.183	7.47	186
	With Cu	131.7	$1.5 \cdot 10^{-4}$	-130	$-48 \cdot 10^{-4}$	59.57	143.2	22.94	0.057	13.84	423.6
O 3	Without Cu	20.83	$1.4 \cdot 10^{-4}$	-20.33	$-53 \cdot 10^{-4}$	0.07	22	53.66	0.275	14.18	16.5
	With Cu	27.32	$1.1 \cdot 10^{-4}$	-26.66	$-28 \cdot 10^{-4}$	1.21	28.93	-7.397	$48 \cdot 10^{-4}$	$2.5 \cdot 10^{-4}$	10.35
O 4	Without Cu	16.97	$5.2 \cdot 10^{-4}$	0	$5.2 \cdot 10^{-4}$	493.3	35.95	-6.699	$42 \cdot 10^{-4}$	$3.8 \cdot 10^{-4}$	0.93
	With Cu	$3.76 \cdot 10^6$	$-6.6 \cdot 10^{-4}$	$-376 \cdot 10^4$	$-6.6 \cdot 10^{-4}$	21.52	56.77	-7.391	$44 \cdot 10^{-4}$	$1.9 \cdot 10^{-4}$	6.47
O 5	Without Cu	-	-	-	-	-	335.9	-4.739	$25 \cdot 10^{-4}$	$35 \cdot 10^{-4}$	1266
	With Cu	182.2	$50 \cdot 10^{-4}$	0	$50 \cdot 10^{-4}$	$784 \cdot 10^2$	352.8	-4.331	$33 \cdot 10^{-4}$	$44 \cdot 10^{-4}$	638.4

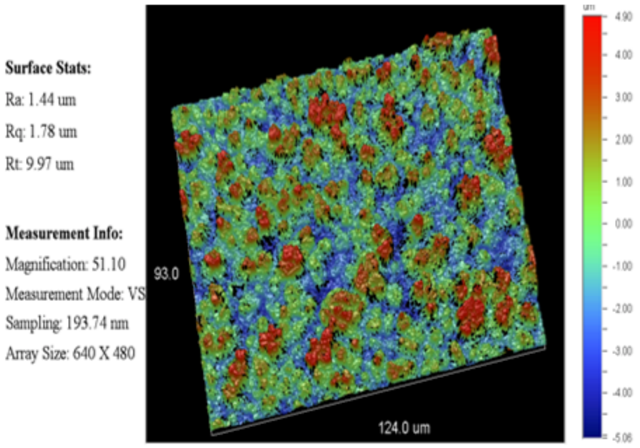
Table 5
THE MODELLING OF THE EVOLUTION OF CO FORMATION IN THE INVESTIGATED OILS

Sample		*$f_1(x)$ – MATLAB predefined function*					*$f_2(x)$ – model Richards*				
		α	β	γ	δ	Err	a	b	c	d	Err
O 1	Without Cu	$1.37 \cdot 10^9$	$-120 \cdot 10^{-3}$	13.09	$2.6 \cdot 10^{-3}$	5.902	3054	4.057	$2.25 \cdot 10^{-3}$	0.782	11.64
	With Cu	$-2.18 \cdot 10^4$	$2 \cdot 10^{-3}$	$2.18 \cdot 10^4$	$2.0 \cdot 10^{-3}$	41.34	5678	3.399	$1.74 \cdot 10^{-3}$	0.587	41.12
O 2	Without Cu	-	-	-	-	-	382.14	-15	$494 \cdot 10^{-3}$	$1.69 \cdot 10^{-7}$	3945
	With Cu	-	-	-	-	-	442.8	-1.604	$1.70 \cdot 10^{-3}$	0.072	398.4
O 3	Without Cu	-	-	-	-	-	158.4	24.83	$9.46 \cdot 10^{-3}$	7.854	21.9
	With Cu	11.36	$2.13 \cdot 10^{-6}$	0.975	$2.9 \cdot 10^{-3}$	0.052	160.25	25.79	$10.18 \cdot 10^{-3}$	9.065	8.2
O 4	Without Cu	-	-	-	-	-	90.68	10.4	$13.34 \cdot 10^{-3}$	3.475	52.04
	With Cu	$-1.86 \cdot 10^4$	$4.44 \cdot 10^{-3}$	$-1.85 \cdot 10^4$	$4.4 \cdot 10^{-3}$	144	172.9	8.006	$14.51 \cdot 10^{-3}$	2.108	35.64
O 5	Without Cu	$-3.06 \cdot 10^5$	$7.2 \cdot 10^{-4}$	$30,6 \cdot 10^4$	$0.7 \cdot 10^{-3}$	325	307	3.25	$3.84 \cdot 10^{-3}$	1.291	221.3
	With Cu	$-1.45 \cdot 10^5$	$3.5 \cdot 10^{-4}$	$14.51 \cdot 10^4$	$0.3 \cdot 10^{-3}$	673.4	325.1	3.721	$5.38 \cdot 10^{-3}$	1.479	66.12


Surface Stats:
Ra: 284.57 nm
Rq: 354.67 nm
Rt: 3.44 um

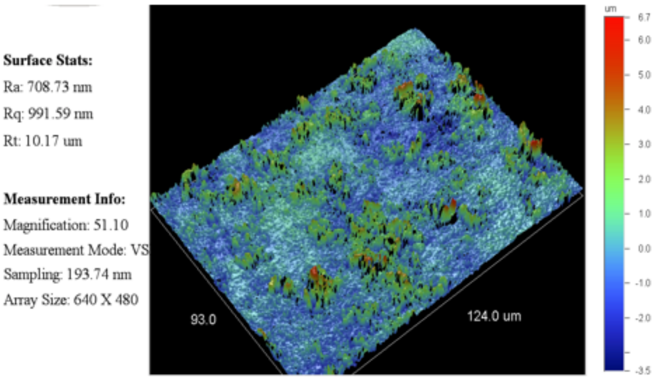
Measurement Info:
Magnification: 51.10
Measurement Mode: VS
Sampling: 193.74 nm
Array Size: 640 X 480

Fig.7. The roughness profile of the initial copper foil, the glossy side


Surface Stats:
Ra: 1.44 um
Rq: 1.78 um
Rt: 9.97 um

Measurement Info:
Magnification: 51.10
Measurement Mode: VS
Sampling: 193.74 nm
Array Size: 640 X 480

Fig.8. The roughness profile of the initial copper foil, the matte side


Surface Stats:
Ra: 708.73 nm
Rq: 991.59 nm
Rt: 10.17 um

Measurement Info:
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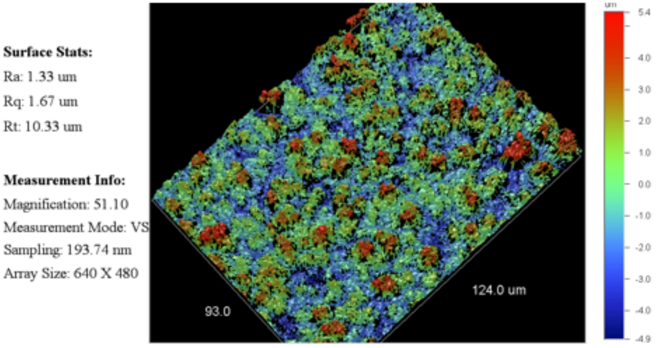
Measurement Mode: VS
Sampling: 193.74 nm
Array Size: 640 X 480

Fig.9. The roughness profile of the copper foil exposed to the thermal treatment in O5, the glossy side


Surface Stats:
Ra: 1.33 um
Rq: 1.67 um
Rt: 10.33 um

Measurement Info:
Magnification: 51.10
Measurement Mode: VS
Sampling: 193.74 nm
Array Size: 640 X 480

Fig. 10. The roughness profile of the copper foil exposed to treatment in O 5, matte side

Table 6

THE AVERAGE RESULTS OF THE INTERFEROMETRIC MICROSCOPY DETERMINATIONS

Sample of Cu foil		Glossy side						Matte side					
		R_a[µm]	Δ_{Ra}[µm]	R_q[µm]	Δ_{Rq}[µm]	R_t[µm]	Δ_{Rt}[µm]	R_a[µm]	Δ_{Ra}[µm]	R_q[µm]	Δ_{Rq}	R_t[µm]	Δ_{Rt}[µm]
initial		0.282	–	0.350	–	3.41	–	1.45	–	1.79	–	10.51	–
Exposed in:	O 1	0.360	0.078	0.424	0.026	4.3	0.89	1.36	–0.09	1.66	–0.13	10.32	–0,19
	O 2	0.275	–0.007	0.345	–0.005	3.35	–0.06	1.42	–0.03	1.75	–0.04	10.48	–0.03
	O 3	0.278	–0.004	0.347	–0.003	3.37	–0.04	1.41	–0.04	1.77	–0.03	10.50	–0.01
	O 4	0.280	–0.002	0.348	–0.002	3.39	–0.02	1.43	–0.02	1.78	–0.02	10.49	–0.02
	O 5	0.696	0.414	0.807	0.457	9.93	6.52	1.32	–0.13	1.64	–0.15	10.29	–0.22

The results of the modelling for the evolution of CO and CO_2 formation during the applied thermal treatment are summarized in table 4 and table 5 respectively.

From the analysis of the data in table 4 and table 5, it is observed that in the case of the evolution of carbon monoxide and carbon dioxide formation, the best results are obtained using the equations (5) and (6). If in the case of carbon monoxide the experimental data satisfy both equation (5) and (6), in the case of carbon dioxide, only equation (6), the Richards model, represents satisfactory from mathematical point of view the modelling of the evolution of CO_2 formation in the investigated oils.

Figure 7 and figure 8 are representative images obtained by interferometric microscopy on the initial copper foil, respectively the exposed foil to the thermal treatment in O5 in figure 9 and figure 10.

In table 6 the average results obtained from the interferometric microscopy measurement of five unitary areas are presented.

By analyzing the data in table 6, it is noted that the average roughness of Ra (the arithmetic mean of the deviation from the average profile over the entire measured area) suffers remarkable increases on the glossy face of the treated copper foils in O1 of 0.078 ìm and in O5 of 0.414µm, changes that can also be observed by comparing the image in figure 1. with those in figure 2 and figure 4 respectively. This roughening of the glossy surface of the copper foil suggests that as CuS particles grow, the copper corrosion below them is blocked (fig. 2 - O1b), and after the CuS particles reach a critical dimension, they detach from the surface making possible the dissolution of a new amount of copper (fig. 4 - O5b), the process being carried out with a certain cyclicality. This mechanism is also applicable to the processes occurring on the matte surface of the copper foils and explains the decrease in roughness on the matte surface of the copper foils exposed in O1 and O5. The growth and detachment of CuS occurs faster on peaks and as a result the peaks corrode more rapidly, becoming smooth. The low corrosion rate is also a direct consequence of the non-ionic nature of the medium (oil).

Conclusions

After testing the copper behaviour in various electrically insulating fluids exposed at 110°C for 1000 h in closed vessels (without access to atmospheric oxygen) there is a strong evidence that copper films undergo consistent morphological changes only when exposed to mineral oils O1 and O5, which may be considered with a more aggressive character, and equipment in direct contact with these oils should be inspected more often. This phenomenon is a direct consequence of the sulphur compounds contents for these oils, the secondary oxidation products of these compounds increasing their corrosive aggressiveness.

The evolution of carbon monoxide and carbon dioxide formation in time can be modelled satisfactory from mathematical point of view, the Richards model showing the best results both for modelling the evolution of CO_2 and CO in the investigated oils.

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