Thermal Ageing of Some Insulating Fluids in Contact with Insulation Paper and Copper

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

[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, 49A Theodor Pallady Blvd., 032258, Bucharest, Romania

The behaviour of copper and insulation paper in various electrical insulating fluids (transformer oils) exposed to thermal ageing at 110±3°C for 1000 hours in closed vessels (without access to atmospheric oxygen) has been studied. The processing of the comparative experimental data revealed in all cases that the concentration of dissolved oxygen in the investigated oils decreases exponentially during the heat treatment. In the presence of the copper foil, the oxygen is almost depleted (the dissolved oxygen concentration is approaching zero), indicating a higher affinity of the copper to oxygen than the affinity to oxygen of the investigated oils. In the presence of the copper foil and / or of the insulation paper, the degradation processes of the mineral oils have a pronounced character, explained by the catalytic activity of the Cu_2O film that has been formed and by the paper degradation, respectively. A high thermo-oxidative stability was noticed in the case of natural triglyceride oils, particularly for the synthetic ester-based oil.

Keywords: insulating fluids, mineral oils, vegetal oils, synthetic esters, thermo-oxidative ageing, copper, insulation paper

The issue of providing safe, uninterrupted electricity is a priority for sustainable development, the safe operation of electrical equipment being of significant complexity and importance. Sustainability in operating electrical equipment is primarily determined by the ageing of the insulation systems which are exposed during operation to the synergistic action of electrical, thermal, chemical stress, etc.

Within the electrical power transformers, the elements made of copper with or without insulation paper are in contact with the insulating fluid (transformer oil). Under practical operating conditions, both copper elements and insulation paper in transformers interact with the transformer oil. Therefore, as a result of the action of transformer oil, copper can oxidize and / or corrode. During these complex chemical processes the reaction products are deposited on the elements of copper and paper insulation and / or are dispersed in the transformer oil, thus reducing both the energy efficiency of the transformer (an increase in dielectric losses) and the safe operation of the equipment [1]. Recent studies have shown that the corrosive aggressiveness of transformer oils is primarily determined by their sulphur content [1-8]. On the other hand, several studies have shown that under the action of thermal stress, mineral origin transformer oils into contact with the cellulose within insulation paper leads to the degradation of the oil (cracking processes with gas formation) and obviously of the paper [9-13]. Also, some recent studies highlighted the energetic benefits of using insulating oil in suspension with ferromagnetic fluids [14-17]; the reaction products of mineral oil with insulation paper may affect in this case the stability of the magnetic nanoparticles suspension.

Under the influence of thermal stress, transformer oils suffer thermo-oxidative processes with the dissolved oxygen from the oil or with the oxygen from the air the oil is in contact with; these processes lead to the degradation of their functional parameters [7, 12, 18-23]. It has been experimentally shown that the thermo-oxidative degradation of the oils increases their corrosiveness [24].

Compared to silicone oils and synthetic esters, mineral oils show a cost/performance ratio particularly favourable, which makes mineral oils to be widely used in transformers. The major disadvantage of the mineral oils consists in their high degradation rate [25-28]. The experimental results of several recent comparative studies revealed that, in the most electrical engineering applications – including transformers, some vegetable oils (easily and quickly biodegradable) can successfully replace the mineral oils [7-9, 11-13, 18-20, 25-28].

Given the above mentioned considerations, the purpose of this paper consists in the comparative study of heat degradation undergone by various insulating oils in the presence and absence of copper and / or insulation paper.

Experimental part

The origin and type of the investigated oils, as well as the encoding of the samples is shown in table 1.

Approximately 200 grams of oil sample under investigation were placed in Erlenmeyer flasks with ground glass joint and glass stopper. Also, 1.2 dm^2 of electrolytic copper foil with a thickness of 36 ± 4μm and / or approx. 1dm^2 of insulation paper (kraft type, in accordance with IEC 60641-1 / 2007) were introduced in oil and were exposed to thermal ageing by storage at 110±3° for 1000 hours in an ageing-oven *France Etuve 980 XL* type (fig. 1).

In order to evaluate the oxidative degradation undergone by the oil and/or by the copper foil and insulation paper respectively, during the heat treatment the concentration of dissolved oxygen in oil was monitored with a gas chromatograph manufactured by Perkin Elmer 600 CLARUS (US). Also, the appearance of the copper foil was observed with a standard microscope MM-KKE-M-C-U provided by HYDAC FILTER SYSTEMS GmbH, Germany. Before and after the storage for 1000 h at 110±3°C, the

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

Fig.1. Oil samples and their exposure to thermal ageing

Table 1
INVESTIGATED SAMPLES OF INSULATING OIL

Probe code	Oil type	Oil origin
O1	Mineral	MOL TO-30.01R [29]
O2	Vegetal ester	Biotemp® [30]
O3	Synthetic ester	LUMINOL [31]
O4	Vegetal ester	MF-UPMEE; P1MF [32]
O5	Mineral	Nynas [33]

colour of the oil samples was quantified by determining the iodine value (according to [34, 35]).

Results and discussions

The variations in oxygen concentrations of the investigated oils during the heat treatment are shown in figures 2-6. The probe codes are listed in table 1.

By performing a comparative analysis of figures 2-6 it is ascertained that for the solubility of gaseous oxygen, namely its initial concentration in the O1 and O5 mineral oils is relatively high, respectively of over 16000ppm, unlike for the case of the synthetic ester O3 (approx. 11000ppm) and of the vegetable oils O2 and O4 for which the oxygen solubility is relatively low (7500ppm and 2500ppm, respectively). The very low concentration of oxygen in O4 sample may be due to the antioxidant additive content of

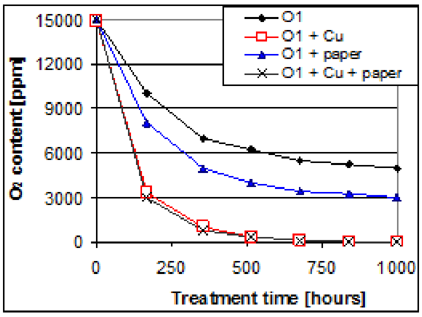


Fig. 2. The variation of dissolved oxygen in the O1 oil during the heat treatment

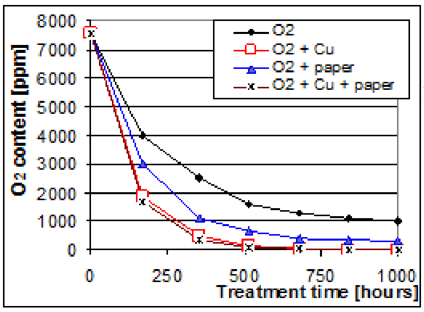


Fig. 3. The variation of dissolved oxygen in the O2 oil during the heat treatment

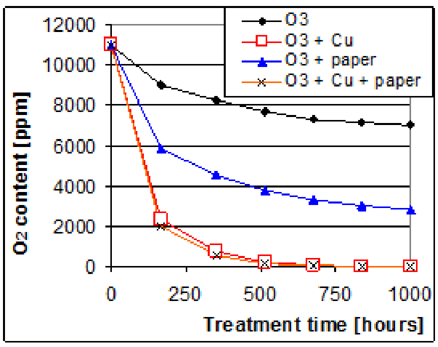


Fig. 4. The variation of dissolved oxygen in the O3 oil during the heat treatment

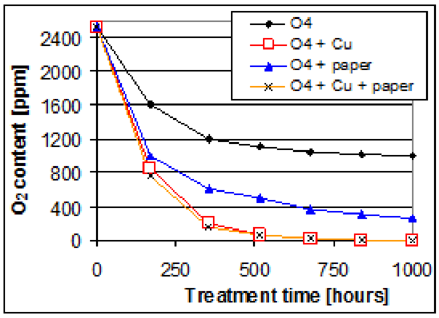


Fig. 5. The variation of dissolved oxygen in the O4 oil during the heat treatment

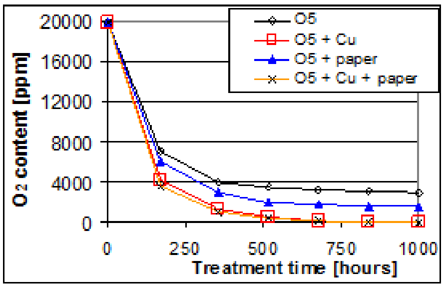


Fig. 6. The variation of dissolved oxygen in the O5 oil during the heat treatment

this oil [32]. It is also observed that, in all cases, the concentration of oxygen in the investigated oils under the test conditions (heat treatment in closed containers) decreases in time (almost exponentially). This ascertainment indicates that the free oxygen in the oil is consumed during the heat treatment. In the given experimental conditions, the consumption of dissolved oxygen in oil can occur through the following reactions:

a) oxidation of unsaturated bonds with formation of peroxides and/or volatile products [18-21];

b) oxidation of copper foil with formation of Cu_2O and CuO oxides [5, 7, 8];

c) oxidation of oil as well as of the cellulose in the insulation paper [10, 18-21].

Changes in the colour of the investigated oils after the applied heat treatment, as an indicator of the oxidative processes undergone by the oils, are summarized in table 2.

By analyzing the data in table 2 it results that the most significant changes in colour were registered for the oils O1 and O5, indicating that their thermo-oxidative stability is minimal. Also, it is noted that the highest changes in colour, perceived visually (fig. 7) were registered for the oils in contact with copper foil; this finding may be explained by the catalytic activity of Cu_2O on the degradation processes of mineral oils.

The comparative analysis of figures 2-6 reveals that in the presence of the copper foil the oxygen dissolved in the investigated oils is almost entirely consumed. In conjunction with the data in table 2, this behaviour can be explained by the formation (in a first step) of a film of cuprous oxide Cu_2O [5] with known catalytic effect [36,

Table 2
IODINE COLOUR OF OIL SAMPLES COLOUR BEFORE AND AFTER EXPOSURE FOR 1000 HOURS TO $110^0 \pm 3^0$C WITH AND WITHOUT CONTACT WITH COPPER FOIL AND INSULATION PAPER RESPECTIVELY

Oil sample	Iodine colour [mg.iodine/100cm^3]				
	initial	After heat treatment in contact with:			
		without	Cu foil	paper	Cu+paper
O1	10	16	26x3 =**78**	24	22x4=**88**
O2	14	18	22x2=**44**	18	15x3=**45**
O3	10	10	11	10	11
O4	11	12	18	12	20
O5	10	22	30x3=**90**	30	24x4=**96**

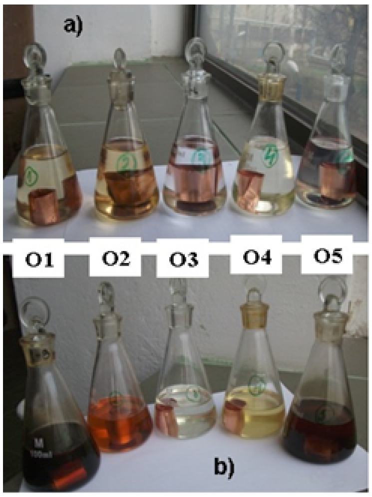


Fig. 7. Photo of oil samples colour: a) - initial appearance; b) - appearance after 1000 hours of treatment at $110^0 \pm 3^0$C in contact with copper foil

37]; most likely, it catalyzes the addition of oxygen to the unsaturated bonds in the structure of the oil [7]. In the case of vegetable oils, has been demonstrated the catalytic activity of copper traces on the decomposition of peroxide products [38, 39] formed by oxidation of the double bonds in esterified fatty acids (especially linoleic and linolenic acids [40]).

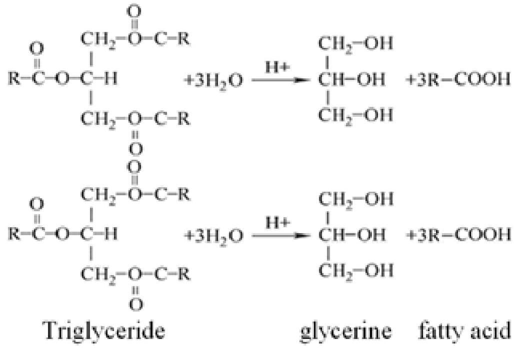
By comparing figure 2 and figure 6 showing the behaviour of mineral oils, it results that during the 1000 hours heat treatment in the absence of the copper foil and/or insulation paper, the dissolved oxygen content in O5 oil decreases about 7 times, as compared to the O1 oil for which the decrease is about 3.5 times, indicating an affinity for oxygen of approximately 2 times higher for O5 than for O1. This ascertainment is in agreement with the data in table 2, namely the change in colour for O5 oil from 10 to 22 and for O1 oil from 10 to 16 respectively.

By comparing figure 3 and figure 5 it results that in the cases of O2 oil (mainly vegetable oil) and O4 oil (99.5% vegetable oil and 0.5% antioxidant), the affinity of oxygen for O2 oil in the absence of copper foil/insulation paper is approximately 3 times bigger than for O4 oil. This observation is in agreement with the changes in colour occurred during the heat treatment, i.e. a change from 14 to 18 for O2 oil and from 11 to 12 for O4 oil.

By analyzing figure 4 it is found a low affinity of oxygen for O3 oil (the decrease of the oxygen content being of only 0.4 times), determining no changes in colour for O3 oil during the heat treatment, in the absence of copper foil and/or insulation paper.

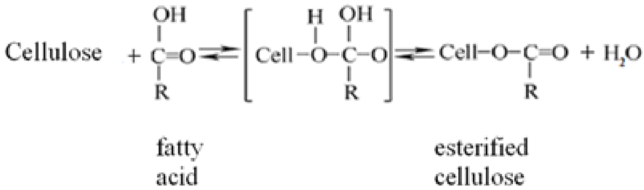
The behaviour of the insulation paper into the investigated oils is varying with the oil type. Thus, into the mineral oils O1 and O5, the insulation paper accelerates the thermo-oxidative degradation of the oil. This can be explained by the fact that the oxidation products, under the action of the moisture from the oil and the water formed in the complex processes of the mineral oil oxidation, opens the pores of the paper and degrades the cellulose by hydrolysis and oxidation. These processes that generate gases, especially CO and CO_2 as well as water, leading to an acceleration of the degradation of paper [41, 42] and oil; this is also supported by figure 2 and figure 6 and by the data in table 2. When exposing the insulation paper in oil-based esters, the processes are fundamentally different. Thus, in the case of vegetable oil which contains the triglycerides of the fatty acids [11, 20, 43] these can hydrolyze with the water present in traces, forming glycerol and fatty acids [11] according to eq. (1):

Further, the fatty acids formed in the process (1) react with the cellulose and, by an esterification process, a



(1)

relatively stable product is formed, namely esterified cellulose [11], as eq. (2) shows:



This behaviour can explain the fact that, during the applied heat treatment, the oils O2, O3 and O4 in contact only with the insulation paper and do not change their colour.

The appearance of the copper foil prior to the heat treatment in the investigated oils is shown in figure 8. We noticed that the appearance of the exposed copper foils in the oils O2, O3 and O4 has not changed. However, a significant change was also for exposed copper in O5 oil. A representative image of the copper foil appearance exposed for 1000 h at 110±30°C in the oil O5 is shown in figure 9.

Through a comparative analysis of figure 8 and figure 9 it is found that the mineral oil O5 interacts with the copper foil during the heat treatment and forms dark spots on the foil's surface, which can be explained by the sulphur content of the investigated mineral oils and the formation during heat treatment of the copper sulphide [5, 7, 8, 44]. It is to be noticed that, besides the layer of copper sulphur from the foil's surface, it is also formed some powder of copper sulphur, which is dispersed within the oil, reducing significantly the insulation level of the oil/paper system.

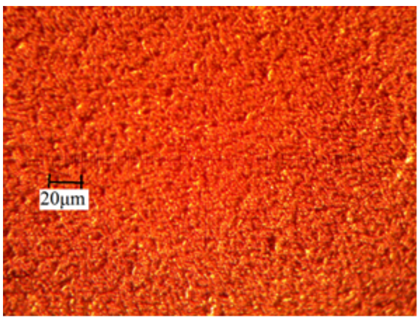


Fig. 8. The appearance of the copper foil prior to the heat treatment

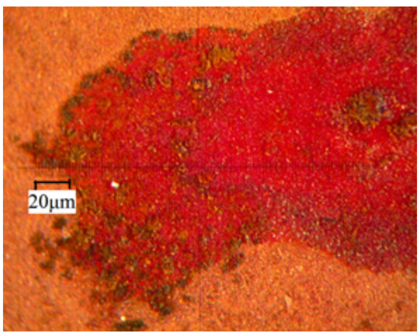


Fig. 9. The appearance of the copper foil after the heat treatment in O5 oil

The experimental results obtained by carrying out the research presented in this paper confirmed that vegetable esters-based insulating fluids in electrical applications presents a number of advantages over traditional mineral oils, namely: high thermal stability, no degradation of the immersed insulation paper, no corrosion of the immersed copper components, and no formation of copper sulphide sludge after thermal ageing. It was also noted that it can be relatively inexpensive to obtain vegetable oils from renewable resources through environmental-friendly technologies, and these vegetable oil are easily and quickly biodegradable under natural conditions [25-27].

Given the above mentioned considerations, for a sustainable development and for ensuring a sustainable development and environmental protection, by continuous education and information on environment [44, 45] the manufacturers and users of electrical equipment should be encouraged to abandon the use of traditional mineral oil for vegetable oils.

Conclusions

We demonstrated that the thermal ageing of some insulating fluids, both in the presence and in the absence of copper foil and/or insulation paper, can be studied by gas evolution content and colour change.

The processing of experimental data obtained before and after exposure to thermal ageing for 1000 h at 110±30°C in closed vessels led to the following conclusions:

- thermal stability of the ester-based oils (both natural triglycerides and synthetic ester) is superior to the one of the mineral oils;

- during the heat treatment, the dissolved oxygen in the investigated oils in the copper foil presence is almost entirely consumed, the formed Cu_2O film catalysing the thermo-oxidative degradation processes of mineral oils;

- into the mineral oils with sulphur content, the copper foil is corroded resulting copper sulphide, which is partially deposited on the support and partially dispersed in the oil; in natural triglycerides based oils and in synthetic ester-based oils the corrosion of the copper foil did not occur;

- the changes in colour of the investigated oils during the heat treatment are in good correlation with the thermo-oxidative processes undergone by the oils;

- the insulation paper degrades and contributes to the thermal ageing of the mineral oils (evidenced by the changes in colour), unlike the natural triglycerides based oils and synthetic ester-based oils, which do not present changes in colour when being in contact with the insulation foil during the heat treatment.

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

References

1.DE CARLO, R.M., SARZANINI, C., BRUZZONITI, M.C., TUMIATTI, V., IEEE Transactions on Dielectrics and Electrical Insulation, **21**, no. 2, 2014, pp. 666-673.

2.SCATIGGIO, F., TUMIATTI, V., MAINA, R., TUMIATTI, M., POMPILI, M., BARTNIKAS, R., IEEE Transactions on Power Delivery, **24**, no. 3, 2009, pp. 1240-1248.

3.MAINA, R., TUMIATTI, V., IEEE Transactions on Dielectrics and Electrical Insulation, **16**, no. 6, 2009, pp. 1655-1663.

4.WIKLUND, P., LEVIN, M., PAHLAVANPOUR, B., IEEE Electrical Insulation Magazine, **23**, no. 4, 2007, pp. 6-14.

5.MITREA, S., OPRINA, G., RADU, E., MARINESCU, V., VOINA, A., LINGVAY, I., Rev. Chim. (Bucharest), **67**, no. 9, 2016. p. 1707

6.ZHOU, Q., RAO, J.X., XIE, H-L, WANG, S, 2014 International Conference on High Voltage, DOI: 10.1109/ICHVE.2014.7035480 2014. pp. 1 – 4

7.VOINA, A., RADU, E., MITREA, S., OPRINA, G., LINGVAY, I., ªERBAN, F., PICA, A., **IEEE Xplore, DOI:** 10.1109/DEMISEE.2016.7530462

8.LINGVAY, I., OPRINA, G., MARINESCU, V., MITREA, S., Electrotehnicã, Electronicã, Automatica (EEA), **64**, no. 4, 2016. pp. 5-10.

9.OOMMEN, T.V., IEEE Electrical Insulation Magazine, 1, no. 1, 2002, pp. 6-11.

10.COTESCU, S.L., MEREANU, A., BUNEA, M., C. PREDUT, POPESCU, C., NOTHINGER, P., DUMITRAN, L., TANASESCU, G., CIOLACU, F., EEA-Electrotehnicã, Electronica, Automatizari, **55**, no. 1, 2007, pp. 19-24.

11.LIAO, R., HAO, J., CHEN, G., MA Z., YANG, L., IEEE Transactions on Dielectrics and Electrical Insulation, **18**, no. 5, 2011, pp. 1626-1637.

12.CIURIUC, A., VIHACENCU, M.S., DUMITRAN, L.M., NOTINGHER, P.V., Annals of the University of Craiova, **36**, no. 36, 2012, pp. 46-51.

13.DUMITRAN L.M., CIURIUC, A., NOÞINGHER, P.V., Advanced Topics in Electrical Engineering, May 23-25, 2013, Bucharest, Romania, pp. 1-6 (DOI 10.1109/ATEE.2013.6563459)

14.PATEL, R., PAREKH, K., UPADHYAY, R.V., MEHTA, R.V., Indian Journal of Engineering and Materials Sciences, **11**, no. 4, 2004, pp. 301-304.

15.KIRALY, J., MARTON, K., CIMBALA, R., KOLCUNOVÁ, I., EEA – Electronicã, Electrotehnicã, Automatizari, **60**, no. 1, 2012, pp. 32-36.

16.CIMBALA, R., KIRÁLY, J., GERMAN-SOBEK, M., EEA-Electronicã, Electrotehnicã, Automatizãri, **62**, no. 3, 2014, pp. 90-95.

17.CHAUDHARI, S., PATIL, ZAMBARE, R., CHAKRABORTY, S., **IEEE Xplore, DOI:** 10.1109/ICPADM.2012.6318921

18.LINGVAY, I., BUDRUGEAC, P., VOINA, A., CUCOS, A., MOSCALIUC, H., Rev. Chim. (Bucharest), **67**, no. 11, 2016, p. 2202

19.BUDRUGEAC, P., LINGVAY, I., PICA, A., SBARCEA, B.G., Rev. Chim. (Bucharest), **68**, no. 11, 2017, p. 2514

20.LINGVAY, I., BUDRUGEAC, P., UDREA, O., RADU, E., MARINESCU, M., EEA - Electrotehnicã, Electronica, Automatica, **63**, no. 1, 2015. pp. 64-70.

21.DEGERATU, S., ROTARU, P., RIZESCU, S., DANOIU, S., BIZDOACA, N. G., ALBOTEANU, L. I., MANOLEA, H. O., Journal of Thermal Analysis and Calorimetry, **119**, no. 3, 2015, pp. 1679-1692.

22.LINGVAY, I., RADU, E., UDREA, O., Journal of Sustainable Energy, **6**, no. 2, 2015, pp. 58-61.

23.LINGVAY I., OPRINA G., CUCOS A., RADU E., VOINA A., Journal of Sustainable Energy, **7**, no. 3, 2016. pp. 65-70.

24.KAMISHIMA, S., IEEE Transactions on Dielectrics and Electrical Insulation, **19**, no. 2, 2012, pp. 505-509.

25.RADU, E., UDREA, O., MITREA, S., PATROI, D., LINGVAY, I., Electrotehnica, Electronica, Automatica (EEA), **63**, no. 4, 2015, pp 84-92.

26.AI- JAWHARI, I.F.H., Journal of Applied & Environmental Microbiology, **2**, no. 2, 2014, pp. 46-52.

27.RADU, E., UDREA, O., LINGVAY, M., SZATMARI, I., LINGVAY, I., Journal of Sustainable Energy, **6**, no. 2, 2015, p. 52-57.

28.BOGATU, L., CIUPARU, D., TANASESCU, C., Rev. Chim. (Bucharest), **61**, no. 10, 2010, p. 1003

29.*** MOL TO - 30.01 R - ulei mineral, electroizolant, neaditivat, http://www.lubrifianti.com/produs/transformator-897/mol-to-30-01-r.html

30.*** BIOTEMP® - Biodegradable Dielectric Insulating Fluid, http://www.nttworldwide.com/docs/BIOTEMP-ABB.pdf

31.*** LUMINOL™ TR/TRI high-efficiency electrical insulation fluids http://lubricants.petro-canada.ca/resource/download.aspx?type=TechData&iproduct=1780&language=en

32.*** Ulei electroizolant prietenos mediului pentru echipamente electrice – UVPMEE, MF-UPMEE, P1MF: http://www.icpe-ca.ro/proiecte/proiecte-nationale/pn-2014/uvpmee.pdf

33.*** Nynas Naphthenics AB Transformatorenöl Handbuch www.nynas.com/naphthenics http://www.nynas.com/Segment/Transformer-oils/Our-transformer-oil-products/Nytro-Taurus-Standard-grade/

34.*** STAS 145-67: Uleiuri ºi grãsimi vegetale - Determinarea culorii de iod
35.***GOST 5477-93 - Vegetable oils. Methods for the determination of colour
36. PRIMO, A., ESTEVE-ADELL, I., BLANDEZ, J. F., DHAKSHINAMOORTHY, A., ALVARO, M., CANDU, N., COMAN, S. M., PARVULESCU, V. I., GARCÍA H., Nature Communications, DOI: 10.1038/ncomms9561, 2015.
37.HONG, C., JIN, X., TOTLEBEN, J., LOHRMAN, J., HARAK, E., SUBRAMANIAM, B., CHAUDHARI, R. V., REN S., Journal of Materials Chemistry A, 2, 2014. pp. 7147-7151.
38.BENJELLOUN, B., TALOU, T., DELMAS, M., GASET, A., Journal of the American Oil Chemists' Society, **68**, 1991, pp. 210-211.
39.MUKASA-TEBANDEKE, I.Z., SSEBUWUFU, P.J.M., NYANZI, S.A., SCHUMANN, A., NYAKAIRU, G.W., LUGOLOBI, F., American Journal of Analytical Chemistry, **5,** 2014, pp. 1302-1312 (http://dx.doi.org/10.4236/ajac.2014.517136)
40.KODALI, D.R., Industrial Lubrication and Tribology, **54**, no. 4, 2002, pp. 165-170.
41.KASSI, K. S., FOFANA, I., MEGNEFHI, F., BÉTIÉ, A., YÉO, Z., PERRON, J., 2014 IEEE Conference on Electrical Insulation and Dielectric Phenomena (CEIDP), DOI: 10.1109/CEIDP.2014.6995769
42.FOFANA, I., BORSI, H., GOCKENBACH, E., FARZANEH, M., Proceedings of 13th Int. Symposium on High Voltage Engineering, Netherlands, 2003, pp. 387-390.
43.PICA, A., DUMITRU, F., Rev. Chim. (Bucharest), **67**, no. 4, 2016, p. 716
44.OLLERER K., Calitatea Vietii, **23**, no. 1, 2012. pp. 25-44.
45.BOGNER, F. X., The Journal of Environmental Education, **29**, no. 4, 1998, pp. 17-29.

Manuscript received: 27.02.2017