THERMOCHEMICAL STABILITY OF INSULATING OILS

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Abstract - The widespread use of insulating oils (transformer oils) having mineral origin, because of their toxic organic substances and xenobiotic, poses a serious risk to the environment. Synthetic ester oils, although limited risk to the environment, its use is limited due to their relatively high price. This paper presents the preliminary results of the studies of the possible use of the natural ester oils of vegetable origin in the electrical equipment.

Keywords: thermal stability, insulating oils, mineral oils, synthetic esters, vegetal oils, biodegradability.

1. INTRODUCTION

The three-phase power system, the electrical transformers represents the most important equipment of transport systems and energy distribution. Power transformers are filled with insulating liquid which, on the one hand provides a uniform electric field lines from the transformer, and the other hand, ensures the transporting of the heat from the transformer windings to the environment - which is, natural cooling and / or forced of the transformer.

Traditionally, the most commonly used insulating fluid in electrical installations (transformers and capacitors) is mineral oil - fraction of hydrocarbons obtained by refining crude oil, having the following composition [1] (Fig.1.): paraffin, isoparaffin, naphthenes - cycloparaffin, aromatics, olefins etc. - some of them are toxic and present xenobiotic pronounced effect, which makes their use to imply a pronounced risk of environmental pollution, mainly of the soil and groundwater.

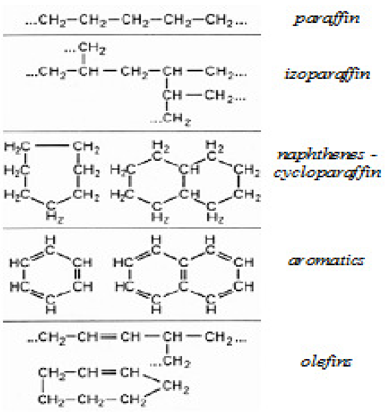


Fig.1. Main constituents of household electrical mineral oil [1]

For these applications may be used also the synthetic ester oils (Fig.2.), which although do not contain toxic chemicals and are considered dangerous for the surface waters [1, 2], are significantly more expensive than mineral oils.

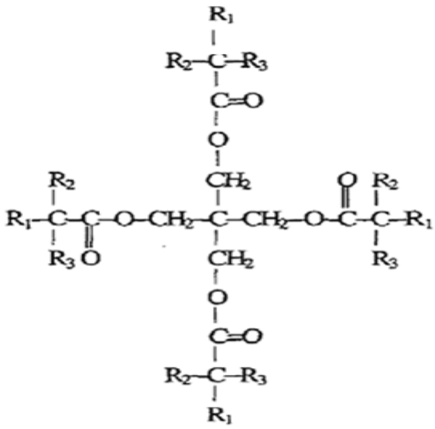


Fig.2. Synthetic ester electrical household structure [1, 2]

Vegetable oils are esters of fatty acid, so in principle, after suitable processing can be used in electric installations. This has the advantage that is obtained from renewable resources, environment friendly.

Degradation, remineralisation of the oils accidentally reached electric installations in soil and / or groundwater occurs through microbiological processes as the action of microorganisms. The biodegradability of oil varieties is shown in Fig. 3.

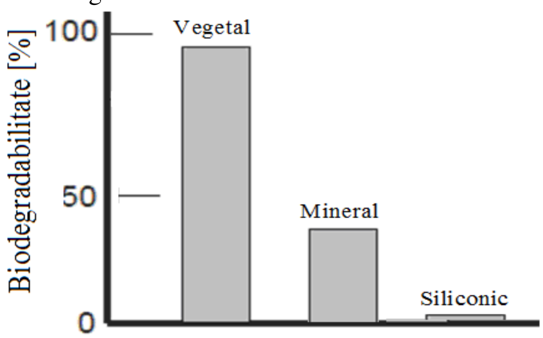


Fig.3. The biodegradability of oils

In the perspective of sustainable development, the environmental protection and widespread use of renewable resources are of great importance.

Given these considerations, the aim of this paper is to assess, through preliminary experimental determinations of the possibility of replacing mineral oils in electric power plants with environmentally friendly vegetable oils.

2. ELECTRICAL HOUSEHOLD OILS – GENERAL CONSIDERATIONS

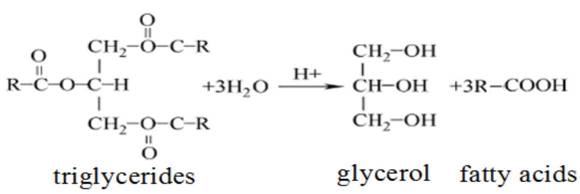
The characteristics physical-chemical and dielectric imposed to electro technical oils are technical regulated [4-6]. From technical regulations results that electrical household oil must provide all of the following technical requirements:

- specific heat greater than 1700 J/kg·K;
- thermal conductivity greater than 0,126 W/m·K;
- freezing point below -20^{0}C ;
- flash point higher than 200^{0}C ;
- fire protection - K2 or K3 minimum grade - IEC 61100 [7];
- breakdown voltage higher than 70kV (measured according to IEC 60156 [8]);
- relative permittivity as low as 3.5 (measured according to IEC 60247 [9]);
- dielectric loss factor $tg\delta$ (at 90^{0}C) of less than 0.009 (measured according to IEC 60247 [9]);
- Compatibility with the materials used to make electrical power equipment – do not degrade materials in the construction of the transformers (paint, paper, cotton, etc.) and do not corrode Cu, Al and / or steel etc.

Analysing the technical conditions imposed, it follows that household electrical insulating oils are nonpolar organic fluid (possibly with a dipole moment very small, whereon the relative permittivity, dielectric loss and breakdown voltage are still within acceptable limits) with high stability (flash point greater than 200^{0}C) and with low aggression for the materials entering in the construction of the transformer.

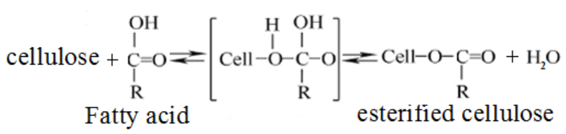
Experimental has been shown and in practice it was verified that ester oils of vegetable origin ensures durability and reliability higher for the insulation systems celluloid (paper, cotton etc.) than mineral oils [3]. This behaviour is explained by the fact that the constituents of the mineral oil (fig.1), when in use, degrades the cellulose structure, and the degradation products (CO, CO_2 , H_2O , H_2, CH_4 , furans, stb.) significantly reduces the performances of the insulation system [3, 10 , 11].

Vegetable ester oils contain, primarily triglycerides, which with the presence of trace water (moisture), hydrolyses forming glycerol and fatty acids (1).



(1)

Fatty acids formed according to (1) reacts with OH groups of cellulose, forming esterified cellulose (2), which substantially increases the insulation stability [12].



(2)

In practice often requires supplementing existing oil exploitation - situations that requires that different sorts of insulating oil on the market to be compatible / miscible with each other perfectly.

3. EXPERIMENTAL PART

Given that sustainability and safe operation of electrical insulating oils used in electric power plants is determined by their chemical stability, by the technical methods of thermal analysis (TG , DTG and DTA), it was studied the ramping behaviour in air samples of some samples of oil as LUMINOL (synthetic ester) [13], NYNAS (mineral oil) [14], edible oil and sunflower oil BIOTEMP [15] (natural ester) .

3.1. Operating mode

The conditions for the simultaneous thermal analysis TG/DTG + DTA were:

- STA 409 PC Lux equipment manufactured by Netzsch-Germany, with corresponding specialized software for data acquisition and processing ;
- temperature range : 25º - 700º C;
- sample port alumina crucible ;
- alumina crucible reference (empty crucible);
- atmosphere: 99.999 % purity synthetic air; 100 ml.min $^{-1}$ flow;
- protective gas: 99.999 % purity synthetic air; 10 ml.min $^{-1}$ flow;
- linear heating rate of 10 K.min $^{-1}$.

3.2. Experimental results and interpretation

TG , DTG and DTA curves for the oil mineral sample NYNAS (commonly used in electric equipment, as shown in Fig.1. constituents) are both showed in Fig.4, from which it appears that following progressive heating in air at approx. 100^{0}C begins a process of oxidation with forming of volatile products - weight loss up to 150^{0}C being significant (approx. 6%), process which is completed at approx. 300^{0}C when the loss of mass is substantially complete (99.45 %) - finding that suggests the fact that the mineral oil NYNAS is only thermally stable up to approx. 100^{0}C .

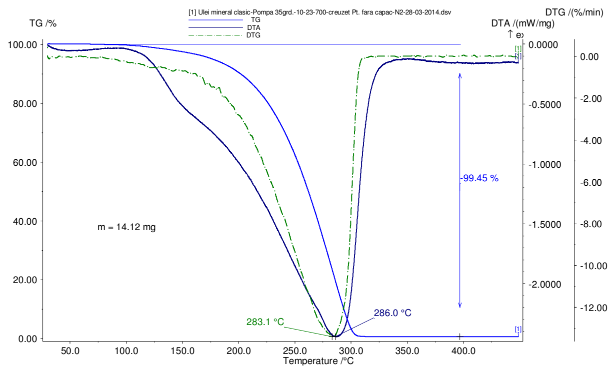


Fig.4. TG, DTG and DTA curves for the sample of mineral oil NYNAS

TG, DTA and DTG curves for LUMINOL oil sample, a synthetic ester having the structure shown in Fig. 2, are shown in Fig.5. It appears that for the gradual heating of the sample of synthetic ester take place two successive exothermic processes with forming of volatile products. As a result of these processes, practically all of the oil quantity is converted to gaseous products. From the analysis of the results it appears that, in the air, LUMINOL synthetic oil is thermally stable up to 170^{0}C. The non-isothermal parameters of these processes are shown in Table 1.

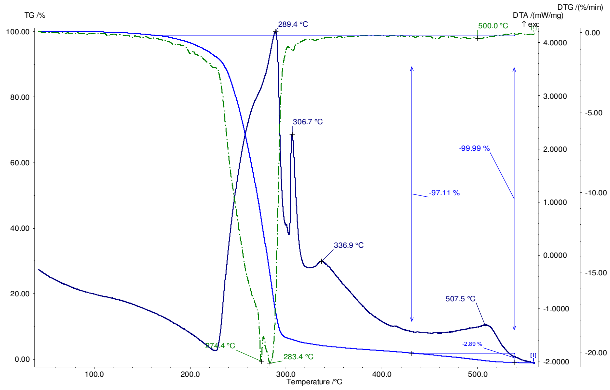


Fig.5. TG, DTG and DTA curves for the LUMINOL synthetic oil (synthetic ester) sample

Table 1. Parameters of the non-isothermal processes taking place gradually warming synthetic oil sample LUMINOL

Process	ΔT [ºC]	Δm [%]	T (DTG) [ºC]	Pic DTA [ºC]	ΔH
1.	170,0 - 425,0	97,11	274,4; 283,4	289,4; 336,9	exo.
2.	425,0 - 540,0	2,98	500,0	507,5	exo

ΔT - the temperature range of the proceedings ; Δm - mass loss during the process ; T(DTG) = temperature corresponding to the minimum DTG; pic DTA = temperature corresponding to the maximum DTA; ΔH - thermal effect of the process (exo = exothermic)

TG, DTG and DTA curves for BIOTEMP sample, vegetable origin - natural esters of glycerol - triglycerides (1) are both shown in Fig.6. It appears that for the gradual heating of the oil sample take place six successive processes, namely the initial exothermic oxidation process forming liquid products and five consecutive processes of thermal oxidation forming volatile products. Following these processes, all of the oil quantity was converted to gaseous products. The non-isothermal parameters of these processes are shown in Table 2.

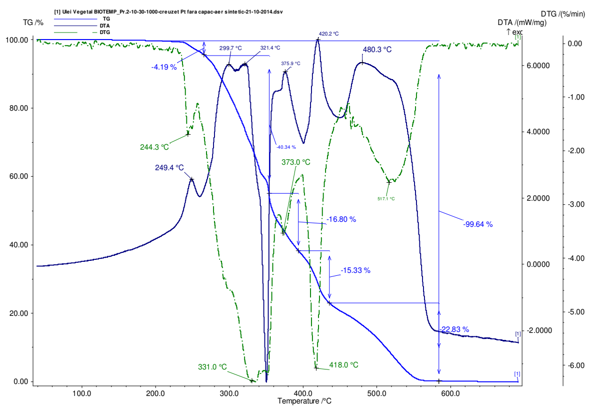


Fig.6. TG, DTG and DTA curves for the BIOTEMP oil sample

Table 2. Characteristic parameters of the processes that take place at progressive heating of BIOTEMP oil sample

Process	ΔT [ºC]	Δm [%]	T (DTG) [ºC]	Pic DTA [ºC]	ΔH
1.	233,8 – 260*	-	-	-	exo
2	240,0 – 270,0	4,19	244,3	249,4	exo
3	270,0– 360,0	40,34	331,0	299,7; 321,4	exo
4	360,0 – 400,0	16,80	373,0	375,9	exo
5	400,0 – 440,0	15,33	418,0	420,2	exo
6	440,0 – 600,0	22,83	517,1	480,3	exo

* At a temperature of 240^{0}C the formation of the second process begins forming gaseous products. The notations are given in Table 1 legend.

It appears that the thermo-oxidative degradation of BIOTEMP oil (triglyceride of vegetable origin) is more complex than that of LUMINOL oil (synthetic ester – Fig.1). According to the results obtained, in air BIOTEMP is thermally stable up to 233,8^{0}C.

TG, DTA and DTG curves for the edible sunflower oil are shown in Fig .7. It is noted that at the progressive heating of the sunflower oil sample take place four successive processes, namely a first exothermic oxidation process with forming of liquid products and three consecutive processes of thermo-oxidation with forming of volatile products. According to the results obtained, outdoor the analysed cooking sunflower oil is thermally stable up to 149,7^{0}C. In these processes, all quantity of the oil (99.96%) is transformed into gaseous products. Non-isothermal parameters of these processes are shown in Table 3.

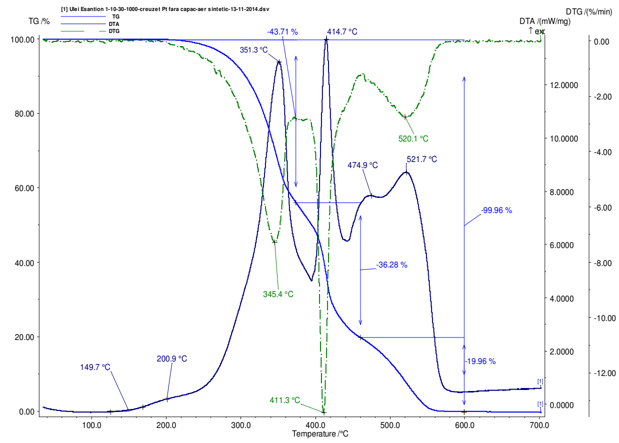


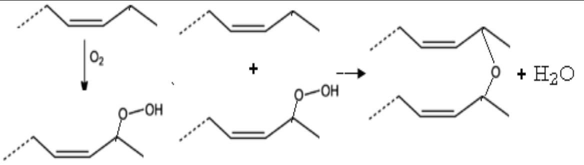
Fig.7. TG, DTG and DTA curves for the edible sunflower oil sample

Table 3. Characteristic parameters of the processes that are taking place to gradually heating of the edible oil from sunflower sample

Process	ΔT [ºC]	$\%\Delta m$ [%]	T (DTG) [ºC]	Pic DTA [ºC]	ΔH
1.	149,7 – 226,0	0	-	200,9	exo
2.	226,0 – 371,0	43,71	345,4	351,3	exo
3.	371,0 – 460,0	36,28	411,3	414,7	exo
4.	460,0 – 600,0	19,96	520,1	474,9; 521,7	exo

ΔT =Temperature range in which the process takes place; $\%\Delta m$ = mass shift in the process ($\% \ \Delta m > 0$ for weight loss; T(DTG) = temperature corresponding to the minimum DTG, pic DTA= temperature corresponding to the maximum DTA; ΔH =endothermic effect (endo) / exothermic (exo)

The first process revealed in DTA curve from Fig.7. consist in the auto-oxidation of the oil by the addition of oxygen to the unsaturated compounds, followed by cross-linking. Initial addition of the oxygen occurs at the C-H bond adjacent to the double bond belonging of the unsaturated fatty acid ester with glycerine. It follows that hydro peroxides are likely crosslink - according to the scheme (3) [16]:



(3)

At the heating in an oxidizing atmosphere of the cross-linked products it were formed gaseous products (processes 2, 3 and 4 set out in the TG/DTG+DTA curves) .

4. CONCLUSIONS

Following the technical measurements of the thermal analysis (TG + BG + DTA), it was found that the thermal stability in air, given by the starting time temperature of the first process of thermal oxidation, of the investigated oils is:

- NYNAS - insulating oil of mineral origin – 100^0C;
- LUMINOL – insulating oil based on synthetic esters – 170^0C;
- BIOTEMP – oil based on triglyceride vegetable origin – $233{,}8^0$C;
- Edible sunflower oil (vegetable origin triglycerides) – $149{,}7^0$C.

It appears that the oils of vegetable origin based on natural triglyceride, readily biodegradable, presents a substantially higher thermal stability than oils of mineral origin, so their use in electric equipment ensures a longer life with their safe and friendly environment. It also notes that it is plausible that, by applying purification treatments, sunflower oil lend itself to obtain insulating fluid for electric equipment.

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