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THERMAL STABILITY CHANGE OF SYNTHETIC ESTER-BASED TRANSFORMER OIL

SUMMARY

For good transformer condition assessment it is necessary to determine the condition of insulating materials, both liquid and solid. Transformer is reliable for as long as its insulation system resists deterioration. Therefore, thermal and oxidation stability are important characteristics of transformer oil. It is a measure of oil resistance for decomposition by the influence of oxygen and temperature. Oils with good thermal and oxidation stability retain their characteristics regardless the thermal stress.

Because of environmental and safety issues, the use of synthetic ester-based transformer oils is increasing. Although they have been in use in smaller transformers (distributive, traction, …) for decades, limit values for chemical and physical characteristics are still discussed. New methods for thermal stability evaluation can be useful for insulation condition assessment.

Key words: transformer oil, synthetic ester, ageing, thermal properties, TGA, DSC

1. INTRODUCTION

Physical and chemical testings of transformer oil have proven to be worthy tools for transformer condition monitoring and evaluation. Degradation products soluble in oil are formed and analysis of liquid insulation is a convenient method for transformer condition assessment. Representative oil sample can provide information about degradation of oil itself, cellulose insulation and construction materials, as well as information about thermal and electrical processes in transformer. Decades of laboratory analysis and information gathering have resulted in recommended values for oil characteristics for normal condition of new and transformers in service, and typical concentrations of degradation products dissolved in oil (characteristic gases and furanic compounds). More important, chemical processes of mineral oil degradation are known so obtained values can be explained and understood.

Mineral oil has been used as an insulating liquid in transformers since the very beginning of oil immersed transformers. It fulfils the requirements for electrical and thermal insulation, and in normal operating conditions its characteristics can remain long-term acceptable.

Besides the fact that its availability has become questionable and thus the price can vary depending on circumstances, there are more situations where use of mineral oil is not preferable.

Environment protection and fire safety are rising up as crucial topics in expanding use of transformers. Densely populated and environmentally sensitive areas, offshore wind farms, underground

facilities, are some of the situations where use of mineral oil is not suitable. Oil leakage or transformer explosion and oil combustion are serious threats to environment and safety. Mineral oil has great impact on water systems because it blocks oxygen delivery from the atmosphere. With flash and fire point around 140 °C and 160 °C respectively, mineral transformer oil is easily ignited and when on fire produce toxic dense smoke.

For many years, alternative insulating liquids have been used, mainly in traction and distributive transformers. Synthetic esters have been used in distributive transformers (for voltages up to 66 kV) over 30 years, and in the last 10 years there has been an increasing demand for transformers up to 238 kV filled with esters [1].

Due to differences in physical and chemical characteristics between mineral and synthetic ester-based transformer oil, there must be significant change in calculation and construction of power transformers. For that reason start properties and changes during normal and irregular operation must be known. Besides that, transformer condition assessment is not complete without chemical and physical testing of insulating liquid.

Typical values needed for evaluation of ester filled transformer condition are not set. There is no standardized interpretation of DGA, known behaviour after years of operating conditions or methods for estimation of oxidation period. Various laboratory tests are conducted and useful information is gathered. But it will take some time to confirm laboratory values with in-service data.

Possibility of rapid evaluation of synthetic ester-based transformer oil was investigated [2]. Samples of synthetic ester-based transformer oil have been exposed to thermal ageing in closed vessels at 120°C and 150 °C for the period of 168, 336, 504 and 672 hours. Along with methods that show obvious changes of synthetic ester-based transformer oil properties (dielectric dissipation factor and color change), differential scanning calorimetry (DSC) and thermogravimetry (TGA) were used. DSC is widely used as an analytical, research and diagnostic tool from which relevant information, such as oxidation onset temperature (OOT) can be obtained. Decomposition kinetics can be determined by thermogravimetry (TGA), a technique in which the mass of a sample is measured as a function of temperature whilst subjected to a controlled temperature program [3]. Obtained curves are called thermograms, they show the sample mass dependence on temperature, and provide information about physical phenomena, such as vaporization, sublimation, absorption, adsorption and desorption, and about chemical phenomena, such as chemisorptions, desolvation and decomposition. Water content was determined for better understanding of decomposition reactions.

2.   THERMAL STABILTY CHANGE

One of the most important characteristics of transformer oil is its thermal stability. Thermal stability of transformer oil prevents unacceptable changes of viscosity during the transformer operation at elevated temperatures. Synthetic ester-based transformer oils have superior thermal stability due to exceptional chemical stability of ester bonds [4].
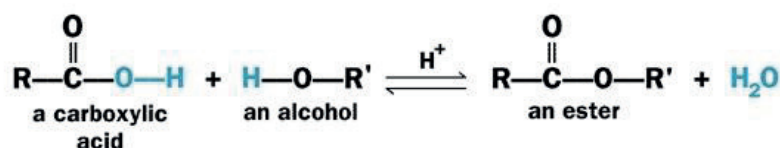

Figure 1 - Esterification reaction (R, R' are saturated hydrocarbon chains)

Synthetic esters are organic compounds formed during an esterification reaction between polyvalent alcohols and fatty acids (Figure 1). The ester linkage, bond between a hydroxyl group (-OH) and a carboxyl group (-COOH), is exceptionally stable, bond energy is more stable than the C-C bond. The absence of hydrogen atom (replaced by alkyl groups) on the β-carbon (second carbon atom to carboxyl group) of the alcohol portion of an ester leads to superior thermal stability. Decomposition occurs by a free radical mechanism which requires more energy and can occur only at higher temperatures [4].

Decomposition mechanism of ester consists of initiation, propagation and termination, but intermediates depend on oxygen presence [5]. Differences in decomposition reactions depending on oxygen presence are presented in Table I.

In presence of oxygen, initiation step gives alkyl (R•) and peroxy (HO$_2$•) radicals and hydrogen peroxide (H$_2$O$_2$). Unstable radicals react with each other, with oxygen and other molecules and propagation reactions give alkyl and peroxy radicals differentiated in length from initiation products. Unstable molecules react with each other forming stable molecules and terminating reaction.

In absence of oxygen, alkyl (R•) and hydrogen (H) radicals are formed in initiation step, followed by the formation of extended molecules (R2, R3, …). Reactions are terminated by stable molecules formation [5].

Table I - Ester decomposition reaction steps at elevated temperature

Reaction steps	Reaction conditions	
	Oxygen present	Oxygen not present
Initiation	RH + O$_2$ → R• + HOO• RH + RH → 2R• + H$_2$O$_2$	RH → R• + H•
Propagation	R• + O$_2$ → ROO• ROO• + R^{2}H → ROOH + R^2•	R• + R^{2}H → RH + R^2•
Termination	ROO• + ROO• → ROOR + O$_2$ R• + R• → R-R	R• + R• → R-R

Esters of pentaerythritol and terephthalic acid (polyol esters) are widely used as insulating oils. They oxidise very slowly, at temperatures above 125°C, and darken as they do [6].

Thermal degradation of polyol ester in air is mainly due to oxidation which causes chain scission and the formation of radicals. The peroxy radical reacts with polyol ester, producing intermediate ROOH. The intermediate then decomposes to ROOR' peroxide, R"OOH peroxide and aldehyde, which decompose to form small molecules such as water or carbon dioxide. Unstable radicals also can link molecules, form large colloidal compounds (sludge) which increase viscosity [5]. The most important influence of free radicals on insulating liquids is the fact that molecules can capture their free electrons and form ions. The accumulation of ionized molecules increases the dissipation factor of oil-paper insulation [7].

3. EXPERIMENTAL SETUP

Samples of synthetic ester-based transformer oil were exposed to thermal ageing in closed vessels at 120 °C and 150°C for the period of 168, 336, 504 and 672 hours. Virgin transformer oil and aged samples were characterized.

The released heat from oxidation reactions can be measured using DSC in either isothermal or non-isothermal mode. For DSC oxidation measurements, the heat flux from the oxidized oil is compared to the heat flux from an inert reference (empty pan) both heated at the same rate. When the oxidation of the sample occurs, the recorded heat shows a peak whose area is proportional to the amount of heat released by the sample. The heat released by the oxidized oil is recorded as the heat flow signal (y-axis) as a function of temperature (x-axis) [4]. Results (oxidation onset temperature, OOT) were obtained both in an open aluminum pan and a sealed pan with a pinhole, with a heating rate of 10 °C/ min.

Thermogravimetric analyzer quantifies mass change as a function of time and temperature. It consists of a microbalance and a well regulated furnace. The test consists of precise weight loss measuring of the oil sample (initial mass 10 g) during the exposure to temperatures from 25 °C up to 625 °C with a heating rate of 10 °C/ min.

As the indicators of thermal degradation, water content, viscosity, color change and dielectric dissipation factor were determined.

Water content was determined by automatic coulometric Karl Fisher titration. The sample is mixed with a base/alcohol solution of iodide ion and sulphur dioxide. Iodine is generated electrolytically and reacts with water. Iodine is generated in proportion to quantity of electricity and the amount of water is determined directly from the quantity of electricity required for the electrolysis [8].

Dielectric dissipation factor is a measure of the dielectric losses in an electrical insulating liquid when used in an alternating electric field and of the energy dissipated as heat. A low dissipation factor indicates low AC dielectric losses. Dielectric dissipation factor of oil may be useful as a means of quality control, and as an indication of changes in quality resulting from contamination and deterioration in service or as a result of handling [9]. Higher dielectric dissipation factor indicates the presence of moisture and contaminating agents.

4.   RESULTS

Oxidation onset temperatures (OOT) of virgin oil and aged samples were determined by DSC. Results are shown on Figure 2. There is no significant difference between measurements in open and sealed pan. Oxidation onset temperatures of samples exposed to 120 °C are increasing, while for samples exposed to 150 °C are decreasing with ageing duration.
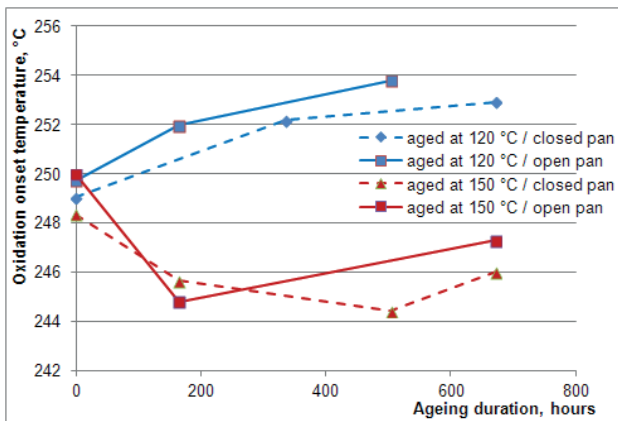

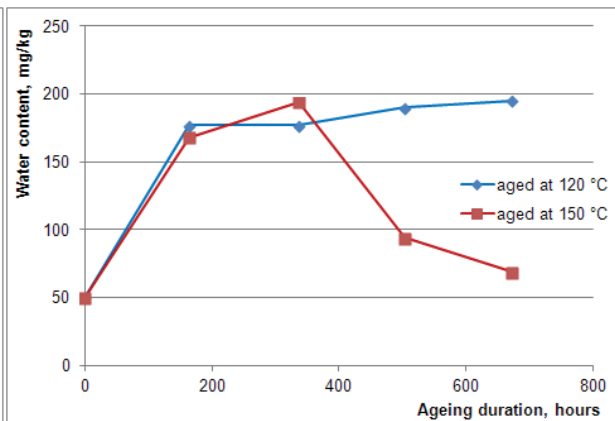Figure 2 - Oxidation onset temperatures of aged samples;

Figure 3 - Water content of aged samples

Obvious differences in oxidation onset temperature (increase and decrease after ageing at different temperatures) indicate the difference in degradation mechanism. It must be investigated if compounds that contribute to better thermal stability of synthetic ester are formed at higher temperatures. Water content of aged samples (Figure 3) confirms differences in degradation mechanism at different temperatures.

Thermograms of tested oil samples (aged at temperatures of 120 °C and 150 °C for up to 672 hours) are presented on Figure 4. All samples have lost about 5% of initial mass at the temperatures from 245 to 255 °C. For samples aged at 120 °C noticeable weight loss begins rapidly above 200 °C, while for samples aged at 150 °C weight loss is slower but begins around 160 °C.
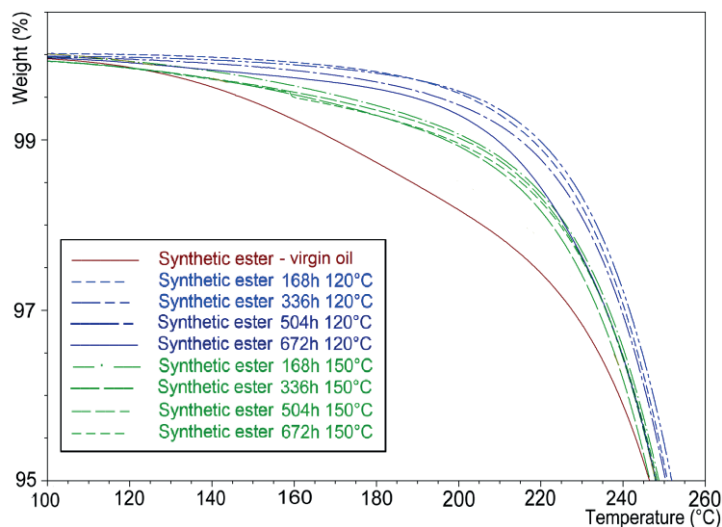

Figure 4 - Thermograms of virgin oil and aged samples

As expected, thermograms show a better thermal stability for samples aged at 120 °C than for those aged at 150 °C. Surprisingly, the fastest weight loss is measured on virgin oil. It can be assumed that water present in virgin oil evaporates during thermogravimetric analysis and causes rapid weight loss, while in aged samples it evaporates earlier, during laboratory ageing.

Comparison of aged samples weight loss at 200 °C and 220 °C is presented on Figure 5. As observed on Figure 4, samples aged at 120 °C, both at 200 °C and 220 °C, show greater difference than samples aged at 150 °C. Ageing must be extended to see whether samples aged at 150 °C show rapid weight loss.
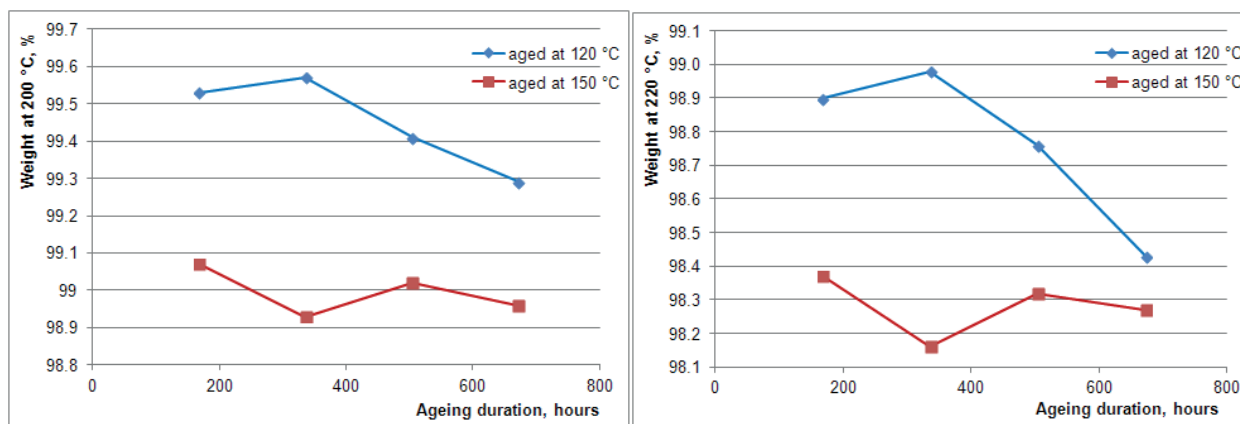

Figure 5 - Weight change at 200 °C and 220 °C of aged samples

Differences in degradation mechanism are obvious in colour change and increase of dielectric dissipation factor (Figure 6).
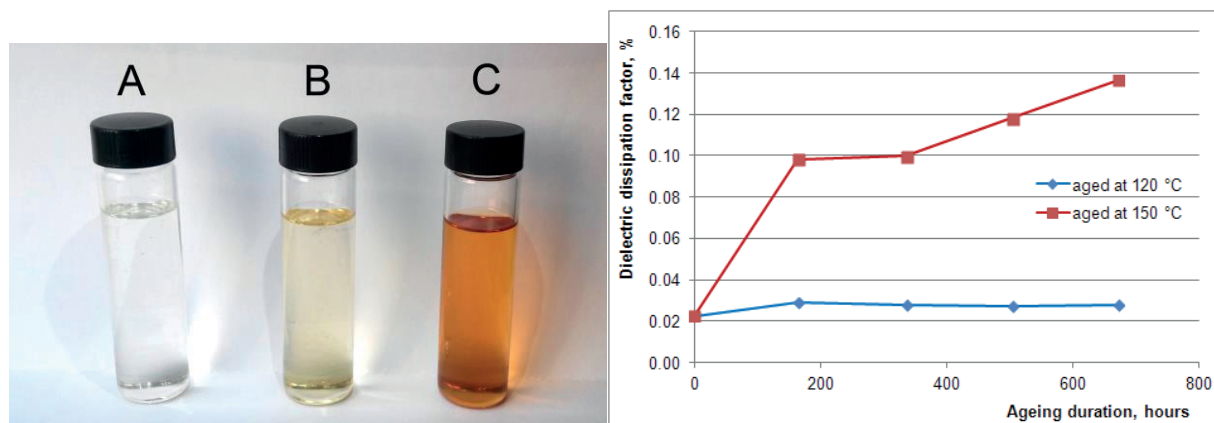

Figure 6 - colour change of virgin oil (A) after 672 hours of thermal ageing at 120 °C (B) and 150 °C (C); change of dielectric dissipation factor during laboratory ageing at 120 °C and 150 °C

There was no change in kinematic viscosity measured at 20 °C and 40 °C for virgin and aged oil (Table II). Since there is increase of the dissipation factor of oil samples aged at 150 °C, accumulation of ionized molecules occurred but unstable radicals did not form large colloidal compounds (sludge) which increase viscosity.

Table II – Kinematic viscosity measurements

Sample	Kinematic Viscosity (mm^2/s)		
	Ageing process	20 °C	40 °C
virgin oil	-	70	28
1	672 hours at 120 °C	72	28
2	672 hours at 150 °C	72	28

5.   CONCLUSION

Environmentally friendly synthetic ester-based insulating liquid was aged at 120 °C and 150 °C in presence of air for 672 hours. Differential scanning calorimetry and thermogravimetric analysis were performed on virgin oil and aged samples, as well as kinematic viscosity and dielectric dissipation factor measurements, colour observations and water content determination.

Differences in oxidation onset temperature indicate different thermal ageing process kinetics at different temperatures. Oxidation onset temperatures of samples exposed to 120 °C are increasing, while for samples exposed to 150 °C are decreasing with ageing duration. Change in thermal stability of aged samples shows some regularity considering duration of ageing: samples tested after 168 hours of temperature exposure (both 120 °C and 150 °C) have better thermal stability than samples tested after 672 hours. What is not expected is that virgin oil has poorest thermal stability and the causes require further investigation. It must be determined if it is due to higher low molecular weight components content or some oxidation products or reactions contribute to better thermal stability of aged samples. Water content of aged samples confirms differences in degradation mechanism at different temperatures. Increase of dielectric dissipation factor indicates accumulation of ionized or polar molecules. However, molecules of high molecular weight, as final degradation products, are not formed in quantities sufficient to form sludge and influence kinematic viscosity.

Differential scanning calorimetry and thermogravimetric analysis have proven to be useful methods in oxidation process monitoring of synthetic esters. Additional measurements after prolonged ageing of oil samples must be performed for more knowledge of synthetic ester-based transformer oil terminal deterioration.

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