Comparison between Synthetic Ester and Mineral Oil Impregnated Transformer Paper Aging Markers

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Abstract—**For transformers in service, aging markers from cellulose in oil such as furans, water, methanol and acids are measured for diagnostic purposes. The content of these indicators, measured in oil, may therefore vary with load, temperature, solid and liquid insulation aging, as well as marker stability and evaporative loss. Correction factors estimating the level of the aging marker to a reference temperature would make the diagnostic more relevant.**
In this study, correction factors for temperature differences have been estimated for different aging markers in insulation systems impregnated with either mineral oil or synthetic ester. In the case of mineral oil based systems, we observe correction factors for water, methanol and furans in line with previously reported findings. On the other hand, for the synthetic ester system, novel correction factors for water and methanol are suggested while for furans, no temperature dependence was observed.

Keywords—Aging markers; furans; methanol; ethanol; water; maintenance; synthetic ester; mineral oil; thermally upgraded paper; correction factors; partitioning

I. INTRODUCTION

In the asset management of transformers, diagnostics and maintenance are very important. There is a need to improve the diagnostic methods for conventional insulation systems, and to establish new methods for new insulation systems. Cellulose based windings insulation is subjected to irreversible aging, which reduces its ability to withstand the short circuit mechanical stresses. Consequently, tensile strength and degree of polymerization (DP) are reduced with time. Experimental studies have established that temperature, moisture, acids and oxygen are the major factors influencing the aging of cellulose in transformers [1-7]. Aging of the oil-cellulose system will generate water [8], high and low molecular weight acids [9], alcohols [10-13] and furans [1, 14, 15] that can be found to some degree dissolved in the oil. These by-products can potentially be used as aging indicators. Furan level has also been used as an indirect [16, 17] way of estimating DP-value of winding insulation, but the correlation remains uncertain and depends among other things on partitioning and temperatures when the sampling is done.

The diagnostic methods for the cellulose aging using the different aging markers are mostly related to mineral oil based transformers. Most power transformers in Europe are filled with mineral oils, but during the last decade there was a shift towards more environmentally friendly liquids such as natural and synthetic esters. These liquids are fully biodegradable and have a much higher flash and fire point [18].

The diagnostic of oil filled transformers are based upon oil samples delivered in the laboratory, normally into one liter aluminum bottles or 500 ml glass bottles in the case of UK. The temperatures of the oil in the transformer during sampling is recorded (sample, bottom, top oil). The oil is then analyzed with respect to water content, acidity, aging markers, and other parameters. The water solubility for ester oils is much higher than for mineral oils and to estimate the water content in the windings, partitioning curves for the distribution of water between the cellulose and the oil have been established [19, 20]. These curves are normally derived for new - not service aged - materials. When the transformer oil becomes old and acidic the water solubility of the oil increases and this leads to an overestimation of water content of the cellulose [19]. Water equilibrium curves for ester oils and cellulose are even less well established [18, 20]. In general the furan level in a transformer with synthetic ester seems to be lower than for a mineral oil based one [15].

The purpose of this study was to investigate partitioning for water and aging markers for cellulose in an aged transformer insulation system, and to derive correction factors for varying temperatures during sampling. Due to problems with collecting cellulose materials from service it was decided to base the studies on laboratory aged systems. Insulation systems were first aged, and thereafter oil sampling was performed at different temperatures. This was done both for mineral oil and for synthetic ester impregnated cellulose systems.

II. EXPERIMENT

The experiment was performed in sequence in two parts. In the first part a cellulose system (low density kraft

cellulose pressboard and thermally upgraded Insuldur paper with 2.9 % nitrogen) was aged either in mineral oil (Nytro 10 XN) or in the synthetic ester (Midel 7131) to produce the relevant markers. In the second part the cellulose and liquid insulation were transferred to a partitioning rig (Fig. **1**) where the marker concentration was measured at different temperatures.

A. Aging of insulation systems

The paper and pressboard were first dried in a sealed metal tank under vacuum at room temperature for two days and then at 100 °C for a final four days. Still at high temperature, 100 ml of water were added to the tank. The water vaporized and equilibrated with the paper/cellulose after one week. 80 liters of dry hot mineral oil were then added under vacuum. Thereafter, this system was aged for 75 days at 130 °C in the tank with careful air flushing using pressurized air (air gun) into the tank twice a week.

Before aging, in the system with mineral oil, the pressboard and paper had a humidity concentration of 1.6 % and 1.7 %, respectively. After aging the acidity of the oil was measured and found to be 0.33 mg KOH/g, the pressboard and paper humidity was 2.3 % and the DP-values were 170 and 180 for pressboard and Insuldur paper, respectively. The differences in aging between the kraft pressboard and the upgraded paper may seem surprisingly small, but it can actually be explained by effects from oxidation where aging is similar for the two cellulose qualities [1, 6]. It must be stated that both cellulose type has reached the leveling off point and ordinary non-upgraded cellulose may have reached this point much earlier.

In the system with synthetic ester oil, both pressboard and paper were at 2 % humidity before aging. After aging, the humidity was 0.5 %, most likely due to water absorption in the synthetic ester at this high temperature [21], but possibly also due to a leak from the tank. In order to be able to have "similar humidity" for both the mineral oil and the synthetic ester oil system before the aging marker partitioning experiment started, water was added at the end of the aging giving 1.1 % humidity for the pressboard and 1.2 % for the paper. At the end of the aging the DP for the pressboard was measured to be 162 while the Insuldur paper had reached DP=327. The oil acidity for the synthetic ester was very low, similar to the initial value and in line with the assumption that the produced acids are eliminated, reacting with water forming more esters.

B. Aging marker experiment at different temperatures in the oil circulation rig

In this context we will use the circulation rig described in [22] and Fig. 1. Originally built for contamination partitioning experiments between oil and cellulose, oil circulates through two cellulose containers which may be kept at different temperatures up to 140 ˚C. The larger of the two containers holds enough cellulose to act as an "infinite" contamination reservoir while the smaller one (0.5 liter) could hold paper for sampling. For the present experiment, only the large container was used where only oil was sampled and the maximum temperature was 100 ˚C. Two liquid-based temperature control systems control the oil temperature at the two containers via heat exchangers, guided by Pt100 sensors in the oil flow just before each container. Temperature and "water activity" sensors provided by Vaisala were also used to monitor the experiment. To avoid condensation of water in the oil, the control liquids were restricted not to have more than 10 °C colder than the actual oil temperature.

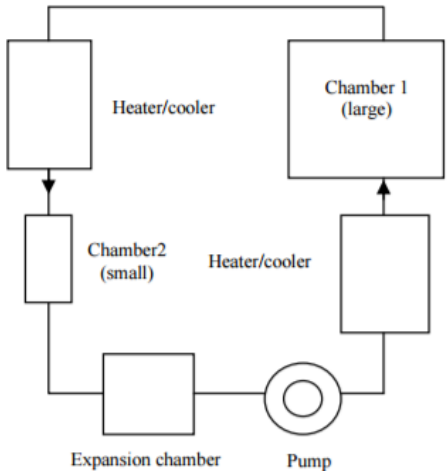

Fig. 1: Schematic of experimental setup of the oil circulation rig previously published in [22].

1.0 kg of oil impregnated Insuldur, 2.7 kg of oil impregnated pressboard and 17 l of the aged oil were used in the circulation rig. These weights were used to simulate conditions in the field and are based upon literature search [23]. The aging state (DP value) was different for the two systems, but this was of minor importance since the goal was to study the marker partitioning. The transfer of the materials to the rig was done within a few hours at ambient temperature.

The idea was to estimate correction factor [24, 25] adjusting for temperature for different aging markers both for mineral and synthetic ester oil systems in combination with cellulose materials. The correction factor is defined as the concentration of the chemical marker compound (CM) at the reference temperature (20 °C) divided by the concentration at the specific temperature (Ts).

$$Correction\ Factor = \frac{CM_{20\,°C}}{CM_{Ts}}$$

The acidity in oil was measured by titration according to IEC 62021. The humidity in oil was measured by extracting 2.5 ml with a warm syringe and injecting it into a coulometric Karl Fischer titration unit.

For the furan and alcohol compounds we used 2 x 50 ml sealed luer lock syringes for the sampling. High Pressure Liquid Chromatography (HPLC) with Diode Array Detection has been the instrument (Agilent 1200 HPLC) of choice for the determination of furan by-products (ASTM D5837 (2005) and Head Space Gas Liquid Chromatography

coupled with Mass Spectroscopy (HS-GC-MS) for the Methanol by-products produced by the degradation of the oil impregnated (Mineral or Midel) paper [26] (Deuterated Ethanol technique). The mineral oil based system were sampled at 25, 40, 50, 60, 70, 80 and 100 °C and the synthetic ester system was sampled at the same temperatures except for 25 °C.

The time between the outtakes described in **TABLE I** was based upon previous experience [22] where acidity and water were measured for the paper and the oil until the equilibrium was reached for both materials. The necessary time intervals to reach equilibrium for methanol and furans are known to be longer [25] but the time between outtakes was expected to be sufficient since temperatures were always increased successively between each successive sampling. We assume that during the circulation rig experiment at different temperatures (25-100 °C) there is no significant increase in the total amount of aging markers. All the production of aging markers happens in the production of the aged material at 130 °C.

TABLE I: EXPERIMENTAL MATRIX FOR THE CIRCULATION RIG WITH TIME TO EQUILIBRIUM BETWEEN OUTTAKES, MEASURING ON WATER, METHANOL AND FURANS

Materials	T (°C)	Equilibrium Time
20 kg Nytro 10XN	25	2 months
	40	4 weeks
1 kg Insuldur	50	1 week
	60	1 week
2.7 kg pressboard	70	1 week
	80	1 week
	100	1 week
20 kg Midel 7131	40	4 weeks
1 kg Insuldur	50	1 week
	60	1 week
	70	1 week
2.7 kg pressboard	80	1 week
	100	1 week

III. RESULTS

In Table II, the absolute values of the different aging compounds are listed for 20 °C. The values at this temperature were obtained by extrapolating the values measured at other temperatures. The lowest temperature measured was 25 °C for the aged mineral oil system and 40 °C for the synthetic ester system.

The corrections factor for furans (2-FAL, 2-FOL and 5HMF), water and methanol for the mineral oil impregnated system are plotted Fig. 2 - Fig. 6.

TABLE II: INITIAL PARAMETERS FOR THE TWO AGED SYSTEMS (P – NON UPGRADED PRESSBOARD, T-THERMALLY UPGRADED PAPER). 20 ºC VALUES FOUND VIA EXTRAPOLATION.

System	*DP*	Concentration in oil at 20 °C µg/g				
		2 Fal	*2 Fol*	*5 HMF*	*H_2O*	*MeOH*
Nytro 10XN + Cellulose	P=170 T=180	1.28	0.44	0.08	15	229
Midel 7131 + Cellulose	P=162 T=327	6.59	< 0.01	1.3	138	6.8

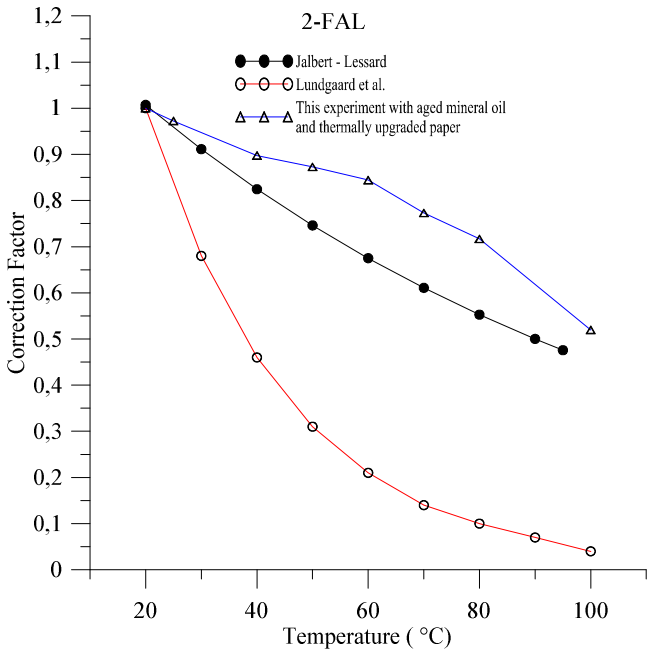

Fig. 2: 2-FAL correction factor for mineral oil system comparison using [24] and [5].

Correction factor has been estimated for the synthetic ester and cellulose system for water and methanol, shown in Fig. 7 . In **TABLE III** the correction factors for all the aging markers at different temperatures are presented for both the mineral oil and synthetic ester systems. The concentration of furans for the synthetic ester system appeared to be temperature independent.

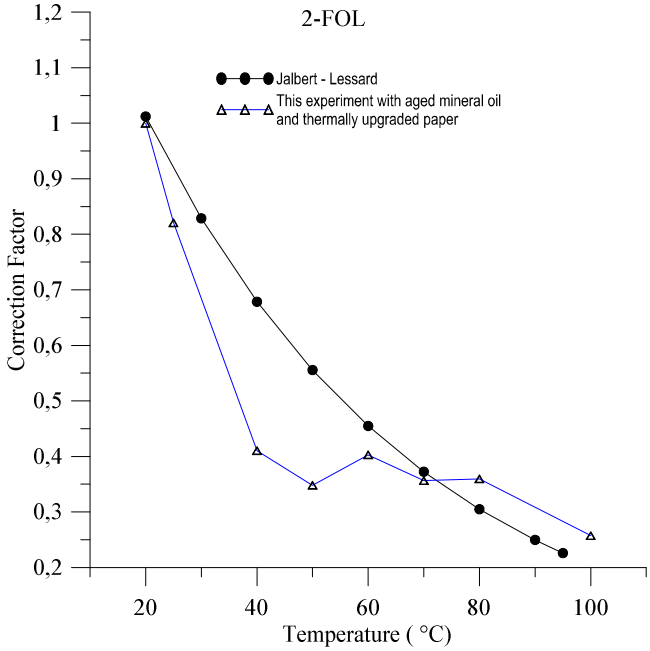

Fig. 3: 2-FOL correction factor for mineral oil system comparison using [24].

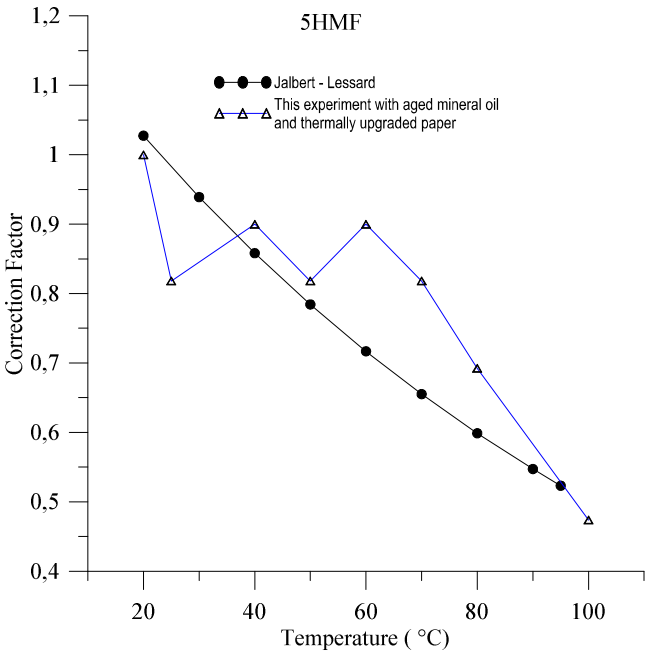

Fig. 4: 5HMF correction factor for mineral oil system comparison using [24].

The correction factors obtained for the various furanic components (2-FAL, 2FOL and 5HMF) as a function of temperature in mineral oil are shown in Fig. 2, Fig. 3 and Fig. 4. The results obtained are compared with similar studies found in the literature.

The results show that the concentration of these furanic markers in mineral oil are temperature dependent. Nevertheless, some differences from previous studies can be observed. The results obtained with 2-FAL, 2-FOL and 5HMF are similar to what Jalbert et al published [12, 24], while the decrease in the correction factor of 2-FAL with increasing temperature was observed to be more dramatic by Lundgaard et al [5]. This can be attributed to the different natures of cellulosic material (cellulose materials and oil taken from a real transformer) used but is not very well understood.

Correction factors as a function of temperature for water (Fig. 5) and for methanol (Fig. 6) in mineral oil were also derived. As observed with the furans, it can be seen that the quantity of these markers in oil is clearly temperature dependent. The results obtained are in line with what has previously been published [5, 24].

Correction factors as a function of temperature for water and methanol in synthetic ester (Midel 7131) and cellulose system are shown in Fig. 7. As for mineral oil, it can be seen that the quantity of these aging markers in oil is clearly temperature dependent. Methanol content seems to be more temperature dependent than water content. Moreover, it is interesting to state here that regarding the furans, contrary to what was observed for the investigated mineral oil, no clear temperature dependence was observed. In **TABLE III** the correction factors for the different compounds are listed at different temperatures.

TABLE III: CORRECTION FACTOR FOR AGING PARAMETERS

T	20°C	30°C	40°C	50°C	60°C	70°C	80°C	90°C	100°C
Mineral Oil + Thermally upgraded paper + low density pressboard									
H_2O	1.05	0,70	0.47	0.31	0.21	0.14	0.09	0.06	0.04
MeOH	1.01	0.75	0.56	0.42	0.32	0.24	0.18	0.13	0.1
2-FAL	1.07	0.98	0.91	0.84	0.77	0.71	0.66	0.61	0.56
2-FOL	0.99	0.78	0.61	0.48	0.38	0.30	0.23	0.18	0.15
Synthetic Ester Oil + Thermally upgraded paper + low density pressboard									
H_2O	1	0.84	0.71	0.60	0.50	0.43	0.36	0.30	0.26
MeOH	0.99	0.63	0.41	0.26	0.17	0.11	0.07	0.05	0.03

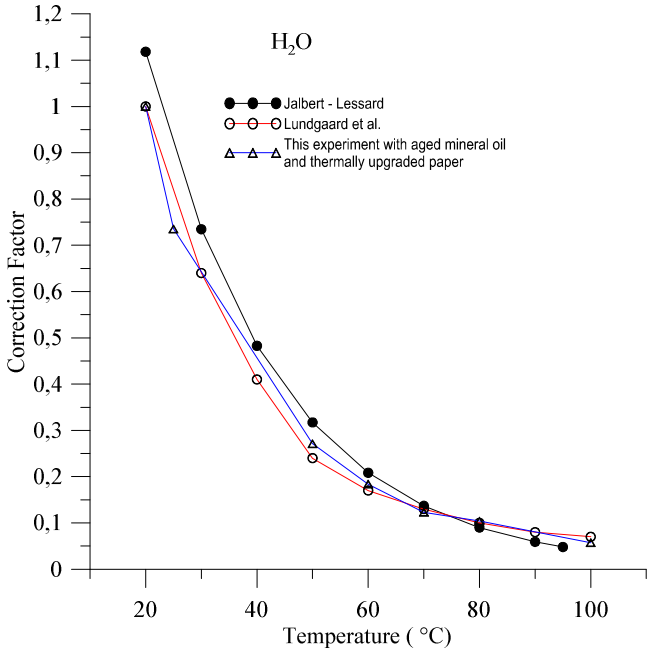

Fig. 5: Water correction factor for mineral oil system comparison using [24] and [5].

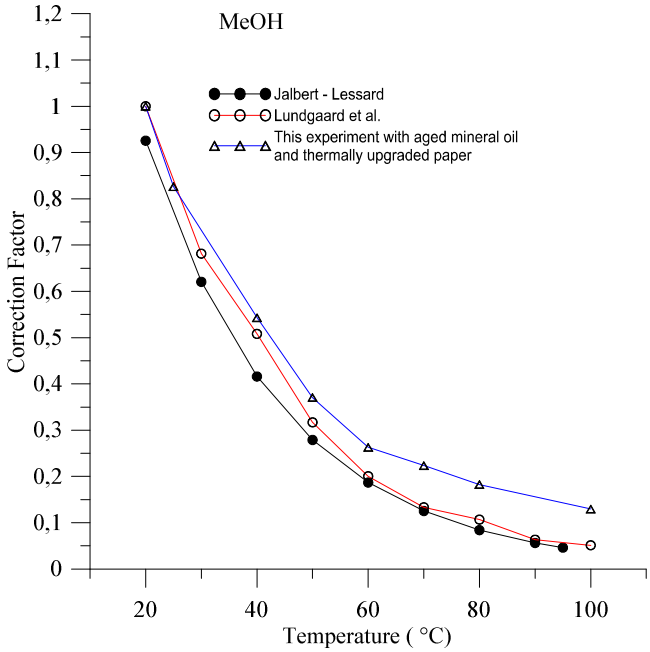

Fig. 6: Methanol correction factor for mineral oil system comparison using [24] and [5].

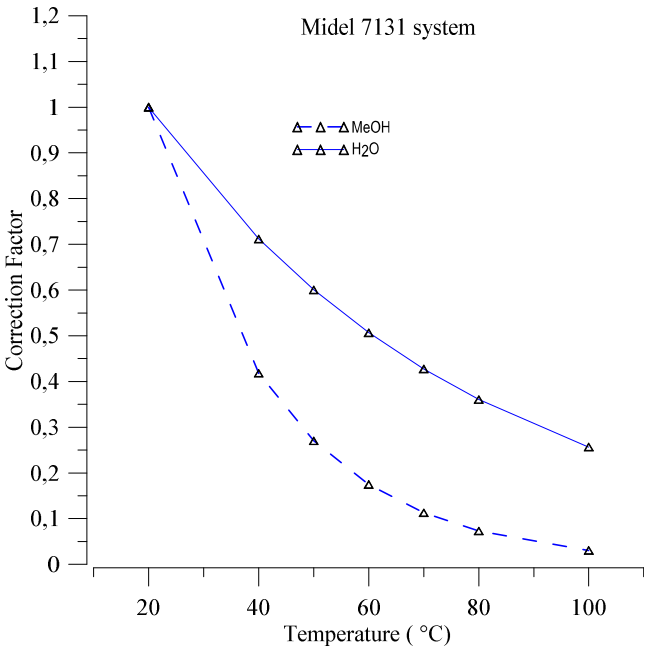

Fig. 7: Methanol and water correction factors for the synthetic ester and cellulose system

IV. CONCLUSIONS

The results presented are a contribution to the understanding of how the concentration of chemical markers in oil varies with temperature and how to calculate the concentration at a reference temperature facilitating comparison regardless of temperature and load. The trends obtained here were compared with other studies, and similar corrections factors for chemical markers were found for systems containing mineral oil.

For the system containing synthetic ester new correction factors for methanol and water have been suggested. Regarding furans as chemical marker in ester, no significant temperature dependence was observed.

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