METHANOL AS NEW AGEING MARKER OF OIL-FILLED TRANSFORMER INSULATION

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ABSTRACT

This paper is focused on the efficiency of Methanol (MeOH) as new ageing marker for transformer risk assessment. Different investigations have been made at laboratory scale to correlate the MeOH concentration (dissolved in oil) with the solid insulation degradation (DPv, 2-FAL). Experimental results confirm MeOH as promising ageing marker for the monitoring of cellulose-based insulation and especially by showing a "logarithmic" trend (earlier detection of the degradation) contrary to 2-FAL showing an "exponential" trend (detection when degradation is severe). This new marker also enables to detect the degradation of thermally upgraded paper, today not detectable with current ageing markers.

INTRODUCTION

Transformer insulation is a composite system made of liquid and solid (impregnated with the liquid). The insulating liquid is generally mineral oil and the solid insulation is based on cellulose (mainly Kraft paper, pressboard and Thermally Upgraded Paper/TUP). The lifetime of the transformer is driven by the lifetime of the cellulosic insulation because this later cannot be easily replaced as the insulating liquid. Then, it is of great importance to check regularly the condition of the cellulosic insulation in order to apply mitigation techniques at the right time. The most important parameter to assess cellulose aging status in transformer is to measure its degree of polymerization (DPv). DPv is a direct assessment of mechanical properties of cellulose through physico-chemical analysis. Nevertheless, the drawback of this method is the non-accessibility of cellulosic samples in service. For the sampling, transformer must be stopped or sampling performed during repair or refurbishment. However, this disadvantage may be bypassed by the monitoring of cellulose insulation through oil sampling followed by laboratory analysis.

Today, two indirect methods (through oil sampling) are used since several decades [1]: Dissolved Gases Analysis (DGA) by Gas Chromatography and Furanic compounds (2-FAL) by High Performance Liquid Chromatography. When cellulose starts to be degraded, Carbon Oxide (CO) and Carbon Dioxide (CO_2) gases are generated and 2-FAL compound is created. Nevertheless, these conventional tools present some drawbacks: CO & CO_2 can also come from the insulating liquid degradation [2]; and 2-FAL appears when cellulose degradation is severe (too late) but is also not detectable during the degradation of thermally upgraded paper [3].

In order to improve the cellulose ageing assessment, a new marker was recently put forward: the Methanol (MeOH) [4, 5]. This molecule, detected by Head-Space / Gas-Chromatography / Mass-Spectroscopy technique, is directly linked to the cellulose degradation, and would be detectable at early stage of the degradation as well as applicable on thermally upgraded paper.

This article is focused on the efficiency of MeOH as new ageing marker for the transformer insulation life assessment. For that purpose, different investigations have been made at laboratory scale to correlate the MeOH concentration with the cellulosic insulation degradation. Thermal ageing at three different temperatures (105°C, 122°C, 130°C) and under different conditions (inert gas blanket, air blanket) were realized during a long period. Three types of cellulose-based materials (paper, pressboard and TUP) were tested in two mineral oils (inhibited and uninhibited). At different interval periods, concentration of MeOH was measured and correlated with the concentration of 2-FAL as well as with the degree of polymerization (DPv).

EXPERIMENTAL CONDITIONS

Tested materials and conditioning

Three different cellulose-based materials (see table 1) and two different mineral oils (see table 2) were used for this investigation.

Before ageing, liquid and solid samples were treated in order to reach acceptable humidity content and be close of new transformer conditions. Mineral oils were degassed and filtered under vacuum. The moisture content of the oil after treatment was less than 10 ppm. The test pieces of paper, pressboard and TUP were dried under vacuum at 105°C during at least 48h. Then, samples were impregnated under vacuum with treated oils previously heated at 70°C. Once the samples completely immersed in oil, the vacuum was switched off in and samples maintained in oil at atmospheric pressure during 24h. After this process, the humidity content of solid samples was less than 0.5% required for new transformer. Then solid materials and oil were put in the ageing test vessel.

Cellulose	Density (g/cm^3)	Thickness (mm)	Thermal class (IEC 60076-14)
Kraft paper	0.97 – 1.2	0.25	105°C
Pressboard	1.2 – 1.35	1	105°C
TUP	1.2 – 1.3	0.25	120°C

Table 1: Cellulose-based material for ageing tests

Mineral oil	Density @20°C (g/ml)	Viscosity @40°C (mm^2/s)	Grade (IEC 60296)
Uninhibited	0.870	10	Standard grade
Inhibited	0.805	9.6	High grade

Table 2: Mineral oil for ageing tests

Ageing tests

Thermal ageing were realized under different sealed system conditions: inert gas blanket (see figure 1) and air blanket (see figure 2). The use of inert gas blanket enables to be focused on the thermal degradation of the cellulose by limiting oxidation process.

Three different temperatures have been tested:

- 105°C in sealed system with inert gas blanket for oil dilatation. This temperature was chosen to be in line with the thermal class of Kraft paper and pressboard.
- 122°C in sealed system with inert gas blanket for oil dilatation. This temperature was chosen to be slightly higher than thermal class of TUP as well as speed-up the ageing process of conventional cellulose.
- 130°C in sealed systems with air blanket for oil dilatation. This temperature and presence of air (oxygen) was chosen to strongly accelerate the degradation of all cellulosic materials.

In order to be close to the conditions in real transformers, copper was added in each test vessels. For all the tests, the following mass distribution was used: around 5% of cellulose, 30% of copper and 65% of oils.

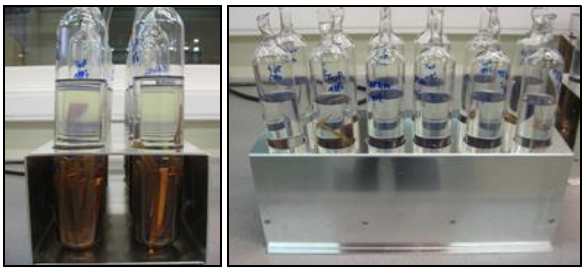

Figure 1: ageing at 105°C and 122°C in 200ml hermetically sealed vials with Argon blanket and uninhibited mineral oil

Figure 2: ageing at 130°C in 25ml glass vessels with air blanket and inhibited mineral oil

Test methods

Degree of polymerization (DPv) was measured in accordance with IEC 60450. This physico-chemical analysis gives some data on the mechanical property of the cellulose. The DPv value of a new cellulose-based material is around 1200 whereas the end of life criteria is around 200 [1].

2-FAL compounds were measured in accordance with IEC 61198 by High Performance Liquid Chromatography. 2-FAL are generated with the cellulose decomposition and slightly soluble in the oil. Few ppm indicate a cellulose degradation.

Methanol being a new ageing marker, it does not exist a standardized method. Nevertheless, Head Space/Gas Chromatography/Mass Spectrometry (HS/GC/MS) was chosen because literature data underline the efficiency of this technique [6, 7]. HS enables to vaporize molecules, then GC separates different molecules and finally MS analyzes and quantifies molecules.

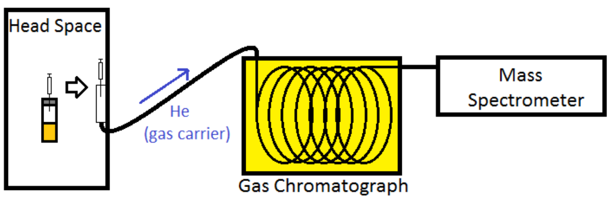

Figure 3: Scheme of HS/GC/MS equipment

EXPERIMENTAL RESULTS

Ageing with inert gas blanket

Figure 4 shows the ageing of Kraft paper. At 105°C, the cellulose decomposition is very slight and there is no 2-FAL generation. Nevertheless, the slight decrease of DPv is correlated with few ppm of MeOH production. At 122°C, as expected, the degradation of insulating paper is more severe with DPv decreasing around 300 at the end of ageing. 2-FAL compounds are generated but at later stage than Methanol. From these results, it appears that Methanol enables to optimize the assessment of insulating paper.

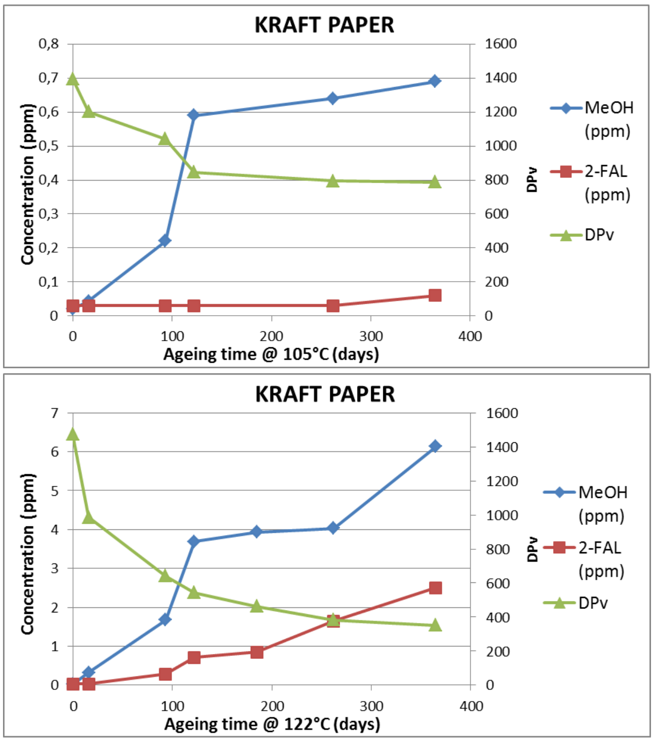

Figure 4: MeOH & 2-FAL concentrations vs. DPv for Kraft in uninhibited mineral oil at 105°C & 122°C (sealed system with inert gas blanket)

Figure 5 presents the ageing of pressboard. The same trends as for Kraft paper are observed with generation of 2-FAL only at 122°C and better assessment of cellulose decomposition with MeOH.

Figure 6 presents the ageing of TUP. As expected, there is very slight degradation of this paper at 105°C. At 122°C, 2-FAL compounds are not produced whereas the DPv is decreasing. On the contrary, MeOH generation clearly underlines this degradation and from the beginning of the ageing process, thus confirming literature data [4, 5].

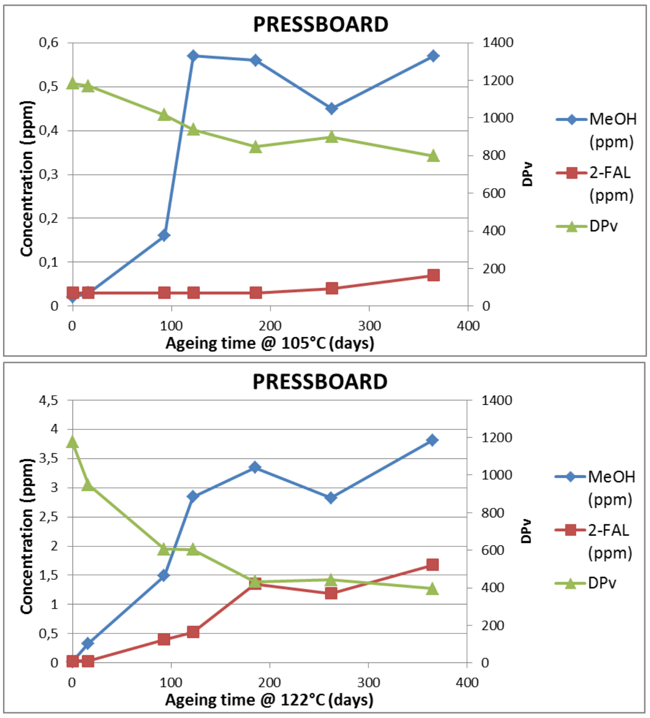

Figure 5: MeOH & 2-FAL concentrations vs. DPv for Pressboard in uninhibited mineral oil at 105°C & 122°C (sealed system with inert gas blanket)

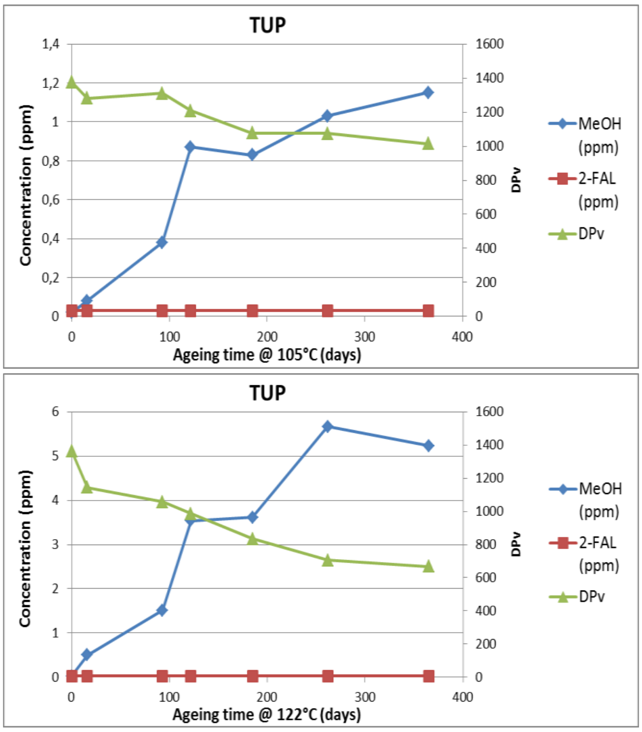

Figure 6: MeOH & 2-FAL concentrations vs. DPv for TUP in uninhibited mineral oil at 105°C & 122°C (sealed system with inert gas blanket)

Ageing with air blanket

Figures 7 to 9 show results of more severe ageing due to the combined actions of temperature (130°C) and oxygen from air blanket.

Figures 7 and 8 present ageing of conventional cellulosic materials (Kraft paper and pressboard). It appears that DPv decreases at low values in a shorter period than previous tests, with clear generation of 2-FAL compounds. Nevertheless, it is interesting to mention that Methanol is produced at earlier stage, then corresponding to the first degradation step of cellulose. Indeed, the significant increase of 2-FAL appears when cellulose is already well degraded. On the other hand, MeOH concentration seems to stabilize when degradation process is well engaged.

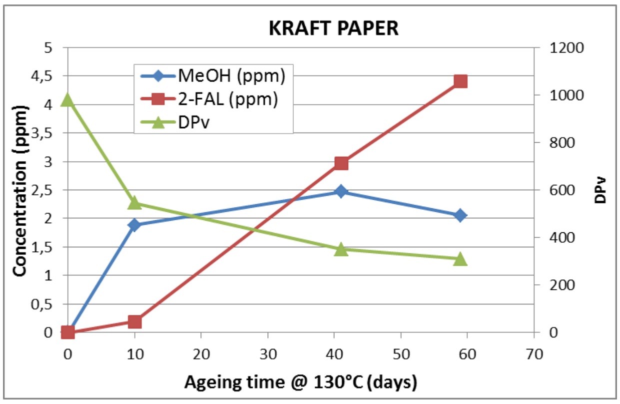

Figure 7: MeOH & 2-FAL concentrations vs. DPv for Kraft in inhibited mineral oil at 130°C (sealed system with air blanket)

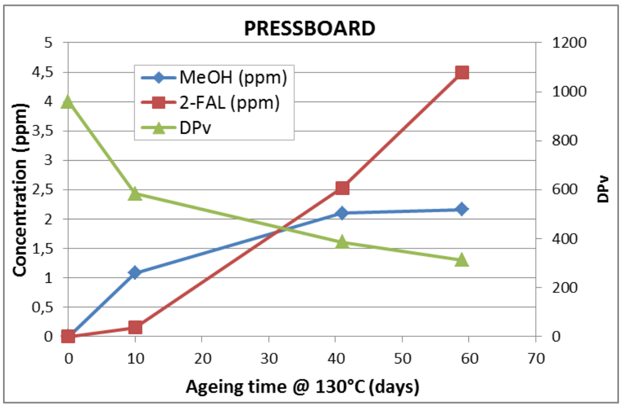

Figure 8: MeOH & 2-FAL concentrations vs. DPv for pressboard in inhibited mineral oil at 130°C (sealed system with air blanket)

Figures 9 presents ageing results with TUP. Even if DPv decreases at a low value (around 400), 2-FAL compounds are not detected. On the contrary, MeOH is generated and well correlated with the DPv decreasing.

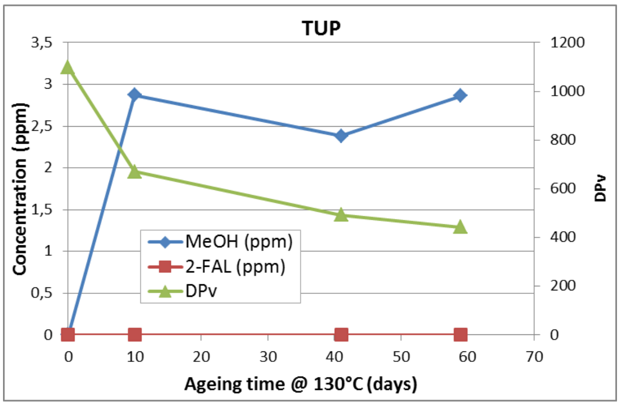

Figure 9: MeOH & 2-FAL concentrations vs. DPv for TUP in inhibited mineral oil at 130°C (sealed system with air blanket)

Discussion

All previous results have clearly shown and confirmed that MeOH appears as good marker to detect the beginning of cellulosic materials decomposition. To go deeper in the analysis, it can be suggested that methanol concentration progresses with "logarithmic" trend (earlier detection of the degradation) contrary to 2-FAL showing an "exponential" trend (detection when degradation is severe). As an example, Figure 10 shows trend curves obtained with ageing of pressboard. Nevertheless, and as expected with logarithmic evolution, the MeOH concentration seems to stabilize when degradation process is well engaged and then from this point, 2-FAL are significantly produced and become higher than MeOH, as also reported in literature [8]. As a summary, MeOH and 2-FAL concentrations are complementary to give an overview of all the cellulose degradation process, but earlier stage remains more relevant for efficient monitoring and mitigation techniques at the right time.

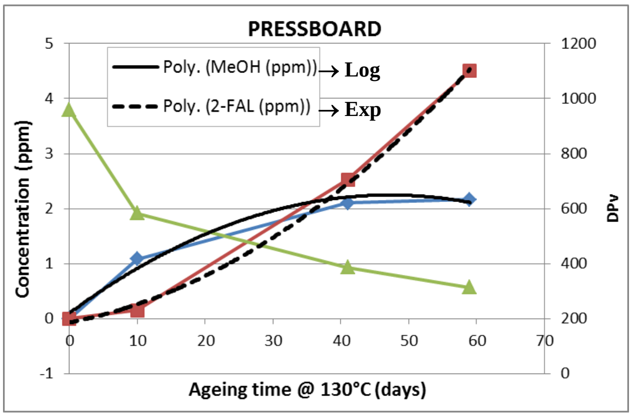

Figure 10: Trend curves of MeOH & 2-FAL concentrations for pressboard (figure 8)

CONCLUSION

Various experimental investigations presented and discussed in this paper have shown that Methanol (MeOH) is a promising ageing marker to assess all cellulose-based materials (Kraft paper, pressboard and TUP) and applicable in different types of mineral oil (inhibited and uninhibited). Correlation is well established between degree of polymerization (DPv) and MeOH generation, as well as earlier detection of cellulose degradation than 2-FAL compounds, thus confirming literature data.

When cellulose decomposition is important, MeOH concentration tends to stabilize and only 2-FAL compounds continue to progress, thus showing that both analysis remain useful. Nevertheless, attention must be paid on the fact that earlier detection (MeOH) is of great importance for efficient monitoring and mitigation techniques at the right time.

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