21, rue d'Artois, F-75008 PARIS
http : //www.cigre.org

Identification of early-stage paper degradation by methanol

SCHAUT Annelore and EECKHOUDT Steve
Laborelec
Belgium

SUMMARY

This study was designed to correlate the degree of polymerization (DP_v) of the paper insulation and content of 2-furfural (2FAL) and methanol (MeOH) in transformer oil. Therefore, several Belgian nuclear power plants were frequently followed-up. To find a correlation between MeOH and 2FAL, oil samples of a group of similar generator step-up transformers were periodically analysed since mid 2009. It became obvious that MeOH can play an important role as early-stage paper degradation marker and as confirmation analysis for the 2FAL content. From this study it was also clear that MeOH was subjected to fluctuations which could be attributed to temperature. An equilibrium between MeOH in oil and paper will be reached dependent on the temperature. This same phenomena was observed with 2FAL. Perhaps the MeOH should be corrected for temperature cfr. corrected water amount in function of the temperature. During another study it was shown that MeOH can be used as confirmation analysis for the 2FAL analysis. This was observed during the analysis of MeOH and 2FAL in oil samples from nuclear power plants. In oil samples with high amounts 2FAL, also high amounts of MeOH were observed.

KEYWORDS

Transformer oil, power transformers, methanol, furanic compounds, end-of-life, early stage paper degradation

1. Introduction

Solid insulation in large power transformers has several important functions such as electrical insulation, mechanical stability, creation of space, direction of oil flow, etc. Cellulose is mainly used because of its excellent electrical and mechanical properties, availability and very good behaviour with mineral insulating oil. Cellulose is a mineral condensation polymer consisting of an anhydroglucose joined together by glycosidic bonds. The degree of polymerization (DP_v) is in order of 1200 for unbleached soft wood Kraft. The mechanical strength of the paper is essential and a reduction down to 50% is considered as a value indicating end-of-life. The insulating paper consists approximately of 80% cellulose, 12% hemicelluloses, 8% lignin and some mineral substances. The aging of solid insulation will influence its mechanical strength. The main cellulose degradation factor is acid hydrolysis, requiring water and acids. Other important factors are temperature, oil degradation products and possible electrical field strength (figure 1) [1].

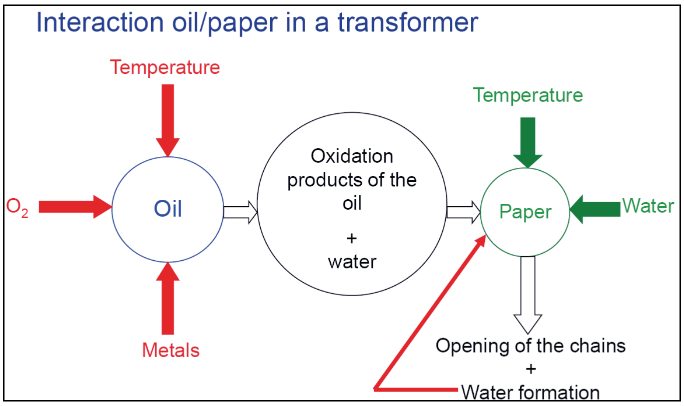

Figure 1: Link between oil oxidation and paper degradation

As paper insulation ages, its electrical properties do not change significantly but the mechanical properties are reduced tremendously. During normal operation the cellulose in the paper will cleave over time depending on the overall transformer conditions such as temperature, moisture and acids. As a result, the mechanical strength of the paper is reduced with time and insulation condition monitoring is therefore valuable.

The degradation of paper insulation in power transformers by chemical markers has been studied since several decades. One of the first studies concerned the link between the amount of carbon oxides, CO and CO_2, in the oil and the DP_v of the insulating paper. However, the problem occurred that these carbon oxides could also originate from oil decomposition due to long-term oxidation which made their application limited [2]. Furanic compounds, a group of chemical compounds formed by oxidation and hydrolysis of cellulose, seem to have a specific link with paper degradation. Especially 2-furfuraldehyde (2FAL) was highly recommended because it was possible to extract this furanic compound from the oil to characterize the thermal composition of insulating paper [3]. However, several disadvantages of 2FAL were observed such as its low detection limit when paper is thermally upgraded, the high yield of production from hemicelluloses, its thermal instability and the effect of moisture on the rate of production. Consequently, the applicability of 2FAL as chemical marker for paper degradation must be considered in perspective [4, 5].

It remains difficult to estimate the actual aging or life expectancy of the insulating paper and thus, of the transformer. Several investigations were performed to model the correlation between 2FAL and DP_v. Some of them were performed under strict laboratory conditions, while others were based on real transformer data [3, 6, 7, 8]. In figure 2 the most commonly used models to correlate 2FAL and DP_v are shown. The large error that can be observed when comparing different models is associated to the aging related problems and thus, to the difficulty in interpreting the amount of 2FAL in the transformer.

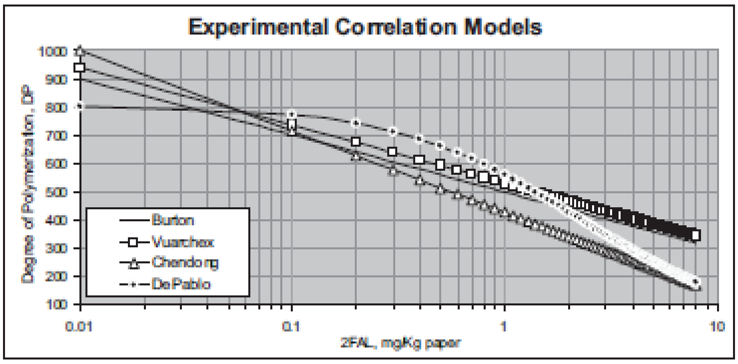

Figure 2: Different 2FAL – DP correlation models.

An important research for new aging markers started in 2001 at the research institute of Hydro-Québec (IREQ). During thermal aging tests on paper/oil systems several molecules with potential diagnostic significance such as acetaldehyde, acetone, methanol, butanol, 2-butanone, ethanol, carbon disulfide were detected but taking into account by-products of oil oxidation, only a few molecules were selected for further testing. Stability tests at different temperatures showed that methanol possessed the highest stability. Thus, methanol was of particular interest for monitoring paper depolymerisation [9, 10].

The aim of this study w as to correlate the DP_v of the paper insulation and content of 2FAL and MeOH in transformer oil.

2. Materials and methods

A G1888 static headspace sampler with a 1mL sample loop coupled to a 6890N gas chromatograph equipped with a 5975B mass selective detector in the electron impact mode (all from Agilent Technologies, Belgium) was used to assess the volatile degradation cellulose by-products. The instrument interface was kept at 250°C and a mass range m/z 10-100 was scanned in total ion current (TIC). The separation was performed with a 60m long Stabilwax polar column (0.25mm diameter, 0.5µm film thickness, Restek, Interscience, Belgium) under the instrumental conditions described in table 1. For the calibration MeOH-in-oil standards were prepared (0.05; 0.1; 0.25; 0.5 and 1ppm). These standards were diluted from a stock solution containing 10ppm MeOH in a blank oil [11].

Table 1: Instrumental conditions of headspace and GC-MS for MeOH analysis

Headspace conditions		
Temperatures (°C)	Oven	100
	Transfer line	80
	Injection loop	100
Times (min)	Equilibration time	40
	Pressurization	0.5
	Loop fill	0.2
	Loop equilibration	0.2
	Injection	1

Shaking	Power	High
Gas chromatograph conditions		
He carrier gas flow	1mL/min	
Oven	35°C (3 min)	
	12°C/min to 100°C (1 min)	
	8°C/min to 200°C (3 min)	

3. Experimental study and discussion

To correlate the amount of MeOH in the oil to paper aging in the power transformer, a group of similar generator step-up (GSU) transformers of Belgian nuclear power plants were frequently followed-up since mid 2009. A comparison of 3 shell-type transformers, F4 (phase 4), F8 (phase 8) and F12 (phase 12) from the same manufacturer with an equal service life of approximately 30 years, 160 MVA, same type of uninhibited oil and N_2-blanketed is shown in figure 3. It was clear that the MeOH amount was higher in each sample. Also the sampling temperature was taken into account which could explain the fluctuations of the MeOH content in the oil.

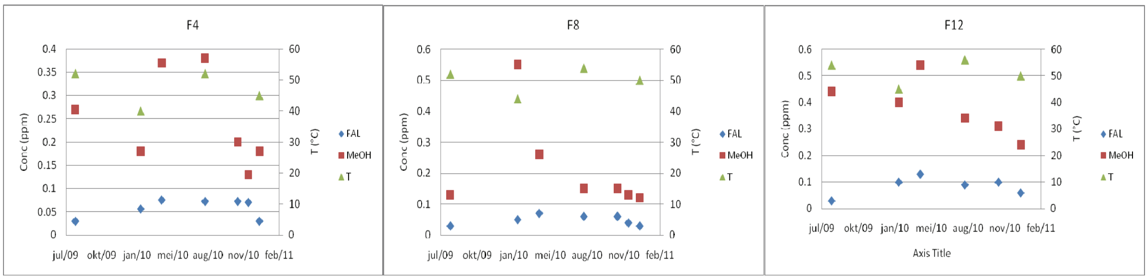

Figure 3: MeOH and 2FAL production of 3 shell-type transformers – 30 years service life, 160MVA, same type of uninhibited oil and N2-blanketed.

The transformers F4, F8 and F12 in figure 4 are all shell-type transformers from the same manufacturers with a service life of 4 years, 500MVA, the same type of passivated oil and are membrane-sealed. In none of the transformers 2FAL was detected, while some small amounts of MeOH were already present. This could indicate some early-stage paper degradation.

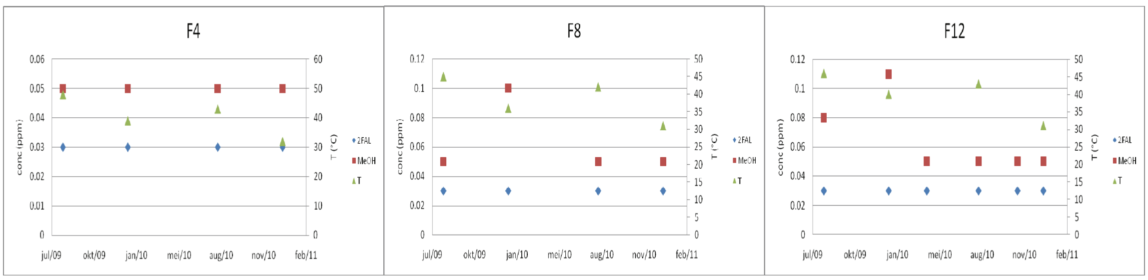

Figure 4: MeOH and 2FAL production in 3 shell-type from the same manufacturer with a service life of 4 years, 500MVA, the same type of passivated oil and membrane-sealed

From these observations it was obvious that temperature will play an important role in the equilibrium of MeOH between the oil and the paper. This influence of temperature must be further investigated but from figure 5 it was clear that MeOH will be temperature-dependent. A large temperature drop, observed in January 2010 was followed by a decrease of MeOH in the transformer oil. An equilibrium between the amount of MeOH in the oil and the paper will be reached depending on the temperature.

It seems like the MeOH content should be corrected (cfr. corrected water content in function of temperature).

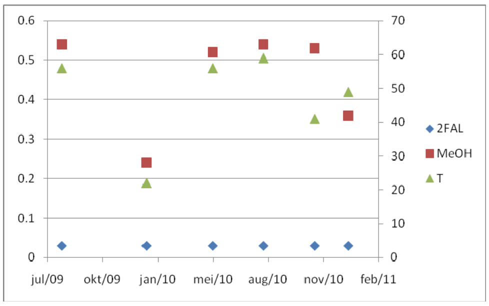

Figure 5: Temperature-dependency of MeOH equilibrium between oil and paper.

During another study it was shown that MeOH can be used as confirmation analysis for the 2FAL analysis. This phenomena was observed during the analysis of MeOH and 2FAL of oil samples from nuclear power plants. In oil samples with high amounts 2FAL, also high amounts of MeOH were observed (figure 6).

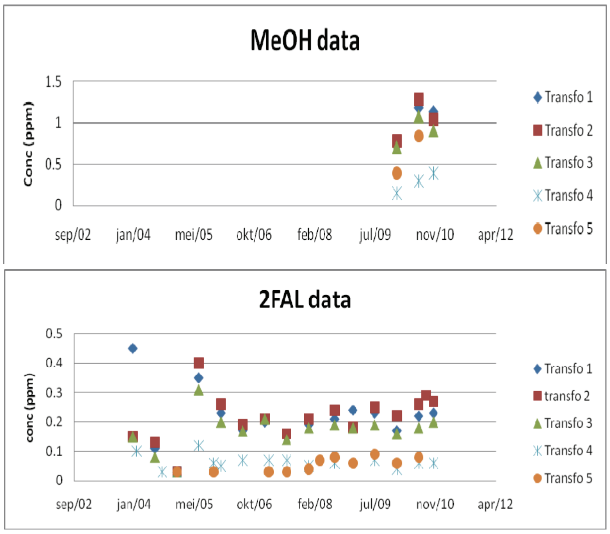

Figure 6: MeOH and 2FAL data for 5 power transformers. In transformers 1 and 2 the highest 2FAL amount was detected but also the highest MeOH concentration.

4. Conclusions

The aging of the solid insulation determines largely the end-of-life of a transformer. Currently some markers are used to estimate the evolution of the aging of the paper present in the transformer. The ratio CO_2/CO, measured by dissolved gas analysis, and 2FAL are the worldwide used. If the DP_v of the paper is decreased from 1200 to 500-700 or less, some furanic compounds like 2FAL are formed. In the earlier stages it is very difficult to know whether the paper has already started to age because of the non-linear correlation between 2FAL and DP_v, and because of the role of hemicelluloses in the formation of 2FAL. As a linear correlation between MeOH and DP_v exists, even at early stages, MeOH could be a very interesting chemical compound to indicate paper aging and could permit an easier estimation of the end-of-life of the transformer [5, 10, 11]. During some laboratory studies the stability of MeOH was shown and it also seemed that the formation of MeOH was only caused by the paper degradation, not by oil oxidation.

During this study oil samples of power transformers of several nuclear power plants have been periodically measured since mid 2009. For several GSU-transformers with a service time of more than 30 years very low to zero concentrations 2FAL were detected, while a significant larger amount of MeOH was observed in the oil. The detection of MeOH could reveal some paper degradation while 2FAL did not. In none of the GSU-transformers with a service life of approximately 4 years 2FAL could be detected while small amounts of MeOH were present, indicating some early-stage paper degradation. Therefore, these transformers are very useful to further investigate the correlation between MeOH and 2FAL once early paper degradation will occur. It is obvious that more data of the same transformers should be collected before any correlation or conclusion could be drawn. From these follow-up studies it is also clear that temperature will play an important role in the equilibrium of MeOH between the oil and the paper. An corrected value for MeOH dependent of the temperature is probably inevitable.

Furthermore it was clear that MeOH confirmed the 2FAL analysis and thus, paper degradation occurring in the transformer. In the 2 transformers with high amounts 2FAL, also the highest concentrations of MeOH were detected.

Overall, it could be concluded that MeOH is an excellent chemical marker for early-stage paper degradation in transformers with a service life of 2 to 4 years but also to confirm paper degradation occurring in transformers with a service life up to 30 years. As the 2FAL detection must be considered in perspective because of its several drawbacks, MeOH can confirm that paper degradation that is actually occurring in the transformer

BIBLIOGRAPHY

[1] Transformer oil handbook, Solid Insulation in Electrical Equipment, Nynas Naphthenics AB, 2004

[2] R. Tamura, H. Aneti, T. Ishii and T. Kawamura, “Diagnostic of aging deterioration of insulating paper”, JIEE Proc. A, 1981, Vol 101, pages 30-36

[3] P.J. Burton, J. Graham, A.C. Hall, J.A. Laver and A.J. Oliver, “Recent developments by CEGB to improve the prediction and monitoring of transformer performance”, Cigré Conf. Paper 12-09, 1984

[4] J. Jalbert, R. Gilbert, Y. Denos, P. Gervais, “Chemical markers for the determination of power transformer insulating life, a step forward”, Doble meeting 2009, paper IM-3, Boston, USA

[5] R. gilbert, J. Jalbert, S. Duchesne, P. Tétreault, B. Morin, Y. Denos, “Kinetics of the production of chain-ends and methanol from the depolymerization of cellulose during the aging of paper/oil systems. Part 2: thermally-upgraded insulating papers”, Cellulose, 2010, Vol. 17, pages 253-269

[6] X. Chendong, “Monitoring paper insulation aging by measuring furfural contents on oil”, 7th International Symposium on High Volt. Eng. (ISH) 1991, Germany, Dresden, pages 139-142

[7] A. Cheim, C. Dupont, “A new transformer aging model and its correlation to 2FAL”, Cigré Transformer Colloquium 2003, Mexico, Merida

[8] A. De Pablo, B. Pahlavanpour, “Furanic compound analysis : a tool for predictive maintenance of oil filled electrical equipment”, Electra, 1997, Cigré WG 15.01.03, N°175

[9] J. Jalbert, R. Gilbert, P. Tréteault, B. Morin, D. Lessard-Déziel, “Identification of a chemical indicator of the rupture of 1,4-β-glycosidic bonds of cellulose in an oil impregnated insulating paper system”, Cellulose, 2007, Vol. 14, 295-309

[10] R. Gilbert, J. Jalbert, P. Tréteault, B. Morin, Y. Denos, “Kinetics of the production of chain-end groups and methanol from the depolymerization of cellulose during the aging of paper/oil systems. Part 1: Standard wood kraft insulation”, Cellulose, 2008, Vol. 16, pages 327-338

[11] A. Schaut, S. Autru, S. Eeckhoudt, “Applicability of methanol as a new marker for paper degradation in power transformers”, IEEE Trans Dielectric Electric Insul., 2011, Vol. 18, pages 533-540