Relationships between Methanol Marker and Mechanical Performance of Electrical Insulation Papers for Power Transformers under Accelerated Thermal Aging

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ABSTRACT

The mechanical performance of two commercial papers used as solid insulation in power transformers, namely standard Kraft and a thermally upgraded Kraft paper, were studied during accelerated aging in Luminol oil at 170 °C. The results show a relationship between the degree of polymerization and the mechanical properties measured by tensile testing. A linear relationship was found between the mechanical properties of paper, the tensile index (Tidx), and the concentration of methanol present in the oil. The methanol chemical marker has been proven to be an accurate assessment tool for the aging of cellulosic paper.

The results show a promising tool for correlating the methanol concentration in oil, as an indirect indicator, with the mechanical performance of the paper. This approach can be used to monitor the real state of the cellulose chains in the power transformer insulation paper.

Index Terms – **Alcohol markers, mechanical properties, tensile index, power transformer, degree of polymerization, methanol, ethanol.**

1 INTRODUCTION

POWER transformers are the most important elements in modern electrical grid. They are vital assets as part of the electric power generating facilities worldwide.

The demand for electricity is continuously growing, thus resulting in a significant number of power transformers in service and being installed. Properly designed power transformers have an average service life of 25 to 35 years depending on loading, temperatures and maintenance. There are cases where power transformers with adequate maintenance can reach a lifespan of around 60 years [1]. However, several large power transformers built during the 60's and 70's are considered to be close to the end of their design life. From this perspective, it is necessary to develop accurate and reliable tools to assess and predict the evolution and remaining lifespan of power transformers and to avoid failures of old units with the resulting consequences.

These days, even with the continuous advance in power transformer control, automation and design, the general configuration of large power transformers, including their components and materials, remains almost unaltered from the first commercial versions. With respect to the transformer insulation system, inexpensive paper, pressboard and oil continue to be used as the elements that make up that part of the transformer. Oil impregnated paper has good electrical and mechanical properties which favor its use as insulating material. Its good dielectric strength is not affected even when the paper loses some of its mechanical performance [2].

Manuscript received on 6 May 2015, in final form 4 August 2015, accepted 13 August 2015.

DOI: 10.1109/TDEI.2015.005386

Multiple factors influence the lifespan of power transformers (electrical, mechanical and thermal stresses). These factors interact with the components of the insulation system, accelerating the normal aging of the oil and paper. Fortunately, the oil can be reclaimed or eventually changed when necessary without stopping the operation of the transformer.

However, the solid part of the insulation system (paper and pressboard) cannot be monitored or changed once the transformer is built. For this reason, paper composed mainly of pure cellulose is one of the most critical constraints for predicting and assessing the power transformer's remaining service life. Therefore, the lifespan of the solid insulation is particularly related to the overall effectiveness of the actual transformer.

Paper is basically a mat of cellulose fibers composed of bundles of cellulose molecules joined by hydrogen bonds that connect hydroxyl (-OH) groups among adjacent cellulose molecules. The cellulose molecule consists of a linear chain of glucose molecules joined by glycosidic bonds [3].

Paper is an anisotropic fibrous structure that has different regions (amorphous and crystalline) with different morphologies. This diversity produces variations during the measurement of mechanical properties. The mechanical strength of cellulose paper is a combination of different factors: the strength of the fibers (cellulose fibers and fibrils) and the strength of the fiber-to-fiber bonds. These interfiber bonds are arranged by the remaining lignin and hemicellulose that compose the paper. Based on these factors, the failure mechanics of paper develop through the following two tracks: the interfiber bonds fail in a weak bonded paper or individual fibers fail in a strongly bonded paper [4].

The pulp and paper industry is focused on bringing a final paper product with the most homogeneous characteristics, even if the paper is a porous, anisotropic material with an inhomogeneous structure. Nevertheless, at the macroscopic level, paper appears to be a continuous and ordered material.

At the molecular level, paper consists of an intricate and complex group of cellulosic fibers bound together by hydrogen bonds. During the manufacture of paper, local variations in the grammage (paper density), fiber orientation distribution, pore distribution and interfiber strength (bonded area among individual cellulose fibers) produce zones denoted as mesostructures. The mesostructures are niches where the paper will start to fail under mechanical stress [4].

This local effect needs to be added to the normal deterioration suffered by the cellulose fibers and interfibre bonding due to typical aging that affects the paper. In summary, the values obtained from the measurement of paper strength are averages. In contrast, the rupture of the paper is not controlled by the average values but by lower values detected in a specific region due to the local variations mentioned above [4].

Many studies have been reported that explore the progression of normal aging of the oil-paper insulation system. Although the aging of paper in oil is not yet fully understood, some of the mechanisms involved in the aging process have been described in the literature. Oxidation, thermal degradation and acid hydrolysis degrade or depolymerize cellulose simultaneously during the entire aging event. Among them, acid hydrolysis is considered to be the main mechanism responsible for cellulose aging [5].

Among the tools used to assess the condition of paper is the measurement of the degree of polymerization (DP_v, average number of glucose units per cellulose chain). This technique is accurate in evaluating the condition of paper. The mechanical strength of paper is related to the average DP_v. For new Kraft paper, DP_v ranging from 1300-1000 is measured; the mechanical strength is considered constant between 1000 and 500. After the DP_v drops to 500, the strength and DP_v decrease to show a linear relationship [2]. When the DP_v values are between 200 and 150, the paper cannot withstand additional mechanical stress (e.g vibration inside the transformer), even when its dielectric strength has not degraded. At this point the paper and the transformer itself are at high risk of experiencing a total failure.

Unfortunately, the main limitation of this technique is obtaining paper samples from an operating transformer. As a result of this situation, there are other indirect methods for monitoring the condition of paper. Dissolved gas analysis (DGA) is used to measure the concentration of carbon oxides generated by cellulose degradation. However, the generation of carbon oxides is not specific to cellulose since the long-term oxidation of oil also produces them [6]. Another current technique is the analysis of furanic composites. After a complex process, the glucose molecule, which is not soluble in oil, degrades into different types of furan derivatives. Some of these are available to be used as chemical markers based on their polarity and solubility in oil. 2-furaldehyde (2-FAL) is a specific furan chemical marker of cellulose degradation. A high concentration of 2-FAL indicates a high level of degradation in paper. However, some disadvantages of 2-FAL are its low sensitivity in the aging of thermally upgraded (TU) paper (more often used by new transformers), along with its exponential behavior. The 2-FAL concentration in oil shows a noticeable increase only with the extreme aging of paper ($DPv \leq 400$) [13].

In an effort to overcome these drawbacks, other chemical markers are being investigated. Methanol, which is found in oil, is an excellent aging marker for standard Kraft and TU papers. The generation of methanol is proportional to the scissions of the glycosidic bonds in the cellulose chain. Based on methanol levels, the condition of the paper can be tracked at every stage, from the initial state of aging to the end. Also, a relationship between the concentration of methanol in oil and the DP_v of aged paper within the transformer has recently been reported [7]. In the case of ethanol, its generation is related to a specific fault in the paper, such as a hot spot. However, even though DP_v is an excellent tool for assessing the condition of cellulose fibers in paper at the molecular level, no relationship has been found between the analysis of chemical markers and the ultimate mechanical properties of the paper; i.e. no macro scale analysis has been performed.

In the present work, two different types of papers, standard Kraft and TU Kraft paper, were studied under an accelerated aging protocol. In both cases, the levelling-off degree of polymerization (LODP), which corresponds to the length of the crystalline region (crystallite), was reached in order to obtain a full picture of paper aging. The relationship between the alcohol markers, DP_v and the mechanical properties of the oil-impregnated paper sample are presented.

2 AGING CELL SETUP

2.1 MATERIALS

In this study, the following materials were used to prepare the aging cells:

Inhibited iso-paraffin synthesized insulating fluid Luminol TR/TR-I (Luminol), by Petro-Canada, with an initial acidity of 0.001 mg KOH/g, was used to impregnate the paper samples. Due to a specific refining process, Luminol has a higher oxidation stability that produces less acidity than other mineral oils [8]. In addition, Luminol meets the Type I to IV performance requirements as required by the norm CSA C50-08 for oxidation stability.

The characteristics of the Munksjö (standard Kraft) and Rotherm (TUK) papers that were studied are presented in Table 1.

Table 1. Physical properties of the studied papers.

Name	**Munksjö EG**	**Rotherm CE**
Manufacturer	Munksjö AB	Tullis Russel
Type	Kraft (5A2-1H1)	Kraft TUK(Insuldur)
Grammage (g/m^2)	40	62
Thickness (µm)	50	75
N_2 (%)	0.04	1.15
H_2O (%)	1.25	0.96
DPv,o (Initial DP_v)	1222	1048
LODP	159	179

The paper samples were cut into 25.4 mm x 130 mm strips using a twin-blade cutter (TMI brand).

Homemade paper holders were used to keep the paper samples free of folds during the aging process. They were made using magnetic copper wire (type HF, AWG 14) to form coils and copper tubing (3.17 mm OD, 2.41 mm ID) to create the rest of the holder. Paper samples (13 per holder) were placed between the coil turns to allow oil to flow freely among the samples (Figure 1).

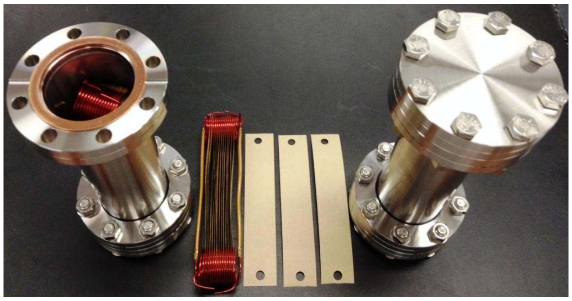

Figure 1. Aging cell and copper holder with paper samples.

The aging cells were created using assembly nipple spools, used for ultra-high vacuum applications (304L stainless steel cylindrical tube (diam. of 47 mm x 163 mm) from Kurt J. Lesker). In addition, the cells were made of two stainless steel vacuum flanges, two copper gaskets with a set of bolt and nuts (closed manually and then with a torque wrench) to close both sides. This setup (Figure 1) ensures hermeticity at high temperatures and prevents gas leakage from the aging cells [9]. The mass distribution of the materials inside the aging cells is presented in Table 2.

Table 2. Mass distribution of materials in aging cells

Name	**Munksjö EG**	**Rotherm CE**
Paper (g)	1.85	2.70
Oil (g)	225	225
Copper (g)	55	55
Ratio Oil/Paper	121.6	83.3

2.2 SAMPLES CONDITIONING AND AGING CONDITIONS

Both the paper and the oil were conditioned to equilibrium with dry air at 0.9% relative humidity (RH) inside a double glove box (Vacuum Atmosphere Company, model VTB 15x24) at 20.8°C before being introduced into the aging cells.

The holders with the paper strips were placed in the antechamber of a double glove box under vacuum atmosphere and at 40°C for 48 hours. This first step of the drying process reduces the original relative humidity (RH) of the paper from more than 1% RH to less than 0.5% RH. The paper samples were then moved from the antechamber to the glove box itself. There, the paper specimens were conditioned to reach the nominal 0.9% RH for at least one week. However, the absolute water content (%) was measured at the start of the aging experiments (see Table 1) according to ASTM D3277.

A glass bottle containing Luminol was also conditioned under constant agitation (via a magnetic stirrer) at atmospheric pressure in the glove box for at least 24 hours. When the oil and paper reached the required equilibrium, the stainless steel aging cells were introduced into the glove box. The holder with the paper specimens and 270 mL of oil (using a pipette) were added to each cell. An air blanket was left in the cell to compensate for the thermal expansion of the oil. The aging cells at air atmosphere were closed inside the glove box to avoid introducing external sources of humidity.

The stainless steel aging cells were placed inside an air-forced oven (Salvis lab, type tc-100s), and the temperature was maintained at 170 °C during aging. The cells were removed at different times for analysis. They were then cooled and maintained at 17 °C for 24 hours before extracting the oil aliquots for analysis. Once opened, the cells were not returned to the oven. The temperature of 170°C was selected because quick degradation would be noticed in paper. Moreover, it was demonstrated that the degradation is governed by a single reaction pattern, and the same mechanism and behavior of degradation of laboratory aging from 70 to 210 °C [10]. Therefore the use of accelerated aging test at a high temperature, 170 °C, is effective for estimating the insulation condition of normal operating transformers. An advantage of this new aging cell consists in an improvement in hermeticity tested at high temperatures. This closure, which prevents air from entering and the loss of volatile compounds, was an issue when glass aging cells were used in a preliminary aging study [9].

2.3 ANALYSIS TECHNIQUES

The following analysis and measurements were performed:

2.3.1 CHEMICAL MARKERS

Alcohol markers (methanol and ethanol) were analyzed using headspace gas chromatography with mass spectrometry detection A comprehensive description of the method is available at Jalbert et al. 2012 [11]. Oil aliquots (10 mL) were taken immediately after opening the aging cells to avoid the loss of volatile compounds.

2.3.2 OIL ACIDITY AND WATER CONTENT

Oil samples were analyzed to measure the neutralization number by titration according to ASTM D974 and to measure the water content in oil by coulometric Karl Fischer titration according to ASTM D1533.

2.3.3 TENSILE INDEX OF THE PAPER

The pulp and paper industries have adopted the concept of standard tensile strength for measuring the inherent strength of paper in order to evaluate end products for different applications. The tensile index (Tidx) is one of the standards used to measure the inherent mechanical properties of paper. The Tidx measures the force at break per unit of the width of paper divided by the specimen grammage. The grammage of paper (in g/m^2) is its density, i.e., its mass divided by a square meter of paper.

The tensile strength test was performed using ASTM D828 designed to assess the tensile strength of paper and pressboard at a constant elongation rate. The specific parameters needed to perform the test are listed in ASTM D828. The values used were for a specimen with a width of 25.4 mm and effective specimen length (grip separation at start of test) of 50 mm. A value of 50 mm was chosen instead of 100 mm to avoid an edge effect. The paper sample has two holes at each extremity for the copper holders. The nominal specimen length was 130 mm while the rate of grip separation during test was set to 7 mm/min.

Thirteen paper samples per aging point were measured; at least eight validated quantities were used to obtain an average value. The other values were rejected due to local failure and conditions from ASTM D828.

The tensile index of the specimen was measured using a tension tester machine (Testing Machine Inc Series 84-76). Before testing, the papers were de-oiled using a bath of distillated hexane, after which the papers were conditioned under air at room temperature (21 °C) inside a laboratory hood for at least 48 hours.

2.3.4 VISCOSIMETRIC DEGREE OF POLYMERIZATION

After the measurement of the tensile index, the remaining paper samples were collected and shredded to measure their degree of polymerization. The average viscometric degree of polymerization is based on ASTM D4243. Two measurements per analyzed point were performed to obtain an average value.

3 RESULTS AND DISCUSSIONS

Visual observation of the samples showed a change in color from an original light brown typical of Kraft papers to a dark brown color at the end of the aging. The software package "Curve Expert Professional v. 1.6.8" was used for curve fitting.

Figure 2 shows the evolution of the degree of polymerization and methanol concentration with the aging time for both types of paper. The aging duration for the standard Kraft and TUK papers was 784 and 1288 hours respectively for reaching their LODP values.

The DPv of the TUK paper decreased slower than for the standard Kraft paper due to the presence of the nitrogen containing thermally upgrading agent that slows down the aging mechanism. However, at a longer aging time, both papers reached a similar level of DP_v values.

The absolute values of the methanol concentration in the oil of cells containing TUK paper were higher than the values for the standard Kraft paper. This large difference occurred because the generation of methanol is directly proportional to the number of scissions in the cellulose chains. In the case of the TUK paper, its grammage or density is 50% greater than the standard Kraft paper; thus, more cellulose chains were accessible to be broken and to produce methanol molecules. To overcome this disparity, the methanol concentration values were normalized by their respective paper grammage, as shown in the figure. In addition, the differences in methanol concentrations can be explained by the partition effect [12]. A higher migration rate of methanol in oil was observed when TUK paper was used in comparison with standard Kraft paper. This phenomenon is probably due to the presence of nitrogen compounds in TUK papers that modify the partitioning of methanol between two phases [13], whereby differences in paper composition, humidity, etc. can also modify the migration behavior of methanol molecules from the paper to the oil.

In the very first part of the curves for methanol presented in Figure 2, a linear progression of methanol was assessed. This relationship agrees with the methanol generation model [13] that showed a direct relationship between the number of scissions of glycosidic bonds in the cellulose chains and the generation of methanol over time. At a certain point, the methanol production reached a plateau and stabilized. At that point, the degradation of the paper has reached more stable crystalline regions and the plateau in methanol behavior is expected because of the availability of the bonds. This behavior has been observed in previous studies [10], [13] and it could also be attributed to a modification of the methanol paper/oil partitioning due to a build-up of oil oxidative products in the liquid phase. However, this behavior has only been observed when the paper insulation has reached its end of life for an application in transformers.

Because the LODP was reached, this figure gives a complete representation of how methanol is generated, due mainly to the aging mechanics of acid hydrolysis.

The concentration of methanol allows the different aging steps to be tracked, from the initial rapid rate of degradation followed by the slow progression to a steady rate, in both standard Kraft paper and thermally upgraded Kraft papers. For the curve fitting of TUK of Figure 2b, three unusual and unknown high values of MeOH were not taken into account.

The generation of ethanol during aging was also measured but is not being presented here. Concentrations between 150 and 200 ppb were registered for both types of papers. These low values could be related to the absence of an abnormal aging event, such as a hot spot, during the experiment's duration [14]. The generation of ethanol was not affected by a higher grammage of the TUK paper or the additional nitrogen present in this paper.

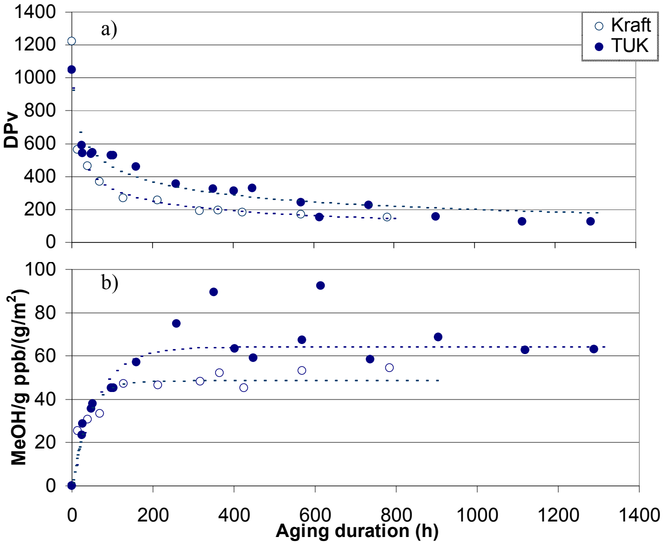

Figure 2. a) Evolution of the degree of polymerization and b) Generation of methanol in standard Kraft and TUK papers.

Figure 3 shows the correspondence between the degree of polymerization and the remaining percentage of the tensile index in both types of paper. The correlation curve appears in two distinct sections. In the first section, the degree of polymerization decreases without a very significant change in mechanical strength or tensile index of the paper. This behavior is in agreement with the initial accelerated loss of DP_v over time for both types of paper. The faster initial degradation is related to the amorphous regions of cellulose; i.e., due to their accessibility, they are easily degraded. The Kraft paper has a high degree of crystallinity and morphology [15]. Therefore, the papers maintain their mechanical properties at this level even if there is loss of DP_v. The first section of the curve implies that the mechanical performance is based mainly on the strength of the crystalline regions of cellulose and the fiber-to-fiber bonds. In the second section of the curve, a linear correlation was established between the DPv and the tensile index. The reduction in the degree of polymerization controlled the loss of the paper's mechanical strength; at this level of aging, most of the amorphous regions were degraded and the crystalline regions endured the aging process better. However, the presence of more scissions in the cellulose chains at the molecular level also has an impact at a macro level by decreasing the paper strength.

For both papers, the correlation converged into one curve. Even with the difference in composition and grammage, the correlation at the molecular level between the two parameters, Tidx and DPv, appears to be intrinsic. The final section of the curve reached values slightly lower than the LODP, around 160. At this level of degradation the mechanical performance of paper lost more than 80% of the initial value. Reaching LODP gives the full picture of the aging process; the degradation in this case was mainly driven by acid hydrolysis. At this point, the paper samples were very fragile and could not carry any large load. The loss of sample mass was negligible (the grammage of the dried and de-oiled papers was measured before and after aging), which indicates that the cellulose crystalline structures were present but had lost their ability to support an external load. However, even at this low mechanical strength level, the paper is expected to maintain its insulating strength [2]

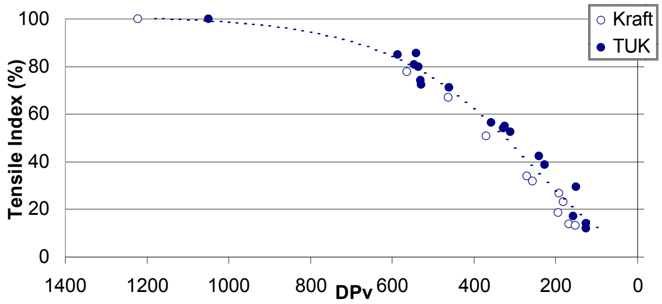

Figure 3. Correlation between tensile index and DP_v for standard Kraft and TUK papers.

Figure 4 shows the relationship between the average number of scissions (NS) in cellulose chains and the remaining tensile index in both types of paper. The NS was calculated as the division of **DPv,o** by the value of DP_v at different times minus one.

The progression in times of the NS and Tidx were opposite; when these two parameters are presented together, a linear correlation was found, as shown in a previous study [9]. This linear correlation relates the number of scissions in the cellulose chain with the mechanical performance of paper. The number of scissions increased linearly over time (not shown here) for both types of papers. In the case of the standard Kraft paper, the rate of degradation was higher than for the TUK paper. This difference was because the addition of extra nitrogen and higher grammage in TUK paper slowed down the aging process. However, after a longer aging period, both papers reached a similar average number of scissions per cellulose chain. The average number of scissions in cellulose that corresponds to a zone where the paper has lost its mechanical strength is NS ~ 5.5, where there is only 20% of initial paper strength, independent of the type of paper. Again, these two parameters with different levels of influence (molecular and macro level) show a direct relationship between them.

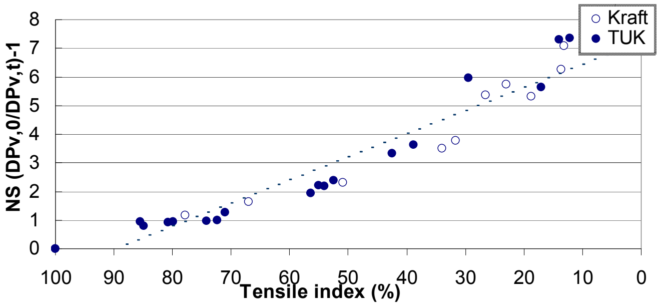

Figure 4. Relationship between number of scissions and tensile index of standard Kraft and TUK papers.

Figure 5 shows the correlation between the concentration of methanol and the evolution of the number of scissions. These correlations show linear behavior in the first part of the curve between these two parameters.

The methanol levels were normalized to compensate for the differing grammage for both papers. In this case, two curves were generated for each type of paper, even after the normalization by grammage. This difference in values can be attributed to the partition effect, whereby different conditions of the aging process such as composition, initial water content, cell internal pressure or other factors influence the migration of the methanol molecules from the cellulose to the oil.

For both papers (standard Kraft and TUK), an initial linear relation between the number of scissions and the normalized methanol is observed up to methanol values of ~ 50 ppb/(g/m²) for standard Kraft paper and 60 ppb/(g/m²) for TUK paper. A plateau is subsequently reached where the degradation of cellulose slows down and the concentration of methanol does not increase. This initial linear relationship was observed in a previous study [13].

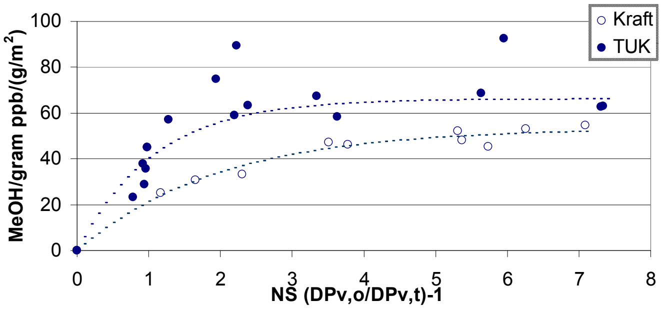

Figure 5. Correlation between the concentrations of methanol normalized by the grammage and the number of scissions of standard Kraft and TUK papers.

Figure 6 shows the relationship between the generation of methanol normalized by the paper grammage and the remaining percentage of the paper's tensile index. In both cases a linear relation was found as expected, based on the previous linear correlation between the concentration of methanol and NS and the correlation between the Tidx and NS. A previous attempt [9] to reach a distinct linear relationship between methanol and tensile strength was unsuccessful due to a leak of the volatile compounds, including methanol, from the aging cells.

Two quasi-parallel linear correlations were generated in this study for the standard Kraft and TUK paper; this difference can be explained by the effect of the partition phenomenon or migration of the methanol molecules from the paper to the fluid. However, the direct description of mechanical performance (macro level property) with a chemical marker at the molecular level is clear.

This relationship also proves the strong and reliable potential of using methanol as a chemical marker of aging in standard Kraft and TUK papers. This correlation should be further explored in order to determine its potential as a tool for assessing the condition of the paper in power transformers still in service.

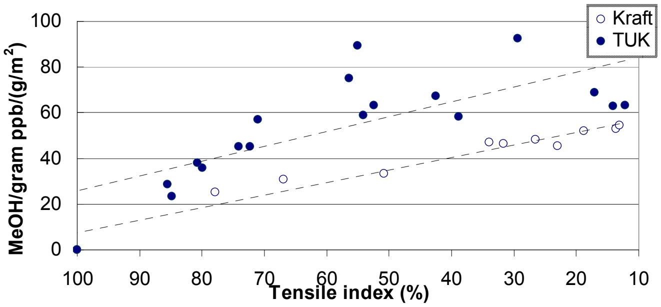

Figure 6. Correlation between the methanol concentrations normalized by paper grammage and the remaining tensile index of standard Kraft and TUK papers.

The evolution of the acidity and water in the fluid during the aging process was also analyzed. The values of acidity for both types of papers were evaluated as very low due in part to the fluid's high stability to oxidation. Indeed, the color and appearance of the Luminol is clear even after 1000 hours of aging at 170 °C. The effect of the low acidity in the paper can also explain the longer time needed to reach a complete degradation (DP_v of 200) of the samples in comparison with other studies in which the samples were impregnated with mineral oil. In addition, in this study the cells were filled to full capacity, compared to a binary atmosphere (gas/liquid) formed when mineral oil was used in [13]. The water content in the fluid was around 10 ppm for both types of paper. However, the water content was probably higher during the aging and decreased after cooling down migrating towards the paper. At these conditions, the mechanics of acid hydrolysis could also have been slowed down.

The 2-FAL analysis was also performed; however, 2-FAL could not be detected. This might be due to the fact that at this high temperature, the 2-FAL had further changed into another molecule, such as furan, which was observed for both types of papers. This hypothesis should be further studied.

4 CONCLUSIONS

Three linear relationships were established in this study. The direct correlation between the generation of methanol and the number of scissions proved that methanol is a robust indirect method for describing the condition of insulating paper. The second linear correlation showed that the number of scissions in cellulose chains has a direct impact on the mechanical performance of the paper. This correlation also shows a parameter measured at the molecular/micro level that can be used for assessing a property at a macro level. Finally, the correlation found between the methanol content in the fluid and the tensile index opens the door to a methodology for assessing the real condition of the paper in power transformers still in service. These findings should be complemented with post-mortem studies to validate the methodology. However, even during the accelerated aging of paper samples performed under laboratory conditions, the partition phenomenon plays an important role in the concentration of methanol in oil. This phenomenon explains how changes in parameters such as temperature, internal pressure, humidity, type of paper and oil, etc. can change the migration of the generated methanol from the scissions of cellulose chains to the oil.

More experimental accelerated aging that varies different parameters such as temperature, humidity and type of oil are needed to understand the impact of these changes in the evolution of the concentration of methanol as well as the phenomenon of partition.

The results support the main goal of this study, which is to use methanol as a tool for assessing the real condition of paper and its mechanical performance as solid insulation over time. Ultimately, it can help predict the lifespan of power transformers.

ACKNOWLEDGMENTS

The authors would like to thank Hydro-Québec and MITACS for supporting this project. They would also like to thank S. Duchesne, S. Gagnon, G. Girard and B. Morin from IREQ for their technical assistance.

REFERENCES

[1] M. Wang, A. J. Vandermaar, and K. D. Srivastava, “Review of condition assessment of power transformers in service,” Electr. Insul. Mag. IEEE, Vol. 18, No. 6, pp. 12–25, 2002.

[2] A. M. Emsley and G. C. Stevens, “Review of chemical indicators of degradation of cellulosic electrical paper insulation in oil-filled transformers,” IEE Proc. Sci. Meas. Technol., Vol. 141, No. 5, pp. 324–334, 1994.

[3] J. Unsworth and F. Mitchell, “Degradation of electrical insulating paper monitored with high performance liquid chromatography,” IEEE Trans. Electr. Insul., Vol. 25, No. 4, pp. 737–746, 1990.

[4] B. Shen, *Variation in the Local Structure and Properties of Paper*, Master's thesis of Applied Science , Department of Chemical Engineering and Applied Chemistry, University of Toronto, Canada, 2000.

[5] B. Noirhomme, M.-C. Lessard, J. Jalbert, S. Besner, F. Brochu, and E. Dupuis, “Influence of transformer oil acidity on insulating paper degradation,” IEEE Electr. Insul. Conf. (EIC), pp. 392–396, 2013.

[6] A. Schaut, S. Autru, and S. Eeckhoudt, “Applicability of methanol as new marker for paper degradation in power transformers,” Dielectr. Electr. Insul. IEEE Trans. on, vol. 18, no. 2, pp. 533–540, Apr. 2011.

[7] M. Bruzzoniti, R. Maina, R. De Carlo, C. Sarzanini, and V. Tumiatti, “GC Methods for the Determination of Methanol and Ethanol in Insulating Mineral Oils as Markers of Cellulose Degradation in Power Transformers,” Chromatographia, Vol. 77, No. 15–16, pp. 1081–1089, 2014.

[8] J. Jalbert, M.-C. Lessard, and M. Ryadi, “Cellulose chemical markers in transformer oil insulation Part 1: Temperature correction factors,” IEEE Trans. Dielectr. Electr. Insul., Vol. 20, No. 6, pp. 2287–2291, 2013.

[9] O. H. Arroyo, I. Fofana, and J. Jalbert, “Relationship between some Chemical Markers and the Mechanical Properties of the Solid Insulation used in Power Transformers,” IEEE Electr. Insul. Conf., Philadelphia, Pennsylvania, USA, pp. 348-352, 2014.

[10] J. Jalbert, E. Rodriguez-Celis, S. Duchesne, B. Morin, M. Ryadi, and R. Gilbert, “Kinetics of the production of chain-end groups and methanol from the depolymerization of cellulose during the ageing of paper/oil systems. Part 3: extension of the study under temperature conditions over 120 °C,” Cellulose, Vol. 22, No. 1, pp. 829–848, 2015.

[11] J. Jalbert, S. Duchesne, E. Rodriguez-Celis, P. Tétreault, and P. Collin, “Robust and sensitive analysis of methanol and ethanol from cellulose degradation in mineral oils,” J. Chromatogr. A, Vol. 1256, No. 0, pp. 240–245, 2012.

[12] J. Jalbert, M.-C. Lessard, and M. Ryadi, “Cellulose chemical markers in transformer oil insulation Part 1: Temperature correction factors,” IEEE Trans. Dielectr. Electr. Insul., Vol. 20, No. 6, pp. 2287–2291, 2013.

[13] J. Jalbert, R. Gilbert, P. Tétreault, B. Morin, and 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, Vol. 14, No. 4, pp. 295–309, 2007.

[14] E.M Rodriguez-Celis, J.Jalbert, S.Duchesne, B. Noirhomme, M-C Lessard, and M. Ryadi, “Chemical markers use for the diagnosis and life estimation of power transformers: a preliminary study of their origins,” CIGRE Conf., Montreal, Canada, 2012.

[15] M. Darveniza, D. J. T. Hill, T. T. Le, and A. K. Whittaker, “NMR relaxation behaviour of cellulose transformer insulation paper,” IEEE 4th Int'l. Conf. Prop. Appl. Dielectr. Mater., Vol. 2, pp. 784–787, 1994.

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