Aging of Transformer Insulation Paper

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AGING OF TRANSFORMER INSULATION PAPER

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ABSTRACT

As a transformer ages, the chemical and physical properties of the cellulose insulation materials in the transformer change, and the paper loses its strength and becomes brittle. The average molecular weight of the cellulose chains decrease with age, and degradation products are formed, including water, carbon monoxide, carbon dioxide, and furans. The molecular weight changes in the cellulose have been studied by several methods, but the GPC method for determination of the molecular weight has been shown to offer advantages over other methods because it yields the total molecular weight distribution. The tensile strength of the cellulose insulation in transformers also changes with age as a result of the changing molecular weight of the cellulose. Work carried out in our laboratory on the aging of cellulose insulation is reviewed in this paper. Our studies have included investigations of insulation materials from retired transformers as well as accelerated aging of insulation paper in transformer oil in the temperature range of 129–166°C under vacuum. In the study the relationships between the molecular weight of the cellulose and the furan degradation products and tensile strength have been

delineated, and they have been correlated with information on the kinetics of degradation of the insulation paper.

INTRODUCTION

Cellulosic materials have been used in the insulation systems of power transformers for a long time because they have been proven to have desirable chemical and physical properties coupled with low cost. However, over time the cellulose degrades, especially at higher temperatures and in the presence of oxygen. Therefore, the degradation of cellulosic materials is an important factor in determining the lifetime of a transformer. Typical operating temperatures for power transformers lie between 65 and 100°C, and they may be open to air. At these temperatures the cellulose insulation materials undergo slow degradation in air with a concurrent loss in mechanical and electrical properties.

Thermal aging experiments have been performed by many authors over the last few decades [1-9], and the results of these experiments have been used to make predictions about transformer lifetime. There have been several reports of accelerated aging experiments in the presence of air and oxygen [3, 4] or under vacuum [5, 6]. These experiments can be divided into two types: Long-term accelerated aging experiments conducted at low temperatures in the range 90-145°C [4] and short-term accelerated aging experiments conducted at high temperatures in the range 120-200°C [7].

Many previous studies of the kinetics of the degradation of cellulose insulation paper have been based upon measurements of the limiting viscosity number of solutions of a cellulose derivative, often the copper-amine complex. These measurements yield a viscosity-average molecular weight, M_v, for the aged cellulose. However, to obtain the rate of bond scission, it is the number average molecular weight, M_n, which is required, and this cannot be obtained from M_v. The viscosity method does not provide any direct information about the molecular weight distribution of the cellulose chains, which is now known to be important in the determination of many polymer properties, including tensile strength.

Molecular weight determination based upon gel permeation chromatography yields information about the complete molecular weight distribution of the cellulose chains present in the insulation materials in a transformer, and thus yields both M_n and M_w. It therefore provides a more detailed picture of the aging process for the cellulosic components of insulation materials.

The results of molecular weight studies on accelerated aging experiments which have been performed on Kraft paper immersed in transformer oil in the absence of oxygen at 130-170°C have been reported in detail [1, 2]. In addition to the molecular weight studies, the artificially aged paper has been analyzed by measuring the changes in its mechanical properties [8] (e.g., tensile strength), and the chemical degradation of the paper has been investigated through a study of the formation of furans [9]. The results of these accelerated aging studies have been compared with those found for papers retrieved from aged power transformers.

In this paper the results of these are reviewed, and correlations between the molecular weight (or degree of polymerization, DP) of the cellulose and the tensile

properties and the concentration of furans which are formed as degradation products are examined.

EXPERIMENTAL

Accelerated Aging Experiments

In this study a series of accelerated aging experiments were performed on dried Kraft insulation paper in the temperature range 130–170°C under vacuum in order to examine the thermal degradation process separately from the processes of oxidation and hydrolysis by water. This study will provide a basis for later studies on the effects of the presence of oxygen and water vapor on degradation kinetics.

A section of a new insulated conductor (20 cm) was placed in a glass ampule and evacuated at 80°C ($<10^{-3}$ torr) for 24 hours in order to remove any adsorbed air or water. Dried and degassed transformer oil (Shell Diala B) was then added to the ampule so that the conductor was completely immersed in the oil. The ampules were then further evacuated ($<10^{-3}$ torr) for 48 hours and sealed under vacuum. The accelerated aging experiments were performed at four different temperatures in an aluminum block heater for various time periods. After aging, the samples were allowed to cool to room temperature and removed from the oil. The paper samples and oils were then removed for chemical analysis.

Molecular Weight Analysis

Cellulose is not readily soluble in simple organic solvents. For this reason the cellulosic components of the insulation papers were modified to improve their solubility. Various modification procedures have been suggested, but the phenyl-isocyanate derivatives offer several advantages [2]. The procedure described by Evans [10] has been modified for use in preparing the tricarbanilate, CTC, derivatives of the cellulosic polymers present in Kraft paper. The procedure used was as follows: 40 mg of dry paper was placed in a 50-mL reaction bottle with 10 mL of dry pyridine, together with 1 mL of phenyl isocyanate, and was heated to 80°C for 40 hours. When the reaction time was complete, 1 mL of methanol was added to stop the reaction. The resulting clear, viscous solution was cooled, and the cellulose tricarbanilate was precipitated by adding the solution to 100 mL of stirred methanol. The cellulose tricarbanilate precipitate was collected by centrifugation of the sample for 5 to 10 minutes. Then the solid precipitate was further purified by dissolution in acetone, followed by precipitation in a water:methanol mixture (75: 25) and centrifugation to separate the precipitate. The cellulose tricarbanilate precipitate was collected and the solution discarded. The cellulose tricarbanilate derivative was then dried in a vacuum oven at 50°C overnight. For the GPC measurements the cellulose tricarbanilate samples were dissolved in tetrahydrofuran at a concentration of 0.1% w/v. The sample solutions were filtered through a 0.45-μm filter immediately prior to the GPC measurement.

The molecular weights of derivatized cellulose samples were determined using a Waters Associates Chromatograph equipped with two detectors connected in series; a variable wavelength Waters 484 tunable absorbance detector (wavelength

at 236 nm) and a differential refractometer Waters 410 detector (sensitivity range 256–512).

For the cellulose tricarbanilate samples, a set of four Ultrastyragel columns (10^3, 10^4, 10^5, and 10^6 A) was used in series at room temperature in the chromatograph, and tetrahydrofuran (THF) was used as the eluent. The Ultrastyragel columns were calibrated using a series of 12 monodisperse polystyrene standards in the 900 to 2 × 10^6 g·mol^{-1} range, and the molecular weight of cellulose tricarbanilate was calculated using a universal calibration [2].

Tensile Strength Analysis

Paper samples collected from new conductors, aged transformers, and accelerated aging experiments were treated according to ASTM D 685-87 and TAPPI T 402 standard procedures, with a minor modification for the aged transformer samples (which were very brittle). The paper samples, 5 mm × 10 mm, were conditioned for 24 hours by placing them in a desiccator which contained a saturated LiCl solution. This solution produced a relative humidity of approximately 45–50% in the desiccator.

The tensile strength tests were performed in an environmentally controlled chamber at 298 K and at a relative humidity of 45–50% using an Instron Universal Testing Instrument, model 1026. The tests were carried out with a crosshead speed of 1 mm/min. The tensile strength of the insulation paper was measured in the cross machine direction; this is, across the paper.

Furan Analysis

Several techniques have been used to extract the furan degradation products of cellulose insulation papers from insulation oil. In this work the method described by Carballeira [11] was used for the analysis because it was shown to give the most reproducible results.

HPLC chromatograms were obtained by using a Waters Associates Chromatograph equipped with a variable wavelength Waters 484 tunable absorbance detector. The wavelength was set at 280 nm for determination of furfuraldehyde and its derivatives and 210 nm for furanoic acid. A Waters Resolve C18 column (5 mm particle size, 3.9 mm × 150 mm dimension) was used for the analysis. The eluent used was an isocratic mixture of water and methanol (75/25). After each run the column was washed with 100% methanol for 30 minutes to remove any remaining residues from the column. The chromatograph was calibrated with six different, freshly distilled furfuraldehydes in methanol; 2-furfuraldehyde, 5-hydroxy methyl-2-furfuraldehyde, 5-methyl-2-furfuraldehyde, acetal-furan, furfuryl alcohol, and furanoic acid.

RESULTS AND DISCUSSION

Molecular Weight Changes

Figure 1 shows the GPC chromatogram of new and used cellulose insulation papers. The chromatogram of the cellulose new insulation paper shows the presence of two components. One component, at lower elution volume or high molecular
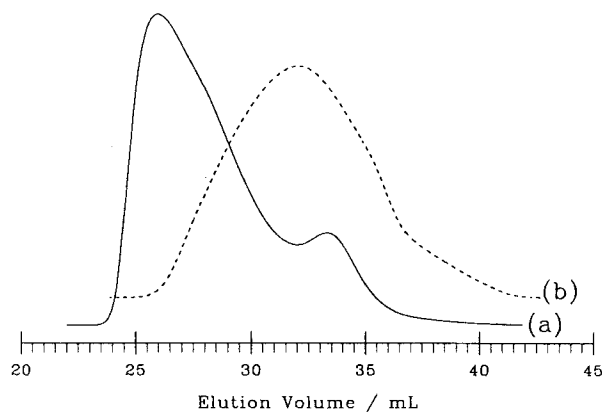
FIG. 1.   The GPC chromatograms of the CTC derivatives of new (a) and used (b) insulation paper.

weight, is due to cellulose, while the other component, at higher elution volume of lower molecular weight, is due to hemicellulose. In the chromatogram of the cellulose insulation paper taken from an aged transformer, the molecular weight of the cellulose component has decreased significantly. The molecular weight distribution of the cellulose has also broadened, and the peak due to the hemicellulose has become barely discernible, suggesting that the hemicellulose component of the paper may have been largely degraded.

Figure 2 shows chromatograms of cellulose insulation papers artificially aged at 411 K. They reveal trends similar to those observed for cellulose insulation papers obtained from aged power transformers (see Fig. 1). As the cellulose chains in
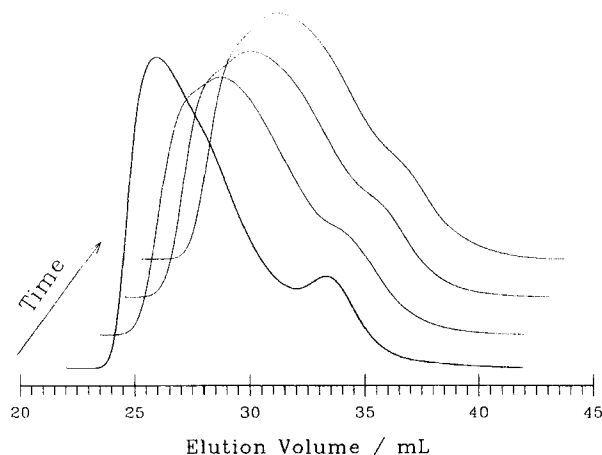
FIG. 2.   The GPC chromatograms of the CTC derivatives of insulation paper artificially aged at 411 K for 0, 14, 21, and 28 days.

the paper undergo scission, the number of polymer chains present increases. The concentration of the cellulose chains in the paper can be calculated from the GPC molecular weight distribution plot [2].

Various workers have developed kinetic models for chain scission to account for the observed changes in the average molecular weight (or average DP) of the cellulose. Some workers, for example, Shafizadeh and Bradbury [12], have reported that thermal chain scission in air or nitrogen at low temperatures follows a zero-order model, while others have suggested that cellulose degradation in transformer oil is best represented by a first-order model, for example, Emsley [13]. We recently showed [2] that the degradation reaction can be satisfactorily described by-zero order kinetics over the time periods of interest for estimation of transformer life-times.

Figure 3 shows the linear relationship obtained for the number of polymer chains per gram of paper (N_c) and the degradation time at 411 K. This relationship can be used to calculate the rate constant for chain scission (k). Values of k for a range of temperatures are given in Table 1.

An activation energy for chain scission in cellulose insulation paper of 79 ± 3 kJ·mol^{-1} was obtained from the temperature dependence of the rate constant [2]. This value is in close agreement with the value of 85 kJ·mol^{-1} previously reported by Fallow [14] and Bouvier [15] for the thermal degradation of cellulose.

Tensile Strength Changes

Figure 4 shows the nonlinear sigmoidal relationship observed between the tensile strength, σ, and the degree of polymerization, DP$_w$, of the cellulose, which was reported previously [8]. As the value of DP$_w$ decreases, the tensile strength of
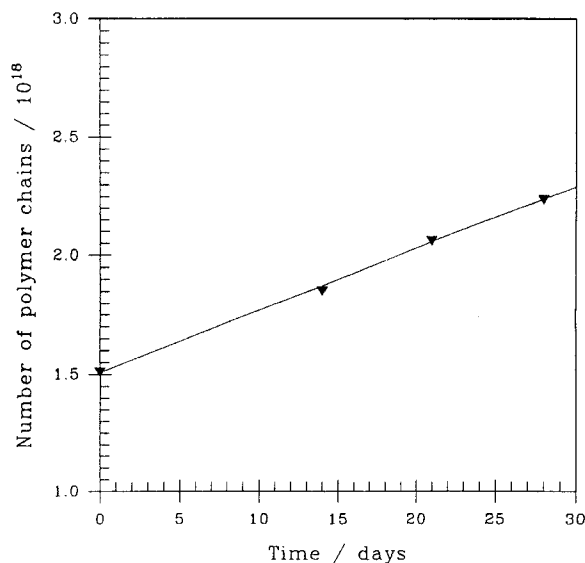

FIG. 3. Plot of the number of polymer chains (N_c) versus degradation time for insulation paper artificially aged at 411 K.

TABLE 1.   The Zero Order Rate Constants, k,
for the Degradation of Cellulose from Insulation
Paper at a Range of Temperature

Temperature (K)	k (10^{11} chains g$^{-1}\cdot$s^{-1})
402	1.5 ± 0.2
411	2.9 ± 0.6
426	6.1 ± 0.8
439	12.0 ± 2.0

the paper decreases. The tensile strength of the paper decreases slowly with decreasing DP_w until a critical value of about 500 is reached, when it drops dramatically. The tensile strengths obtained for paper samples aged at various degradation temperatures all fall on one master curve, indicating that the tensile strength depends on the final molecular properties of the cellulose in the paper and is independent of the degradation temperature.

A plot of $\ln(\sigma/\sigma_0)$ versus the concentration of polymer chains present in the paper, Fig. 5, is close to linear for data obtained over the range of temperatures, so the tensile strength of the paper can be expressed approximately in terms the exponential relationship:

$$\sigma/\sigma_0 = \exp(AN_c)$$

where A is a constant and independent of the degradation temperature over this range of temperatures.
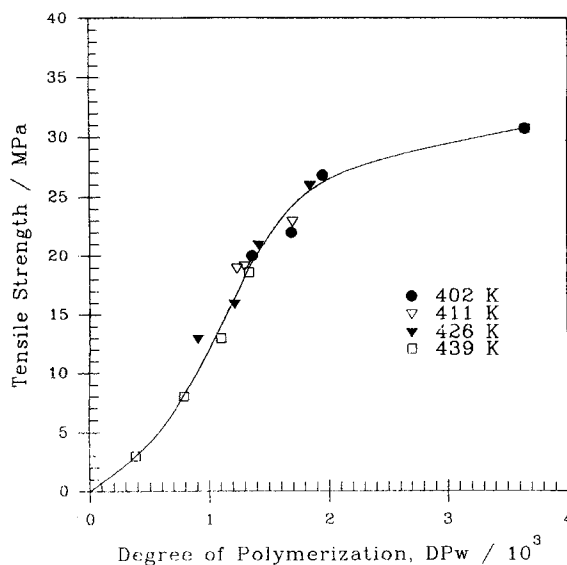

FIG. 4.   The relationship between the tensile strength and degree of polymerization, DP_w, for insulation paper artificially aged at temperatures in the 402–439 K range.
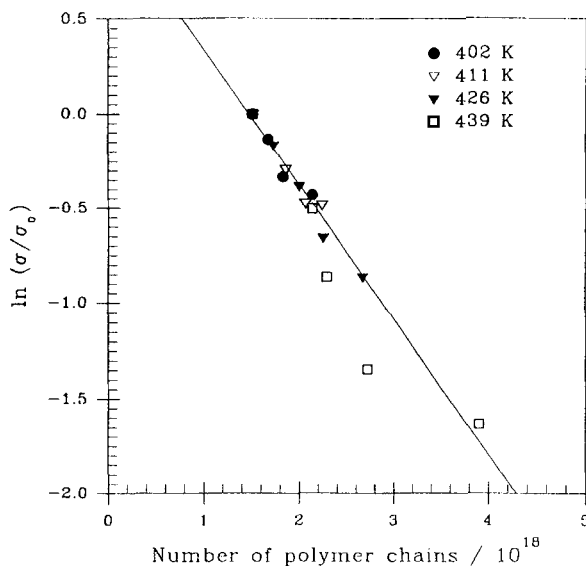
FIG. 5.   Plot of the logarithm of the relative tensile strength, σ/σ_0, versus the concentration of polymer chains, N_c, for artificially aged insulation papers.

This relationship suggests that the tensile properties of the paper are closely linked to the average molecular weight of the polymer chains, as has been reported for many other polymer systems. Thus it would be expected that the kinetics of the polymer chain scission reactions will determine the nature of the time dependence of the tensile properties of the insulation paper.

Furan Formation

Two furans, 5-hydroxy methyl-2-furfuraldehyde, HMF, and 2-furfuraldehyde, F, are present in the oil at significantly greater concentrations than any other furan [4]. 2-Acetal furan, AcF, and 5-methyl-2-furfuraldehyde, MF, have been reported to arise from the degradation of the hemicellulose components of the paper. The other two furans reported to be present in the oil obtained from operational transformers, furfuryl alcohol and furanoic acid, were not found in significant quantities in the oil used for the accelerated aging experiments in this study. This may be due to the absence of oxygen in the present study which was carried out under vacuum. The increase in the concentrations of the other four furans, HMF, F, AcF, and MF, with time are shown in Fig. 6 for a temperature of 411 K. The plots of all four furans show a distinct curvature, with the rate of furan formation increasing at longer degradation times.

Since the furans are believed to be the products of depolymerization of the cellulose chains, the rate of furan formation would be expected to be proportional to the concentration of chain ends in the polymer. An analysis of this model for furan formation has been presented elsewhere [9], and would predict a parabolic dependence of the furan concentration on time. Although the curves presented in
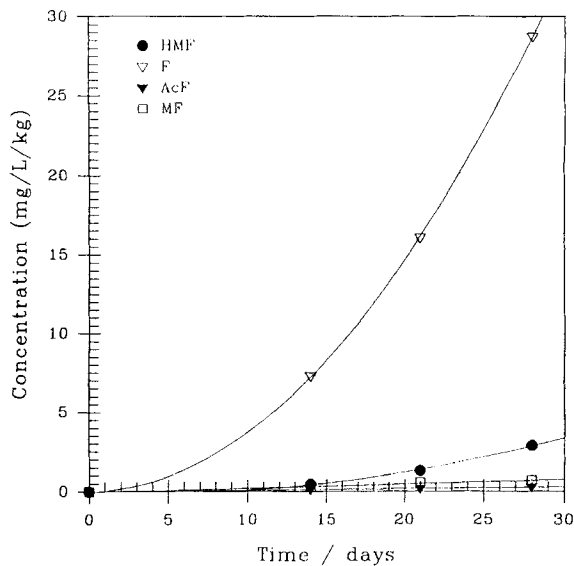
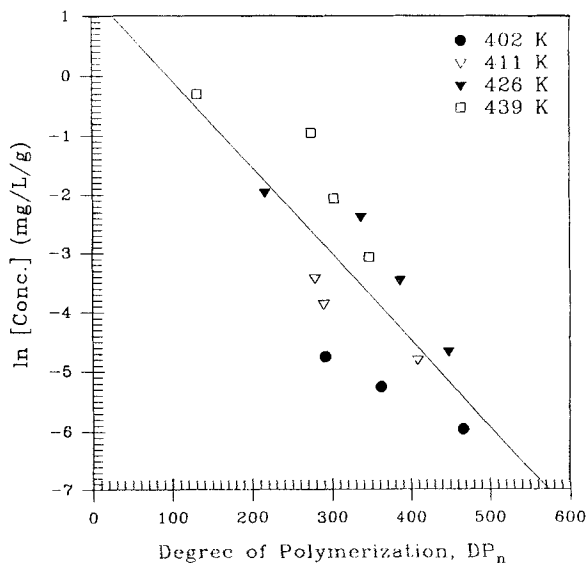**FIG. 6.** Plot of the concentration of furans versus degradation time at 411 K.

FIG. 7. Plot of the logarithm of the total furan concentration versus the degree of polymerization, DP_n, for insulation paper artificially aged at various temperatures.
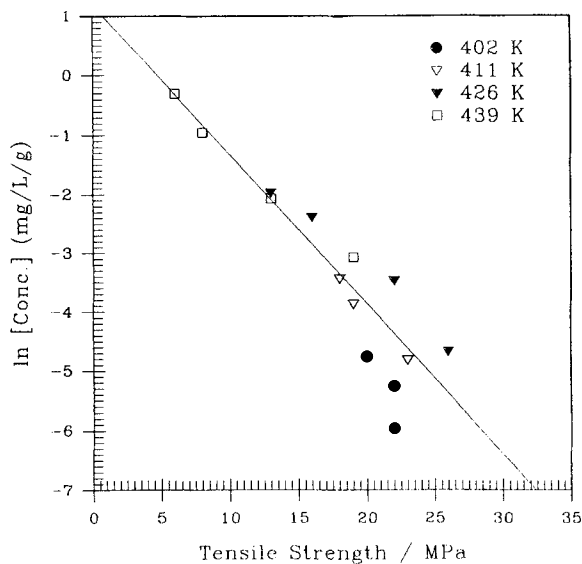
FIG. 8.   Plot of the logarithm of the total furan concentration versus tensile strength for insulation paper artificially aged at various temperatures.

Fig. 6 are parabolic, there is also evidence which supports a catalytic role for water, which is also a product of the degradation processes.

Several previous workers have observed a correlation between the furan concentration and the degree of polymerization of the cellulose, for example, Shroff and Stannett [3]. A correlation between the furan concentration and the tensile strength of the paper has also been reported in the literature, for example, by Mitchell and Unsworth [16]. Figure 7 shows the relationship between the total furan concentration and DP_n for degradation at 411 K, and Fig. 8 shows the relationship between the total furan concentration and the tensile strength of the paper at this temperature.

These plots are quite scattered, and this suggests that their use for the prediction of the molecular weight or tensile strength of the paper, based on furan analysis of the oil in a transformer, would be accompanied by a significant level of uncertainty in the results.

ACKNOWLEDGMENTS

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