

Reaction rates of paper aged in natural ester dielectric fluid

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Abstract: The aging rate of fluid-impregnated Kraft insulation paper varies with the dielectric fluid composition. Reaction rates of thermally upgraded paper aged in natural ester fluid (vegetable oil) are compared to those in conventional mineral oil. Rates are determined using tensile strength and degree of polymerization measurements of sealed aging systems at 130, 150, and 170°C. Rates obtained for mineral oil are compared to those found in previously published work. The aging rates obtained for natural ester are slower than those for mineral oil.

Introduction

Dielectric fluids based on natural esters (vegetable oils) have recently become commercially available [1-3]. Recent work examining accelerated aging in sealed systems indicates that Kraft insulation paper ages more slowly in a natural ester fluid than in conventional mineral oil [4]. The results obtained in [4] are used to estimate the thermal aging reaction rate of thermally upgraded Kraft paper insulation. Reaction rates in both the natural ester and mineral oil are determined. The rates obtained for mineral oil are compared to previously published sealed system thermal aging studies.

The extent of paper aging is determined using tensile strength and degree of polymerization (D_vP).

Experimental

The aging systems contained materials commonly used in liquid filled electrical power equipment. The materials and quantities are listed in Table 1. The total inner volume of the container included a 17% headspace at room temperature.

The moisture content of the paper was adjusted to about 0.5wt%, closely approximating the moisture level

Table 2. Times and temperatures of sealed vessel aging study.

Time (hrs)	Temperature			
	ambient	130°C	150°C	170°C
0	x			
500				x
1000			x	x
2000		x	x	x
4000		x	x	x

of processed paper used in the electrical industry. The materials in Table 1 were conditioned in open containers for a minimum of three days at 22°C and 50% relative humidity, then dried at 105°C for 2.5 hours. Upon removal from the oven, dried and degassed dielectric fluid was added at ambient temperature and pressure, followed by 30 minutes of vacuum processing at 500µmHg.

The vessels were sealed, degassed, and pressurized to eight atmospheres with dry nitrogen to test for leaks. The pressure was reduced to two atmospheres at room temperature prior to the start of the test. The vessel pressure is significant, because it maintains the pressure above the vapor pressure of water at 170°C, thus replicating the expected pressure ratio limit of some operating electrical devices. Base line values were measured at this point.

The sealed aging systems were placed in lab ovens upside-down so that the welded seam of the vessel was over the head space. The sealed systems were aged at 130, 150, and 170°C for 500 to 4000 hours. The selected aging times and temperatures are summarized in Table 2.

After the prescribed aging time, the systems were cooled to room temperature and opened. Moisture content of the fluid and the paper were measured separately, using ASTM methods D1533 and D3277 respectively. The paper tensile strength and D_vP were determined by ASTM methods D828 and D4243 respectively.

Table 1. Aging system components and quantities.

Material	Quantity
Upgraded Kraft Paper (0.255mm)	26 g
Dielectric Fluid	350 ml
Aluminum Strip	106 cm ²
Copper Strip	76 cm ²
Mild Steel Container	323 cm ²

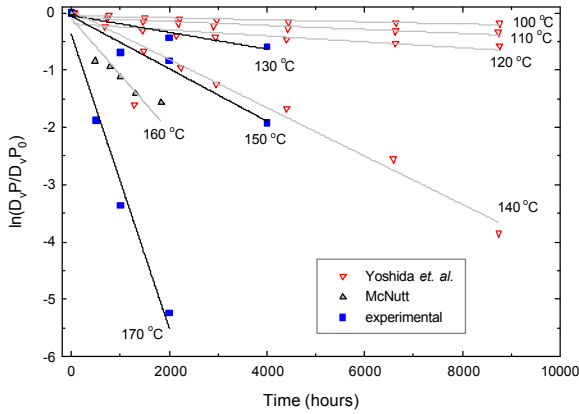


Figure 1: Degree of polymerization of thermally upgraded paper aged in conventional mineral oil. The data are plotted using first order kinetics. Previously published data are shown for 100, 110, 120, 140, and 160 °C.

Results

Degree of Polymerization

The D_vP results obtained in mineral oil are shown in Fig. 1 and compared to prior work [6,7]. First order reaction kinetics fit the D_vP data for mineral oil reasonably well. The results obtained here compare well with the previous work.

For paper aged in natural ester, second order reaction rates give a better fit compared to first order. Second order reaction rates are shown in Fig. 2.

Tensile strength

Only two rate data points could be determined. Tensile strength in both mineral oil and natural ester remained unchanged at 130 °C. This result is in contrast to previous work [6] showing mineral oil tensile strength decreasing at aging temperatures of 100, 110, and 120 °C for similar aging times.

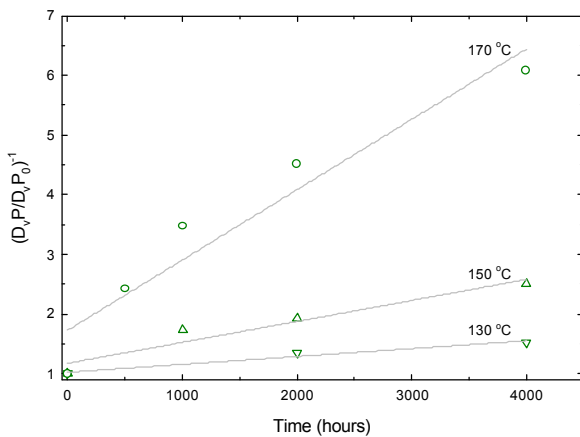


Figure 2: Degree of polymerization of thermally upgraded paper aged in natural ester fluid. The data are plotted using second order kinetics.

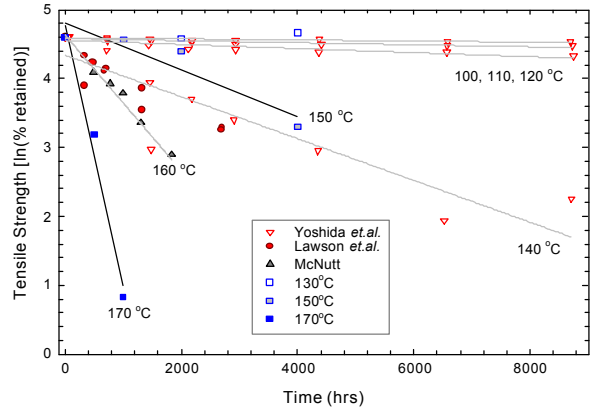


Figure 3: Tensile strength of thermally upgraded paper aged in mineral oil. The data are plotted using first order reaction kinetics. Previously published data are shown for 100, 110, 120, 140, and 160 °C.

The tensile strength aging rates obtained at 150 and 170 °C in mineral oil compare well with previously published work [5,6,7]. Although the rate at 150 °C falls in line with other data, the tensile strength itself changes less than in other work.

The aging rates are shown in Fig. 3-4. As in D_vP , first order kinetics are used for mineral oil aging and second order are used for natural ester.

Water content

Water content of papers (wt%) and fluids (absolute content and % saturation) at room temperature are shown in Table 3. At 130 °C and through 2000 hours at 150 °C, the papers in both fluids lose water as aging progresses. Only the mineral oil shows an increase in water content at 150 °C at 4000 hours.

At 170 °C, the water content of paper aged in mineral oil increases by 15 times at 1000 hours. The mineral oil becomes saturated by 500 hours and remains

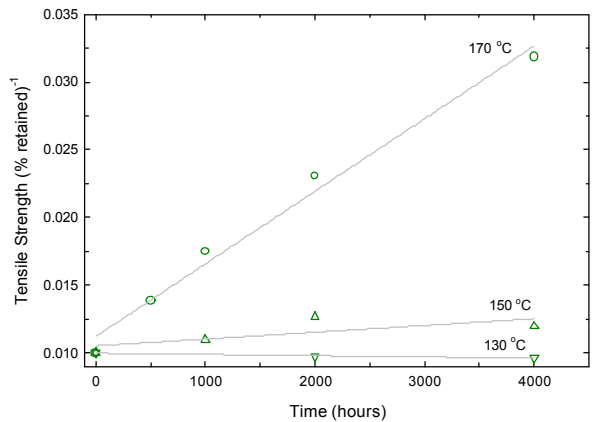


Figure 4: Tensile strength of thermally upgraded paper aged in natural ester. The data are plotted using second order kinetics.

Table 3. Water content of thermally upgraded paper aged in mineral oil and natural ester. Water content of dielectric fluid as absolute content and percent saturation.

Time (hrs)	130°C		150°C		170°C	
	mineral oil	natural ester	mineral oil	natural ester	mineral oil	natural ester
Water Content of Paper [wt%]						
0 ¹	0.46	0.51	0.46	0.51	0.46	0.51
500	-	-	-	-	1.46	0.15
1000	-	-	0.30	0.09	7.03	0.28
2000	0.03	0.10	0.23	0.08	3.28	0.26
4000	0.16	0.04	1.26	0.09	1.85	0.17
Water Content of Fluid [% saturation @ 20°C; (mg/kg)]						
0 ¹	5 (3)	3 (27)	5 (3)	3 (27)	5 (3)	3 (27)
500	-	-	-	-	167 (100)	2 (22)
1000	-	-	25 (15)	5 (54)	114 (69)	4 (39)
2000	11 (7)	1 (7)	10 (6)	1 (11)	105 (63)	10 (109)
4000	2 (1)	2 (20)	50 (30)	3 (28)	145 (87)	25 (258)

¹baseline values

saturated. The water content of paper aged in natural ester fluid decreases and remains constant. The natural ester fluid increases in water content to 25% of saturation at 4000 hours.

Rate determinations

The rate equations used are the first and second order chemical reaction rates. The aging rate at each temperature is determined using linearized rate equations (1,2) so that the rate equals the slope of a straight line fit. Results are shown in Fig. 5-6.

$$\text{First Order: } \ln(x) = \ln(x_0) - kt \quad (1)$$

$$\text{Second Order: } 1/x = 1/x_0 + kt \quad (2)$$

The aging rate as a function of temperature is determined by fitting the aging rates to a linearized

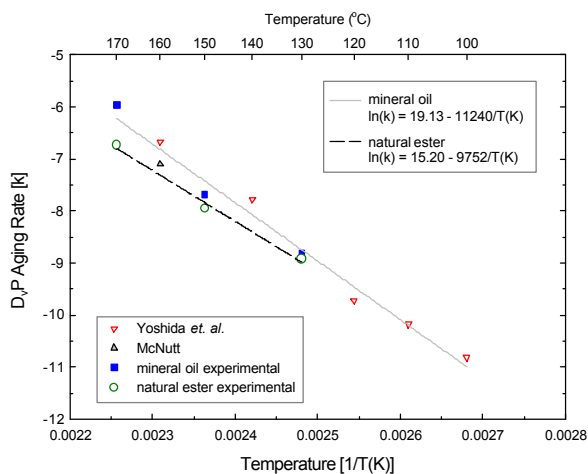


Figure 5 Degree of polymerization aging rate k as a function of temperature of thermally upgraded paper in mineral oil and natural ester fluid.

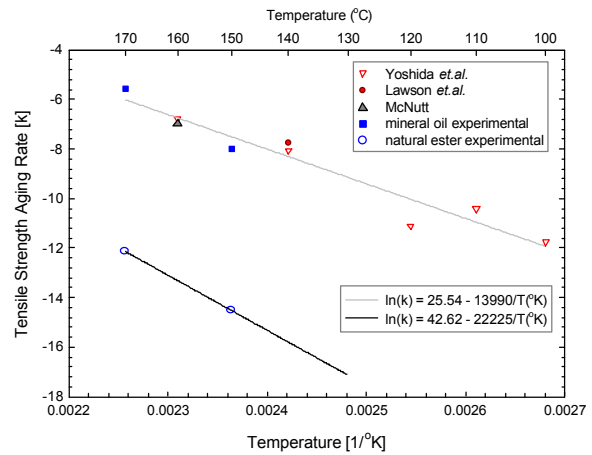


Figure 6. Tensile strength of thermally upgraded paper aged in natural ester fluid.

Arrhenius equation (3) using $\ln(k)$ and $1/T(^{\circ}K)$. The aging rate as a function of temperature is given by (4).

$$\ln(k) = a - b/T \quad (3)$$

$$k(T) = e^a \cdot e^{-b/T} \quad (4)$$

Fig. 6 shows good correlation between our mineral oil results and previous work. For natural ester, the tensile strength versus time shows slower degradation of paper compared to paper in mineral oil. However, the aging rate versus temperature can be determined using only two points. Although a slower aging rate for the natural ester is seen, additional tensile data is required to more reliably determine the $k(T)$ of paper in natural ester.

Insulation life comparisons

Using the $k(T)$ aging rates for D_vP and a paper life endpoint of $D_vP=200$, the time to end of insulation life versus temperature for thermally upgraded paper in natural ester fluid and mineral oil can be estimated. In this experiment, the initial D_vP is 1100. Using the reduced values of $DP=D_vP/D_vP_0$, the paper life as a function of temperature in mineral oil and natural ester is given by

$$\text{life}_{oil}(T) := \frac{\ln(DP_0) - \ln(DP_{end})}{\left[\left(e^{19.13} \right) \cdot e^{\frac{-11239}{T+273}} \right] \cdot 365 \cdot 24} \quad (5)$$

$$\text{life}_{ester}(T) := \frac{\frac{1}{DP_{end}} - \frac{1}{DP_0}}{\left[\left(e^{15.2} \right) \cdot e^{\frac{-9752}{T+273}} \right] \cdot 365 \cdot 24} \quad (6)$$

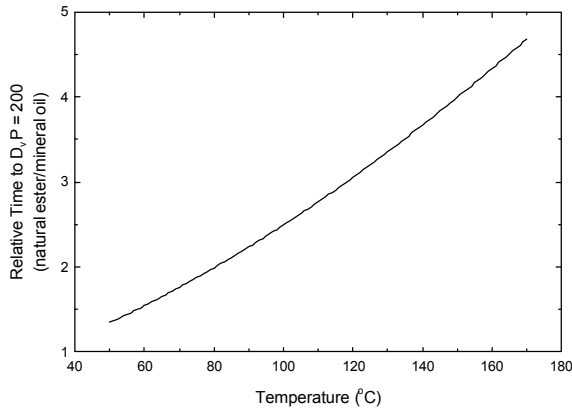


Figure 7. Calculated time to reach DP=200 of thermally upgraded paper aged in natural ester fluid and conventional mineral oil. The ratio of time in natural ester to time in mineral oil is plotted.

The ratio of time to DP=200 of paper in natural ester to that of paper in mineral oil is shown in Fig. 7.

Discussion

The water content results together with the reaction rate data clearly show the influence of water upon the degradation reaction rate of paper at elevated temperatures, particularly aged in mineral oil. In comparing the two different fluids, the reduced rate of paper degradation from thermal aging in natural ester fluid under similar initial water contents points to different chemical interactions between the two fluids, water, and thermally upgraded Kraft paper.

Paper degradation in a sealed thermal aging system is mainly a result of hydrolytic breakdown and thermal scission of the glycosidic bond [4]. Oxidation and other secondary reactions at the ring hydroxyls are also a factor. Key to all of the above is the available water, either present initially or generated from the degradation process. The availability of water and heat drives the reaction rate of cellulose. The slowing of the rate of reaction of paper in natural ester, or in other words, the improvement in paper life, is the result of the ester's ability to consume water [4].

In addition, we propose that further reduction in reaction rate of paper degradation in natural ester is due to the esterification of reactive hydroxyl groups via transesterification. The added stability of the bulky ester groups protects the polymeric chains and the ring, which are the backbone of the cellulose molecule.

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