# Aging of Paper Insulation in Natural Ester Dielectric Fluid

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Abstract: Aging of transformer insulation paper in natural ester (vegetable oil) dielectric fluid is compared to that in conventional transformer oil. Sealed steel aging vessels containing copper, aluminum, thermally upgraded paper, and dielectric fluid (mineral oil and natural ester) were aged at 130, 150, and 170°C for 500, 1000, 2000, and 4000 hours. Paper degradation after aging is determined using paper tensile strength and degree of polymerization measurements. The paper in natural ester aged at slower rates than did paper in conventional transformer oil, taking 5-8 times longer to reach end-of-life. Results obtained for mineral oil samples are similar to predictions based on IEEE transformer loading guide calculations. Mechanisms for the slower aging rate are proposed.

Keywords: aging, dielectric liquids, dielectric materials, insulation, insulation life, life estimation, oil insulation, paper insulation, power transformers, transformers.

# I. INTRODUCTION

Previously published work demonstrates the practicality of substituting natural ester dielectric fluid for mineral oil in liquid-paper insulation systems [1,2,3]. Previous experiments indicated a difference in aging rates between paper in natural ester and paper in mineral oil. This study was undertaken to better understand and quantify the insulation thermal life of thermally upgraded paper in natural ester.

The most significant characteristic used to assess transformer aging is mechanical strength of the paper insulation [4-7,10]. To determine aging rates in a practical amount of time, accelerated aging is used. According to the IEEE loading guide, accelerated aging in sealed systems best simulates real aging in modern sealed transformers [13]. Several sealed system accelerated aging studies have been published [5,9-12].

Paper aging depends primarily on temperature and water content. One of the first studies of insulation aging reported an exponential thermal aging rate that roughly doubled for each 8°C rise [4]. Later work applied chemical reaction rate theory to paper aging and refined the rate estimates [6,7]. Water content studies show the aging rate to be approximately proportional to water content [5,8].

In earlier studies of aged paper a common indicator of mechanical strength is tensile strength. For several decades, the degree of polymerization  $(D_vP)$  has also been used as a

means of indicating paper aging, and is one of the bases in the IEEE loading guide references to aging [8,13].

# II. EXPERIMENTAL

The aging systems contained materials in the same proportions as in a 225 kVA pad-mounted transformer. Each aging test vessel contained thermally upgraded 0.255mm Kraft paper<sup>1</sup> (26g), dielectric fluid<sup>2</sup> (350ml), aluminum metal strip (106cm<sup>2</sup>), copper metal strip (76cm<sup>2</sup>), and the mild steel inner surface of the aging vessel (323cm<sup>2</sup>). Headspace was set at 17% of total internal volume at room temperature. An aging vessel and its test materials are depicted in Fig. 1.

The moisture in the paper was adjusted to approximately 0.5wt%, representing nominal moisture content of paper in new transformers. The open systems were conditioned for a minimum of three days at 22°C and 50% relative humidity, then dried at 105°C for 2.5 hours. Degassed and dried



Fig. 1. Components of a sealed test system.

<sup>1</sup> Whiteley Ltd. Grade K T/U 0.255mm thermally upgraded Kraft paper <sup>2</sup> Ergon Hyvolt II inhibited insulating mineral oil, Cooper Power Systems Envirotemp<sup>®</sup> FR3<sup>™</sup> natural ester dielectric fluid

Table 1. Selected times and temperatures of sealed aging test using thermally upgraded paper.

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

dielectric fluid was added at atmospheric pressure, followed by 30 minutes 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. This maintained the vessel pressure above the vapor pressure of water at 170°C, replicating the expected pressure ratio limit in actual operating transformers. Base line values were measured at this point.

The aging systems were placed in lab ovens upside-down so that the welded end of the vessel was over the head space. The systems were aged at 130, 150, and 170°C for 500 to 4000 hours (Table 1).

## **III. RESULTS**

Tensile strength and degree of polymerization results for the paper aged in mineral oil (Fig. 2) are in good agreement with previously published work [8,9,11,12]. Fig. 3 shows paper after 4000 hours at 150 and 170°C. Visually, paper in natural ester showed noticeably less degradation than paper in mineral oil. Routine sample handling found the papers aged in mineral oil to be more fragile than those in natural ester.



Fig. 2. Tensile strength and degree of polymerization of thermally upgraded paper in mineral oil (sealed vessels at 130, 150, 170°C). Data at 160°C [12] included for comparison.



natural ester @ 150°C



Fig. 3. Thermally upgraded Kraft paper after 4000 hours.

At higher temperatures and longer times, the vessels containing mineral oil had a buildup of sludge and carbonaceous deposits on the walls. The vessels containing natural ester remained clean.

## A. Tensile Strength

Tensile strength results at 150 and 170°C are shown in Fig. 4. Paper aged in both mineral oil and natural ester exhibits no appreciable change in tensile strength at 130°C. At 150°C, the tensile strength of both papers drops slightly at 1000 and 2000 hours. At 4000 hours, the tensile strength of paper in mineral oil decreases to about 25% of initial strength. The tensile strength of paper in natural ester exhibits no appreciable change between 2000 and 4000 hours. At 170°C, the tensile strength of paper in mineral oil falls to about 25% retained strength at 500 hours, and loses its remaining strength at 1000 hours. The tensile strength of paper in natural ester does not drop to 25% retained strength until approximately 4000 hours.

# B. Degree of Polymerization

The  $D_v P$  data are shown in Fig. 5. In all cases, the  $D_v P$  of paper aged in mineral oil is lower than that in the natural ester. The paper aged at 130°C in both fluids did not reach 200 D<sub>v</sub>P. The paper aged at 150°C in mineral oil decreased to 200 D<sub>v</sub>P after 4000 hours. The paper aged in the natural ester decreased to 450 D<sub>v</sub>P in the same interval. The paper aged at 170°C in mineral oil reached 200 D<sub>v</sub>P after 500 hours, while the paper aged in the natural ester decreased to  $450 D_v P$ during the same interval.



Fig. 4. Tensile strength of thermally upgraded paper aged in mineral oil and natural ester dielectric fluids (sealed vessels at 150, 170°C).

## C. Water Content

Water contents of papers (wt%) and fluids (absolute content and percent saturation) at room temperature are shown in Table 2. At  $130^{\circ}$ C, the papers in both fluids lose water as aging progresses, while the water content of both dielectric fluids is nearly constant.

At 150°C, water content of paper aged in mineral oil increases between 2000 and 4000 hours. The water content of mineral oil also increased. The water content of paper aged in the natural ester decreases and remains constant. The water content of the natural ester remained practically unchanged.

At 170°C, water content of paper aged in mineral oil increases by an order of magnitude, peaking at 1000 hours. The mineral oil becomes fully saturated by 500 hours and remains saturated. The water content of paper aged in the natural ester decreases and remains constant. The natural ester increases in water content to about 25% saturation at 4000 hours.

## IV. DISCUSSION

The results obtained for paper in mineral oil correlate well with previously published work examining sealed system accelerated aging of thermally upgraded paper.

Both tensile strength and degree of polymerization are used to define "end of life" of paper insulation [12]. The current IEEE loading guide [13] suggests several "end-of-life" definitions, including 50% retained tensile strength, 25% retained tensile strength, and 200  $D_vP$ . Table 3 compares times to reach these end-of-life criteria for paper in mineral oil to paper in the natural ester.

The data in Table 3 shows that paper aged at 170°C in natural ester takes 5 to 8 times longer to reach standard endof-life criteria than paper aged in mineral oil. Paper aged at 150°C in mineral oil reached end of life points. However, paper aged at 150°C in natural ester does not reach any end-



Fig. 5. Degree of polymerization of thermally upgraded paper aged in mineral oil and natural ester (sealed vessels at 130, 150, 170°C).

of-life points, so a numeric differential cannot be calculated.

#### V. MECHANISMS

It is apparent from the results that the natural ester fluid significantly increased the thermal stability of the paper.

Table. 2. Water content of thermally upgraded paper aged in mineral oil and natural ester. Water content of dielectric fluid as absolute content and percent saturation.

	130°C		150	150°C		170°C		
	mineral	natural	mineral	natural	mineral	natural		
Time (hrs)	oil	ester	oil	ester	oil	ester		
Water Cont	ent of Pap	er [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)		

<sup>1</sup>baseline values

Table 3. Hours to reach insulation "end-of-life" of thermally upgraded Kraft paper aged in mineral oil and natural ester fluid. Time to insulation end-oflife calculated using IEEE C57.91 included for comparison.

		150°C			170°C		
	mineral	natural	IEEE	mineral	natural	IEEE	
End-of-Life Basis	oil	ester	Basis	oil	ester	Basis	
Retained Tensile Strength							
50%	3100	*	1602	240	1300	323	
25%	4000	*	3327	490	4000	671	
Degree of Polymerization							
200	3200	*	3697	480	3400	746	

\*Paper did not reach end-of-life over the duration of the test. To be conservative, extrapolation was not employed.

Paper is essentially cellulose, a linear polysaccharide consisting of many anhydro  $\beta$ -D-glucopyranose units linked to each other via a  $(1\rightarrow 4)$  glycosidic bond (Fig. 6) to form a polymeric chain. Many long oriented chains, arranged parallel to one another, make up the fibers that form the structure of paper.

The strength of paper is a result of the oriented linear chains and hydrogen bonding between the chains, which adds to rigidity. Degree of polymerization and tensile strength provide a relative indication of the number of intact molecular chains and the degree of hydrogen bonding between the chains. Reduction in either of these properties indicates that scission of these chains has taken place.

The principal reactive sites of cellulose are the secondary hydroxyl (OH) groups located at positions C-2, C-3, and the primary OH at C-6. These OH groups are involved in hydrogen bonding, which contributes to further reactivity at elevated temperatures [15]. Water migrates to these sites and disrupts the hydrogen bonds between the cellulose molecules, destabilizing the paper matrix. Paper degradation in a sealed accelerated thermal aging study is primarily a combination of hydrolytic breakdown and thermal scission of the  $(1\rightarrow 4)$ glycosidic bond [12,16]. Oxidation and other secondary reactions at the C-2, C-3, and C-6 hydroxyls are also a factor. The principal reaction products of thermal degradation are H<sub>2</sub>O, CO, CO<sub>2</sub>, and, to a lesser extent, furanic compounds. The latter result from chain scission followed by ring dissociation. The generation of water contributes to hydrolytic breakdown.

We propose that the improvement in the thermal aging characteristics of cellulose aged in the natural ester is the result of at least two modes of protection provided by the natural ester: water scavenging, and steric hindrance of the cellulose hydrolytic reaction.





## A. Water Scavenging

Water scavenging functions in two different ways.

1) At elevated temperatures the natural ester can undergo hydrolysis, consuming available water from the cellulose, thereby reducing the potential damage from water.

2) The natural ester can hold considerably more water than can mineral oil. The room temperature water saturation for the natural ester is about 1050mg/kg; mineral oil is about 60mg/kg. Because of the difference in saturation levels, the natural ester can absorb more water than mineral oil, and so has a greater paper drying effect. Research shows that removing water from the paper as it is generated improves paper aging characteristics [12,14,17].

## B. Hydrolytic Protection

The natural ester can interfere with the process of cellulose hydrolysis due to thermal stress. This is due to reaction of the natural ester with OH on the glucose ring and at chain terminations. The proposed mechanism is transesterification driven by the temperature conditions of accelerated aging [17]. The esterification of the reactive OH sites on cellulose with bulky ester groups stabilizes the molecule and extends thermal life [18].

# VI. CONCLUSIONS AND RECOMMENDATIONS

We find that thermally upgraded Kraft paper ages considerably slower in the natural ester dielectric fluid than in mineral oil under the same thermal stress.

Paper aged in the natural ester takes 5-8 times longer to reach the same end-of-life points as paper aged in mineral oil in sealed vessels at 170 C. Similar quantitative comparisons at the lower temperatures are not available, as the paper aged in the natural ester did not reach any standard end-of-life benchmarks within the 4000 hour test duration.

Preliminary calculations based on these data estimate that at 110°C, the time to end-of-life should be at least 2  $\frac{1}{2}$  times that of paper aged in mineral oil. We recommend that these results, along with additional data as it becomes available, be used to establish thermal aging equations and normal insulation life for thermally upgraded paper in natural ester dielectric fluids. This may result in transformer temperature rise ratings or overload levels higher than those recommended in standard loading guides for thermally upgraded paper in mineral oil insulation systems.

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#### VIII. REFERENCES

[1] C.P. McShane, G.A. Gauger, J. Luksich, "Fire Resistant Natural Ester Dielectric Fluid and Novel Insulation System for Its Use", IEEE/PES Transmission & Distribution Conference, Apr. 12-16, 1999.

[2] C.P. McShane, "New Safety Dielectric Coolants for Distribution and Power Transformers", IEEE Industry Applications Magazine, vol. 6, no. 3, pp. 24-32, May/June 2000.

[3] T.V. Oommen, C.C. Claiborne, "Biodegradable Insulating Fluid from High Oleic Vegetable Oils", CIGRE 15-302, 1998.

[4] V.M. Montsinger, "Loading Transformers by Temperature", AIEE Transactions, vol. 49, pp. 776-792, 1930.

[5] F.M. Clark, "Factors Affecting the Mechanical Deterioration of Cellulose Insulation", AIEE Transactions, vol. 61, pp. 742-749, 1942.

[6] T.W. Dakin, "Electrical Insulation Deterioration Treated as a Chemical Rate Phenomenon", AIEE Transactions, vol. 67, pp. 113-122, 1948.

[7] W.A. Sumner, G.M. Stein, A.M. Lockie, "Life Expectancy of Oil-Immersed Insulation Structures", AIEE Summer Meeting, Paper No. 53-243, Atlantic City, June 15-19, 1953.

[8] J. Fabre, A. Pichon, "Deteriorating Processes and Products of Paper in Oil. Application to Transformers", CIGRE Conference on Large High Voltage Electric Systems, Paper 137, Paris, 1960.

[9] W.G. Lawson, M.A. Simmons, P.S. Gale, "Thermal Aging of Cellulose Paper Insulation", IEEE Transactions on Electrical Insulation, vol. EI-12, no. 1, pp. 61-66, Feb. 1977.

[10] W.A. Fessler, F.S. Nichols, T.O. Rouse, "Tube Aging and Oxidation of Naphthenic and Paraffinic Transformer Oils", IEEE CH1287-2/78/0000-0265, 1978.

[11] H. Yoshida, Y. Ishioka, T. Suzuki, T. Yanari, T. Teranishi, "Degradation of Insulating Materials of Transformers", IEEE Transactions on Electrical Insulation, vol. EI-22, no. 6, 1987.

[12] W.J. McNutt, "Insulation Thermal Life Considerations for Transformer Loading Guides", IEEE Transactions on Power Delivery, vol. 7, no. 1, pp. 392-401, Jan. 1992.

[13] "IEEE Guide for Loading Mineral-Oil-Immersed Transformers", IEEE Std. C57.91-1995 (published 1996).

[14] R.D. Kremer, D. Tabb, "Paper: The Beneficially Interactive Support Medium for Diagnostic Test Development", American Laboratory, pp. 136-143, Feb. 1990.

[15] I. Rusznak, K. Zimmer, "Initial Processes in the Thermolysis of Cellulose Fibres", Proc. Hungarian Textile Conf. 18<sup>th</sup>, vol. 2, pp. 119-139, 1971.

[16] J. Xie, Y.L. Hsieh, "Enzyme-Catalysed Transesterification on Cellulose", Conf. Proc. ACS Polymeric Matls., vol. 82, pp. 406-407, 2000.

[17] M.R. Huang, X.G. Li, "Thermal Degradation of Cellulose and Cellulose Esters", J. of Applied Polymer Science, vol. 68, pp. 293-304, 1998.

[18] R.K. Jain, K. Lal, H.L. Bhatnagar, "A Kinetic Study of the Thermal Degradation of Cellulose and Its Derivatives", Makromol. Chem. 183, pp. 3003-3017, 1982.

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