Aging of Kraft Paper in Natural Ester Dielectric Fluid

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Abstract: Kraft transformer insulation paper aged in natural ester (vegetable oil) dielectric fluid was compared to identical paper aged in conventional transformer mineral oil. Sealed steel aging tubes containing copper, aluminum, Kraft paper, and dielectric fluid (mineral oil and natural ester) were aged at 150ºC for 500, 1000, 2000, and 4000 hours. The extent of paper degradation after aging was determined using paper tensile strength, paper degree of polymerization, and furanic compounds in the aged fluid. Water contents of fluids and paper were compared. Paper aged in conventional transformer oil degraded at a significantly faster rate than in natural ester dielectric fluid. Paper in mineral oil reached three criteria for IEEE end-of-life (50% retained tensile strength, 25% retained tensile strength, and degree of polymerization of 200) within the first 1000 hours. After 4000 hours of aging, paper in natural ester did not degrade to any of the IEEE end-of-life criteria. At 4,000 hours, the paper aged in natural ester retained about 55% of the original tensile strength and a degree of polymerization of about 280. Paper aged in conventional transformer oil degraded to the same values in about 315 and 390 hours, respectively - an order of magnitude faster. The reduced paper-aging rate in natural ester is primarily attributed to the fluid maintaining the paper in a very dry state.

INTRODUCTION

Natural esters (vegetable oils) formulated as dielectric fluids have environmental and fire safety advantages over conventional transformer mineral oil [1]. In thermal evaluation comparisons of transformer insulation systems, production distribution transformers filled with natural ester dielectric fluid exhibited less deterioration than did the corresponding transformers using mineral oil [2].

The environmental properties of natural esters are such that in Germany they are classified as "non-hazardous to waters" [3]. Aquatic biodegradation tests [4] of the natural ester dielectric fluid used in this experiment found >99% metabolized conversion to CO_2, equivalent to compounds defined as "ultimately biodegradable". In acute trout toxicity tests [5], the same fluid had no observable effect on fish at 1000mg/l, the highest concentration tested.

Transformers using natural ester fluids deliver very important improvements in fire safety compared to those using mineral oil. Natural ester dielectric fluids have fire points in the range of 350-360°C; conventional mineral oil has a fire point of about 155°C. Two natural ester dielectric fluids are recognized as "less-flammable" per Section 450.23 of the U.S. National Electrical Code® [6].

Accelerated aging tests of distribution transformers gave early indications that the rate of paper aging is fluid-dependent [2]. An earlier study quantified this dependence for thermally upgraded Kraft insulation paper [7]. This work examines the aging rate dependence on fluid type for plain (not thermally upgraded) Kraft insulation paper.

EXPERIMENTAL

The thermal aging procedure and sample preparation methods are identical to those previously described [7]. Sealed steel aging tubes contained 28.4g of Kraft insulation paper[1] dried to a water content of 0.76wt%, 350ml of dielectric fluid[2], and typical transformer proportions of copper and aluminum. The tubes were aged at 150°C and evaluated after 500, 1000, 2000, and 4000 hours.

The extent of paper aging was determined using changes in the tensile strength (TS) and the degree of polymerization (D_vP). The total concentrations of four predominant furanic products of paper degradation were measured in the aged fluids. The water contents of both the papers and fluids were also determined.

[1] Whiteley Ltd. Grade K 0.255mm presspaper
[2] Cooper Power Systems Tranelec® inhibited insulating mineral oil and Envirotemp® FR3™ natural ester dielectric fluid

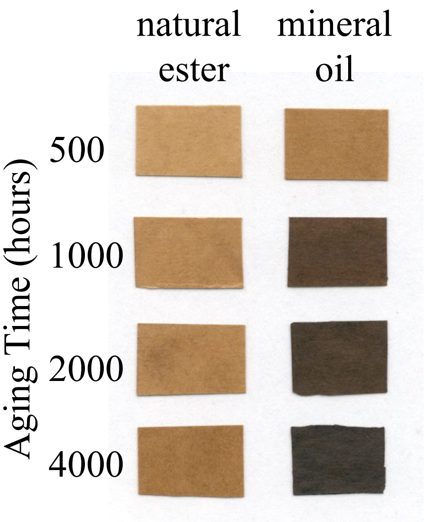

Figure 1. Kraft paper insulation after 150°C sealed tube aging in natural ester and mineral oil.

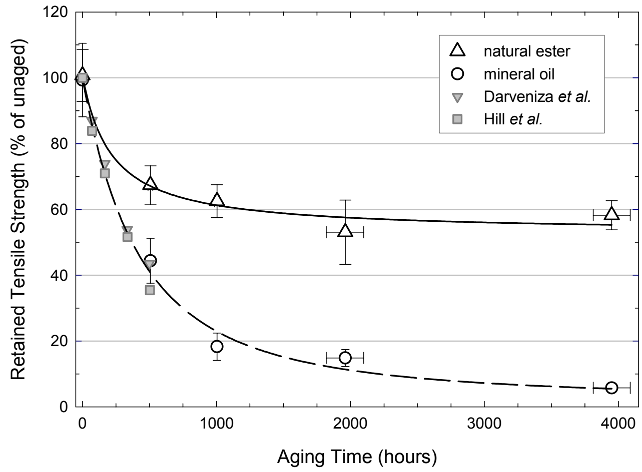

Figure 2. Retained tensile strength *versus* time for Kraft paper aged in natural ester and mineral oil. New paper tensile strength is about 120MPa. Vertical error bars are ± 1 standard deviation; horizontal error bars represent time-at-temperature uncertainty. Published retained tensile strength data [8,9] are included for comparison.

RESULTS

The results of aging at 150ºC, summarized in Table 1, show that paper insulation ages much slower in vegetable oil than in conventional transformer oil.

The difference in appearance between the papers aged in the two fluids is striking (Figure 1). At 1000 hours of aging, the paper in mineral oil was dark brown and brittle; the paper in the natural ester fluid remained flexible and was only slightly discolored. The 2000 and 4000 hour mineral oil papers were fragile and difficult to handle. This was not the case with the natural ester-aged papers. The color and fragility of the papers correlate well with changes in their TS and D_vP, and the proportional furanic difference between the two fluids.

Table 1. Results of Kraft paper sealed tube aging at 150°C in mineral oil and natural ester. Water content of dielectric fluid is given both as absolute content and percent saturation. Total furanic compounds are given as mg furans per liter of fluid per initial kg of paper.

Time (hrs)	0[1]	500	1000	2000	4000
Water Content of Paper [wt%]					
in mineral oil	0.76	0.67	2.44	3.39	3.36
in natural ester	0.77	0.27	0.21	0.04	0.05
Water Content of Fluid [% saturation @ 20°C; *(mg/kg)*]					
mineral oil	2 *(1)*	30 *(18)*	58 *(35)*	61 *(36)*	75 *(45)*
natural ester	2 *(24)*	9 *(89)*	11 *(116)*	2 *(21)*	2 *(25)*
Tensile Strength of Paper [MPa]					
in mineral oil	119	53.2	21.9	17.8	6.9
in natural ester	121	80.8	74.9	63.6	69.8
Degree of Polymerization of Paper					
in mineral oil	1119	217	110	75	12
in natural ester	1225	380	320	306	274
Furanic Compound Content [mg/l/kg]					
mineral oil	nd	1055	1462	670	602
natural ester	nd	191	234	151	62

[1]baseline values

Tensile Strength

The decrease in TS over time (Figure 2) shows a steep initial slope of paper degradation in both natural ester and mineral oil. The highest relative rate of paper degradation takes place in the first 500 hours of aging in both fluids. The relative rates in both fluids decrease substantially after 1000 hours.

In terms of absolute degradation, the paper in mineral oil, already below 50% retained TS at 500 hours, was below 20% retained TS value at 1000 hours. The decline in TS of the paper aged in mineral oil is comparable to that seen in other studies [8,9]. The paper aged in vegetable oil degraded to about 70% of its original TS at 500 hours. After 4000 hours, the retained TS was about 58%.

Degree of Polymerization

Another measure of cellulose degradation is degree of polymerization (D_vP). The change in D_vP over time is shown in Figure 3, and is similar to the change seen in TS. A rapid D_vP decrease in the first 500 hours of aging was observed. Paper aged in mineral oil degraded to about 20% of the

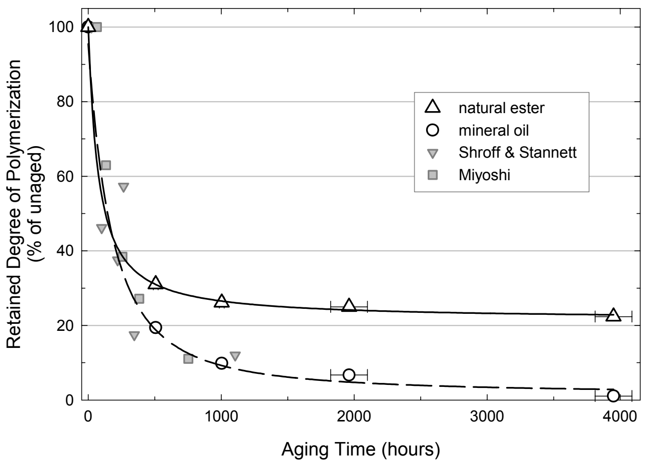

Figure 3. Retained degree of polymerization (D_vP) *versus* time for Kraft paper aged in natural ester and mineral oil. New paper D_vP is 1175 ±50. Horizontal error bars represent time-at-temperature uncertainty. Published retained D_vP data [10,11] are included for comparison (data attributed to Schroff & Stannett from [10]).

original D_vP at 500 hours, in line with other published results [10,11]. The retained D_vP of paper aged in natural ester fluid remained above 20% after 4000 hours of aging.

Furanic Compounds

Furanic compounds in oil are used to observe the insulation degradation of in-service transformers [12]. Figure 4 shows the concentrations of furanic compounds generated by paper degradation over time. The furan evolution from paper aged in the natural ester fluid was up to an order of magnitude lower than paper aged in conventional transformer oil.

The concentration of furans reached a maximum at 1000 hours in both fluids, supporting both the TS and D_vP findings. After 1000 hours, the concentration of furans in both fluids decreases.

Water Content

The water content of the paper in mineral oil increased significantly. The water content of the paper in natural ester decreased. By the end of the test, water content of paper aged in mineral oil was orders of magnitude greater than of paper aged in natural ester.

In mineral oil, the water content of the paper at 500 hours decreased slightly from the initial 0.75wt%. At 1000 hours, the water content increased to 2.4wt%, and continued to increase to about 3.3wt% for the remainder of the test.

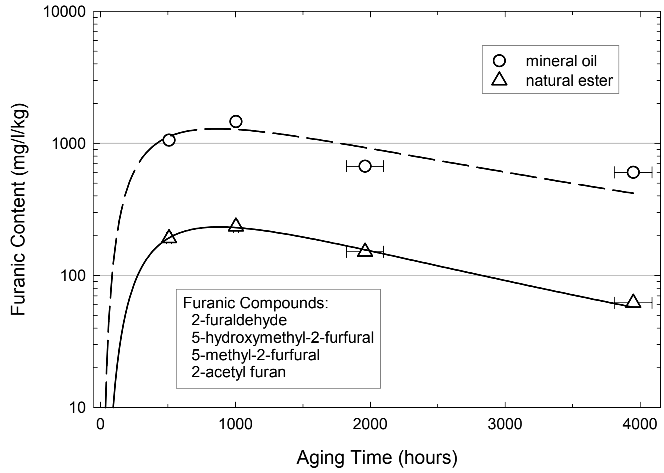

Figure 4. Furanic compound content *versus* time for natural ester and mineral oil after sealed tube aging of Kraft paper. Horizontal error bars represent time-at-temperature uncertainty.

The water content of paper in natural ester decreased to 0.27% after 500 hours and continued to decrease. At 2000 and 4000 hours, the paper contained about 0.05wt% water.

Similar trends were seen in the water content of the fluids (Table 1). Viewing the water content as percent saturation at room temperature, both fluids started with water contents of 2% saturation. The water in mineral oil increased steadily, reaching 75% saturation at 4000 hours. The water in the natural ester rose gradually to 11% saturation at 1000 hours, then decreased to 2% saturation at 2000 and 4000 hours.

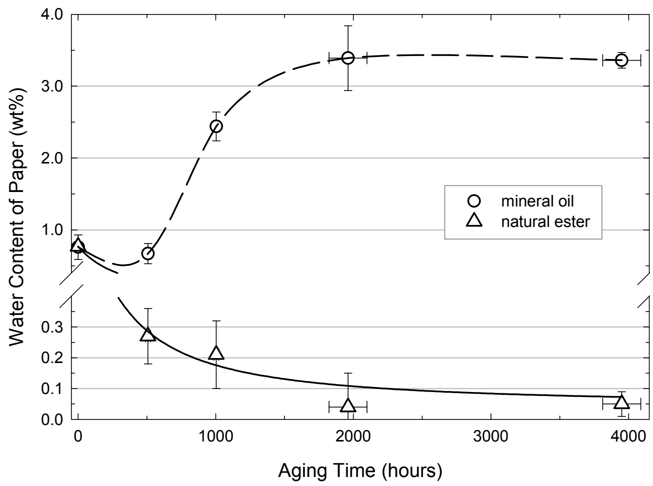

Figure 5. Water content *versus* time for Kraft paper aged in natural ester and mineral oil. Paper was originally dried to a water content of about 0.76wt%. Vertical error bars are ± 1 standard deviation; horizontal error bars represent time-at-temperature uncertainty.

DISCUSSION

The TS, D_vP, and furanic content results establish that paper ages slower in natural ester dielectric fluid than in conventional transformer oil. The paper aged in mineral oil degraded beyond three recognized IEEE end-of-life criteria [13]: 50% TS at 370 hours, 25% TS at 915 hours, and D_vP=200 at 555 hours. At 4000 hours, the paper aged in the natural ester fluid did not reach any IEEE end-of-life conditions.

In both systems, the concentrations of furanic compounds rose to a maximum, then decreased, maintaining a factor of 4-10 times more furans in mineral oil. The furans themselves decompose over time. Although the furanic contents of both fluids decrease in a similar way, the rationale for the reduction is different for each fluid. In the case of paper in mineral oil, more of the cellulose was destroyed and converted to furanic products. In the natural ester fluid, less cellulose aging took place to produce furanic compounds.

The water in paper data suggest an explanation for the contrast in paper degradation seen between fluids [12]. The acceleration of aging due to water has been known for at least 40 years [14]. As paper thermally degrades it produces water, promoting further degradation through hydrolysis. In a conventional transformer paper-in-oil system, the degradation is autocatalytic [15]. The partitioning of the water between the paper and fluid depends on the characteristic polarity (affinity for water) of each.

An essentially non-polar fluid, such as mineral oil, prevents most of the water generated during cellulose degradation from leaving the paper. Although the water content of the mineral oil steadily increased to 75% saturation at 4000 hours, this is only 45mg/kg in terms of absolute water content. The paper also was at approximately 75% water saturation.

The opposite effect is seen for paper in the more polar natural ester. The natural ester has a higher affinity for water than mineral oil. The water, attracted to the ester fluid, is liberated from the paper. Removing water from the paper limits the paper degradation rate.

The water generated during cellulose degradation migrates out of the paper and into the natural ester. One would expect the water in natural ester to increase proportionally. However, the natural ester remains dry at less than <2% saturation.

Since the aging tube is sealed, water cannot escape. The water is consumed in a hydrolysis reaction with the natural ester. The reaction produces long-chain fatty acids. These fatty acids react with the cellulose in a transesterification reaction [16]. This reaction results in steric protection of the cellulose sites most susceptible to attack, a consequence of which is reduced degradation by water [7].

At room temperature, natural esters can hold about 18 times more water in solution than can conventional transformer oil. The electrical strength of a dielectric fluid depends on the percent saturation of water, not the absolute water content. The electrical strength decreases above 50% saturation, about 30 mg/kg in mineral oil and 550 mg/kg in natural esters.

The temperature at which bubbles evolve from an insulation system strongly depends on the water content of the paper [17]. For paper having 3.3% water content (in mineral oil at 2000 and 4000 hours), the equivalent bubble evolution temperature would be about 125°C. For paper having 0.05% water content (in natural ester at 2000 and 4000 hours), the bubble evolution temperature would be >200°C [17].

CONCLUSIONS

These results show that Kraft insulation paper takes at least an order of magnitude longer to reach IEEE end-of-life conditions in natural ester than in conventional transformer oil. Applying natural ester dielectric fluids in transformers should result in improved insulation performance.

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