

Interaction Mechanisms of Natural Ester Dielectric Fluid and Kraft Paper

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Abstract: Sealed tube accelerated aging studies demonstrate a slower aging rate for cellulose insulation in natural (vegetable oil) ester dielectric fluid compared to the rate in conventional transformer oil. The interactions of natural ester fluid and cellulose insulation resulting in increased paper life are described by two interrelated chemical reaction mechanisms. Compared to the conventional transformer oil/Kraft paper system, the natural ester fluid's greater affinity for water shifts more water from the paper into the fluid in order to maintain equilibrium. The natural ester fluid reacts via the primary mechanism of hydrolysis to consume dissolved water in the fluid, shifting further the paper/fluid equilibrium to further dry the paper and produce free fatty acids. These fatty acids serve as reactants in the secondary mechanism of transesterification to modify the cellulose structure. The change in cellulose structure is verified using infrared analysis.

INTRODUCTION

Multiple sealed tube aging studies demonstrate that, under identical conditions, Kraft paper insulation ages significantly slower in natural (vegetable oil) ester fluid than in conventional transformer oil [1-4]. Multiple and interrelated mechanisms have been proposed to explain the increase in paper insulation life [1].

PROPOSED MECHANISMS

Kraft paper insulation aging rates increase with both increasing temperature (thermo-kinetic degradation) and increasing water content (thermo-hydrolytic degradation) [5]. The primary and secondary mechanisms hypothesized to be responsible for the different aging rates are related to differences in how natural ester fluid and transformer oil interact, physically and chemically, with water. The primary mechanism is a net movement of water generated by paper aging from the paper into the natural ester fluid followed by hydrolysis of the ester. The secondary mechanism is the reaction of the hydrolysis products with the cellulose resulting in protection of vulnerable sites on the cellulose chain.

Equilibrium Shift

Water moves between the paper insulation and dielectric fluid trying to reach equilibrium in terms of relative saturation. Fig. 1 shows that the natural esters can accommodate more water than conventional transformer oil [6,7]. This difference causes an equilibrium shift toward the natural ester fluid. That is, more water must be transferred from the paper to the fluid

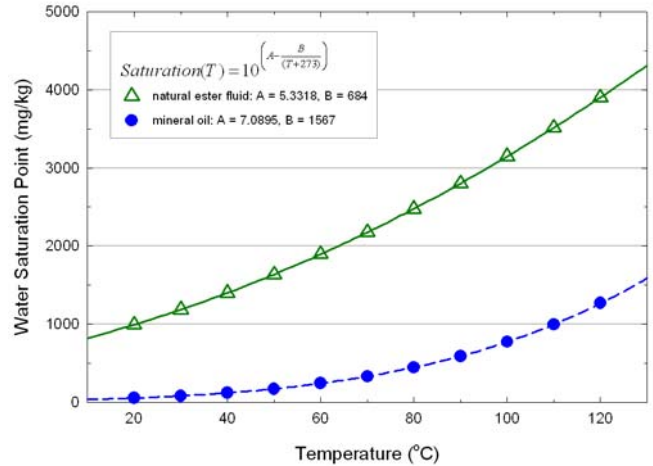


Fig. 1. Water saturation versus temperature for natural ester fluid and conventional transformer oil [6,7].

in order to reach and maintain equilibrium. Fig. 2 shows Kraft paper aged in natural ester fluid and conventional transformer oil, and is typical of a variety of papers aged in these fluids [1-4]. The paper aged in natural ester fluid remains dry, while the water content of paper aged in conventional transformer oil rises to above 3 wt%. As paper breaks down and produces water as a product of degradation, the natural ester fluid absorbs more of the water compared to conventional transformer oil (Fig. 3).

Hydrolysis

Water reacts with the triglycerides comprising the natural ester via hydrolysis to produce long-chain fatty acids (Fig. 4).

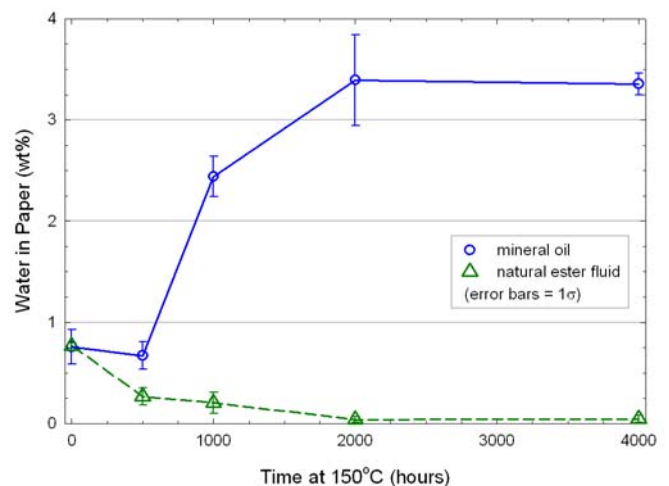


Fig. 2. Water content of Kraft insulation paper aged in natural ester fluid and conventional transformer oil [2].

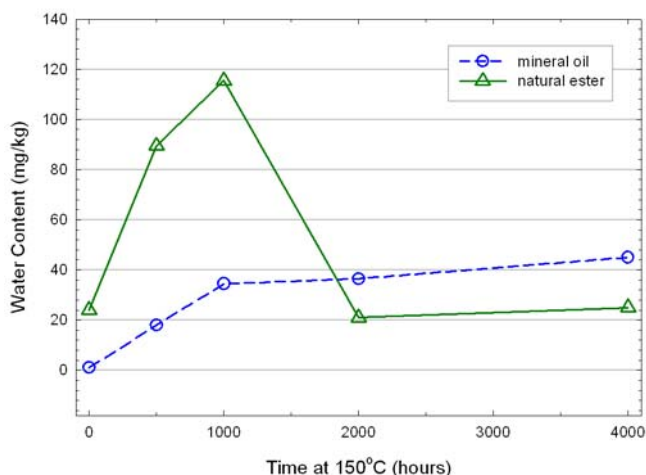


Fig. 3. Water contents of natural ester fluid and conventional transformer oil after accelerated aging [2].

The reaction consumes dissolved water in the fluid causing additional water to move from the paper into the fluid in order to maintain equilibrium.

Transesterification

A secondary mechanism appeared to be theoretically viable and was indirectly supported by the initial data. The acids produced by hydrolysis react with the cellulose via transesterification. Under accelerated aging, the reactive OH (hydroxyl) groups on the cellulose molecule become esterified with fatty acid esters. This reaction takes place at lower temperatures, but of course at slower rates of reaction.

There is significant evidence that long chain fatty acids can be esterified onto cellulose [8-14]. One study used mixed fatty acids from hydrolyzed soybean oil, reactants similar to those that might be found in natural ester dielectric fluids, to esterify cellulose [8]. To obtain a reasonable degree of substitution within a 24-hour time frame, cellulose was typically activated with either mild acid or base and the

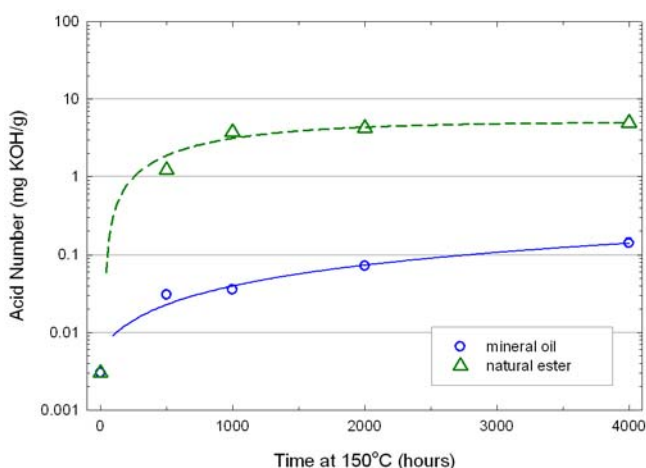


Fig. 4. Acid numbers of natural ester fluid and conventional transformer oil after accelerated aging [2].

esterification was done with fatty acid chlorides, anhydrides, carboxylic acids, etc. The reactions were run at temperatures of 60 to 90°C to obtain substitution, but avoid depolymerizing the cellulose chains. It is reasonable to assume that higher temperatures would drive a transesterification reaction directly between cellulose and less active long-chain fatty acid esters, such as those of natural ester fluids. The esterification of Kraft cellulose almost certainly progresses after the natural ester fluid penetrates the cellulose and hydrolyzes with available water.

ANALYSIS

Molecular Modeling

The long-chain fatty acids from the natural ester would preferentially esterify the primary C-6 hydroxyl group on the cellulose chain. This hydroxyl group is the least sterically hindered of the three hydroxyls and is most likely to react with a bulky substituent [11].

A monomer unit of cellulose, an anhydro-β-D-glucopyranose, was built using a molecular modeling computer program (Fig. 5). The model performed both quantum mechanical calculations and classical mechanics calculations for the molecular structure. The single point energy was calculated using Hartree-Fock 3-21G and a neutral total charge. The electrostatic potential surfaces were mapped along with the molecular conformation set at its energy minima. The relative sizes of the electrostatic potential surfaces correlate directly to the availability of bonding electrons.

The analysis shows that the hydroxyl group attached to each primary carbon (C-6) has the highest electron density and negative charge, which influence reactions on the molecular surface. Both of these groups are located at the top-center of

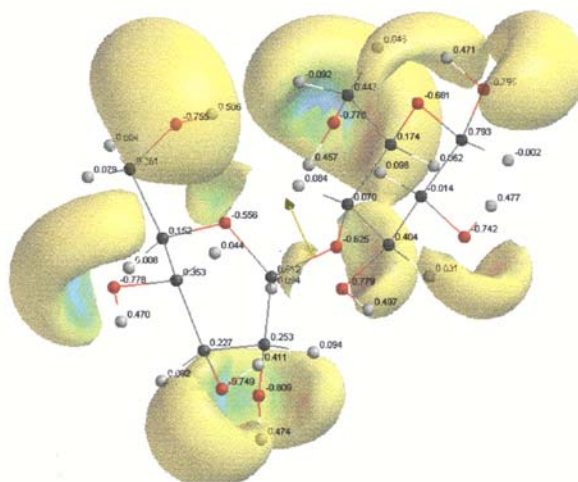


Fig. 5. Molecular model of cellulose monomer unit showing electrostatic potential surfaces. The size of the electrostatic potential surfaces correlates with the availability of bonding electrons.

the monomer unit. In a 3-D model, the top left surface would project out from the surface of the page and the top right would recede into the page. The arrow attached to the small surface in the center of the molecule depicts the dipole of the monomer unit of cellulose, which points toward the more electronegative C-6 hydroxyls.

Fourier Transform Infra-Red Analysis

Fourier Transform Infra-Red (FTIR) analysis using attenuated total reflectance was employed to determine changes in the structure of the Kraft paper aged in natural ester fluid and conventional transformer oil. Samples aged for 0, 500, 1000, 2000, and 4000 hours at 170°C were soxhlet-extracted with hexane. FTIR spectra indicate that the paper aged in natural ester fluid changed very little through 4000 hours, while the paper aged in conventional transformer oil showed a gross change. One highlight for the ester aged paper is the appearance of a weak band at 1717 cm^{-1} that increases with increasing aging time. This carbonyl band indicates the presence of an ester bonded to the cellulose, providing evidence that the transesterification reaction has taken place. The highly aged paper from the mineral oil displays an increasingly strong carbonyl band at 1700 cm^{-1} , consistent with an aldehyde.

Nuclear Magnetic Resonance

Proton nuclear magnetic resonance (NMR) spectroscopy was employed to determine the relative ratio of saturated to unsaturated hydrogen in fresh natural ester fluid compared to fluid aged with thermally upgraded paper for 4000 hours at 170°C. A comparison of the hydrogens (protons) that make up a hydrocarbon molecule is a technique to verify basic molecular structure. The spectrum shows a triplet at a chemical shift of 5.3 ppm, a characteristic of protons bonded to carbon-carbon double bonds, and was used to verify unsaturation. A triplet at 4.3 ppm is due to water, and the multitude of peaks seen between 1 and 3 ppm are due to saturated molecules. A large difference in the ratio of unsaturation to saturation indicates that the molecular composition of the fluid changed. This analysis showed ratios of 5.5 for fresh fluid and 6.0 for fluid aged with cellulose for 4000 hours. This difference is considered insignificant and indicates that the natural ester fluid through the course of 4000 hours with Kraft paper contains the same relative amounts of saturates to unsaturates as fresh fluid. Thus, in a sealed environment, the more vulnerable unsaturated chains of the natural ester fluid were verified to be mostly intact, which would be unlikely if an oxidation process was a factor. This supports the results of full-scale transformer evaluations of natural ester fluid [15], where hydrolysis, not oxidation, was found to be the main fluid breakdown mechanism during thermal aging in sealed transformers.

CONCLUSIONS

The greater affinity of natural ester fluids for water, combined with hydrolysis, cause water to move from the Kraft paper insulation into the natural ester fluid in larger quantities than in conventional transformer oil. This cumulative equilibrium shift of water effectively dries the paper and reduces aging due to thermo-hydrolytic degradation.

Transesterification occurs under the conditions of elevated temperature accelerated aging to chemically modify and protect the Kraft paper and further retard paper aging. Hydrolysis provides the fatty acids necessary for chemical modification of the cellulose to take place. The reactive OH groups on the cellulose molecule become esterified with fatty acid esters via transesterification, hindering cellulose degradation mechanisms utilizing these sites. This reaction is expected to take place at slower rates of reaction at lower temperatures.

The predominant natural ester fluid reaction during elevated temperature aging is hydrolysis, not oxidation. This, in effect, maintains the level of unsaturated molecules in the fluid. This available source of reactant makes the transesterification reaction more favorable.

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