

Cellulose Interaction with Envirotemp[®] FR3[™] Fluid

Multiple sealed tube aging studies produced compelling evidence that, under the same conditions, Kraft paper insulation ages significantly slower in Envirotemp[®] FR3[™] fluid than in mineral oil. The findings of these studies are published in IEEE peer reviewed technical papers [1-4]. In these publications we propose multiple and interrelated plausible mechanisms responsible for increased cellulose, and therefore paper insulation, life.

Primary and secondary mechanisms for the different aging rates are related, directly and indirectly, to the differences between the natural ester FR3 fluid and naphthenic mineral oil in physical and chemical interactions with water. Primarily, the water equilibrium between the insulating fluid and transformer insulating paper is shifted for FR3 fluid, drawing water out of the paper. Since FR3 fluid can hold about 18 times more water than mineral oil before saturation, the fluid will remove significantly more water from the paper. As paper breaks down from heat and produces water as a product of degradation, FR3 fluid absorbs the water to reestablish the equilibrium. Finally, FR3 fluid reacts with the water via hydrolysis to remove water from the system and further drying the paper insulation.

We proposed a secondary mode of paper protection, transesterification, that appeared to be theoretically viable and indirectly supported by the initial data. A study was initiated to determine scientifically if the cellulose can and does undergo transesterification. The results of the study show that, under the conditions of elevated temperature accelerated aging, the reactive OH (hydroxyl) groups on the cellulose molecule become esterified with fatty acid esters. This proves that the cellulose undergoes a chemical change via the mechanism of transesterification, resulting in improved thermal stability. This reaction takes place at lower temperatures, but of course at slower rates of reaction. This study is divided into three main tasks: 1) an extensive literature search, 2) molecular modeling using Spartan Pro, and 3) additional chemical analyses of paper and fluid samples from the previous sealed tube aging studies.

Literature Study: There is significant evidence in the literature that long chain fatty acids can be esterified onto cellulose [5-10]. Wang and Tao [5] used the mixed fatty acids from hydrolyzed soybean oil to esterify cellulose. To accomplish a reasonable degree of substitution within a 24-hour time frame, cellulose was typically activated with either mild acid or base and the 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 not depolymerize the cellulose chains. It is reasonable to assume that higher temperatures would drive a transesterification reaction directly between cellulose and a less active long-chain fatty acid ester, such as FR3 fluid. The esterification of Kraft cellulose in this aging study almost certainly progresses after the ester fluid penetrates the cellulose and hydrolyzes with available water.

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Molecular Modeling: The long-chain fatty acids produced from hydrolysis of FR3 fluid 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 are most likely to react with a bulky substituent [8]. A monomer unit of cellulose, which is formally identified as an anhydro- β -D-glucopyranose, was built within a molecular modeling computer program called SpartanPro. This program was used to perform both quantum mechanical calculations and classical mechanics calculations of 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 indicate a direct correlation to the availability of bonding electrons. The output of this analysis is detailed in Figure 1 below.

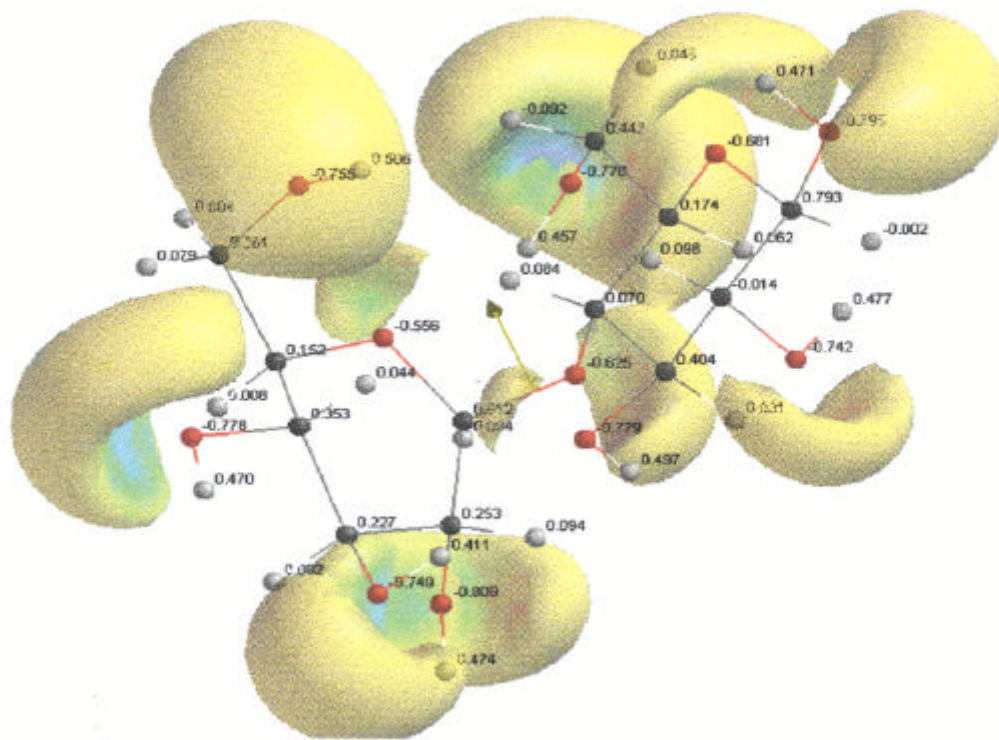


Figure 1: Electrostatic Potential Surface of Cellulose Monomer

The above results from SpartanPro analysis show that the hydroxyl group attached to each primary carbon (C-6) have the highest electron density and negative charge, which influences reactions on the molecular surface. Both of these groups are located at the top-center of the monomer unit. The top left surface would be sticking out from the surface of the page and the top right would stick out to the back in a 3-D model. 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.

Chemical Analysis: Fourier Transform infrared (FTIR) analyses of the paper and FR3 fluid samples were performed after various aging times. Fresh FR3 fluid was compared to fluid aged with UG paper for 0, 500 and 4000 hours at 170°C. The results show that the FR3 fluid changed very little after aging 4000 hours with thermally upgraded (UG) Kraft paper. There were bands present that indicated a weak carboxylic acid component from the fatty acids and NH stretch from the dicyandiamide paper treatment after 4000 hours. Infrared analysis using ATR was employed to determine changes in the structure of the Kraft paper aged in FR3 fluid and mineral oil. Samples that 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 FR3 fluid changed very little through 4000 hours, while the paper aged in mineral 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, which provides evidence that the proposed 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. The FTIR spectral comparison of the FR3 fluid aged paper is attached as Figure 2 and the mineral oil aged paper as Figure 3.

Proton nuclear magnetic resonance (NMR) was employed to determine the relative ratio of saturated to unsaturated hydrogens in fresh FR3 fluid compared to the FR3 fluid aged with UG paper for 4000 hours at 170°C. The NMR spectra are attached as Figures 4 and 5 for the fresh and aged FR3 fluids respectively. A comparison of the hydrogens (protons) that make up a hydrocarbon molecule is a technique to validate basic molecular structure. The triplet at a chemical shift of 5.3 ppm is characteristic of protons bonded to carbon-carbon double bonds and was used to verify unsaturation. The triplet at 4.3 ppm was due to water and the multitude of peaks between 1 and 3 ppm were due to saturated molecules. A large difference in the ratio is an indication that the molecular composition of the fluid changed. This analysis showed ratios of 5.5 for fresh FR3 fluid and 6.0 for FR3 fluid aged for 4000 hours with cellulose. This difference is quantitatively insignificant and indicates that FR3 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 FR3 fluid were verified to be mostly intact, which would be unlikely if an oxidation process was a factor. This result supports the results from the Locke transformer evaluation of FR3 fluid, in which hydrolysis was found to be the main breakdown mechanism during thermal aging in a sealed transformer and not oxidation [11].

Conclusion: The results from this study show that under the conditions of elevated temperature accelerated aging, the reactive OH groups on the cellulose molecule become esterified with fatty acid esters via the mechanism of transesterification. This reaction would be expected to take place at lower temperatures, but at a slower rate of reaction. The study provides evidence both directly from chemical analyses from the conclusions of other researchers. Another significant conclusion from this study, supporting our previous work, is that Envirotemp FR3 fluid undergoes mainly hydrolysis during elevated temperature aging as opposed to oxidation. This, in effect, maintains the level of unsaturated molecules in the fluid and provides a source of reactant to make the transesterification reaction more favorable. It is clear from our work and the work of others that placing a bulky ester group on paper cellulose will increase the stability and ultimately enhance the life of the paper.

References:

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Figure 2
FTIR Spectra of FR3 Aged Papers

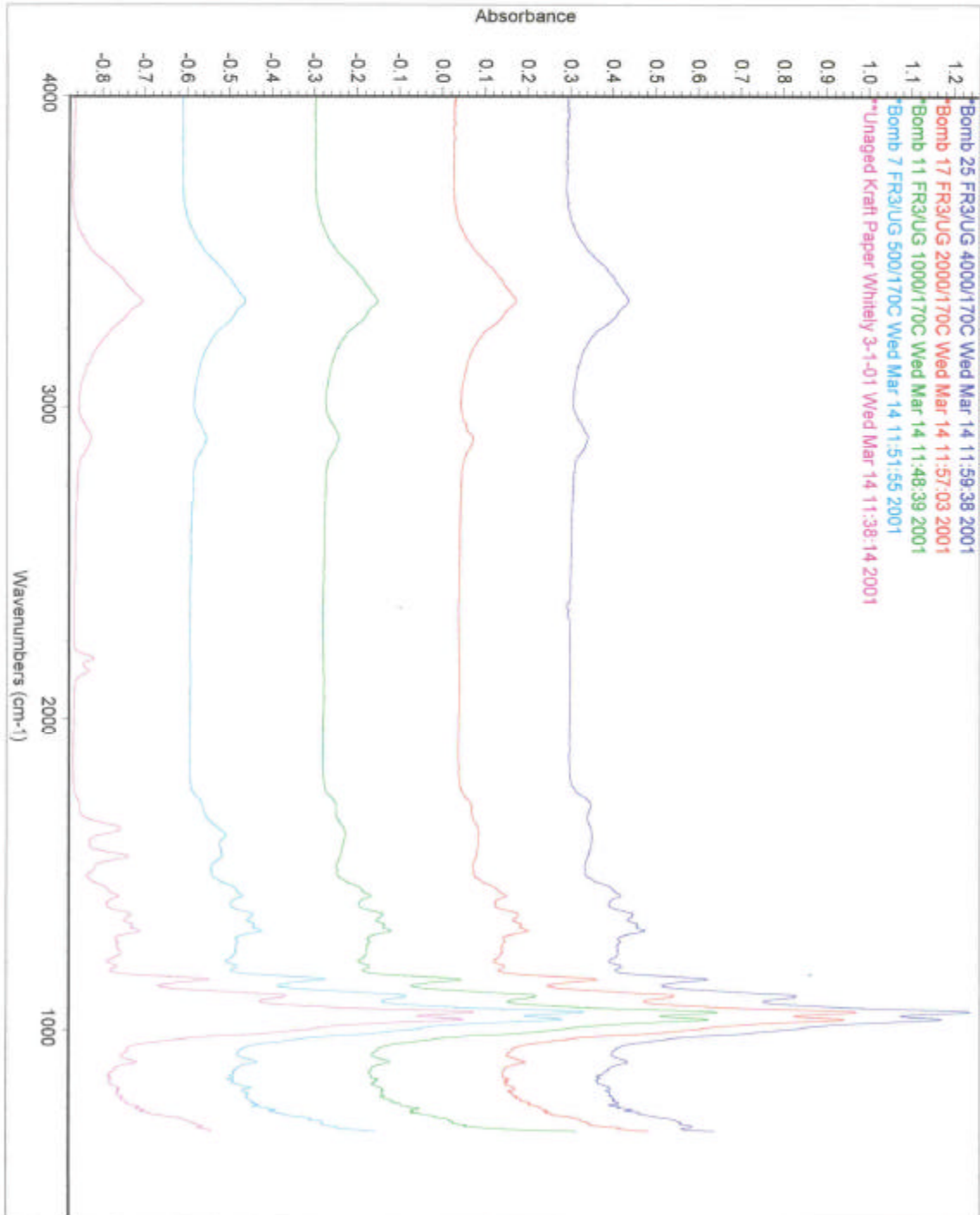
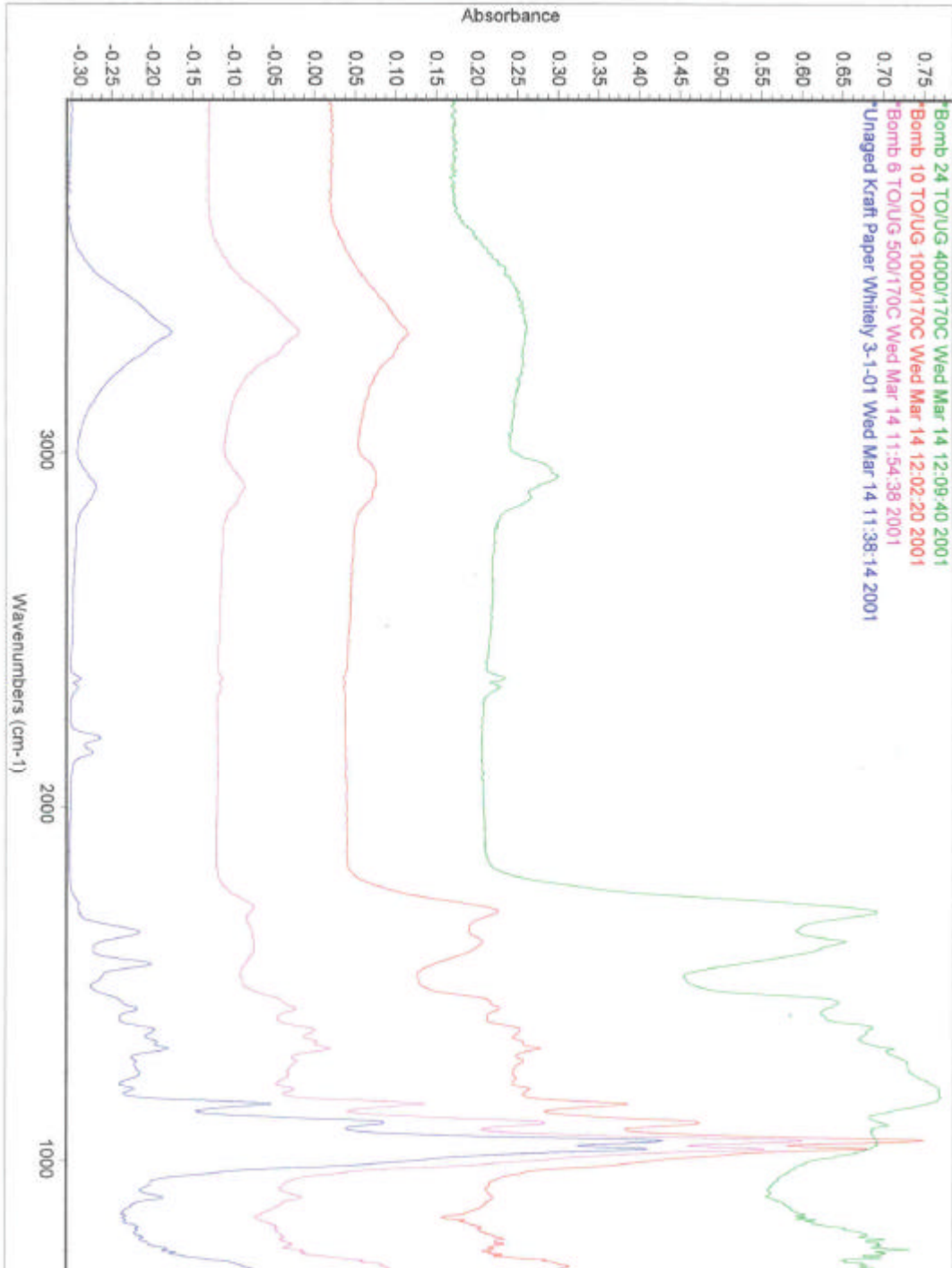
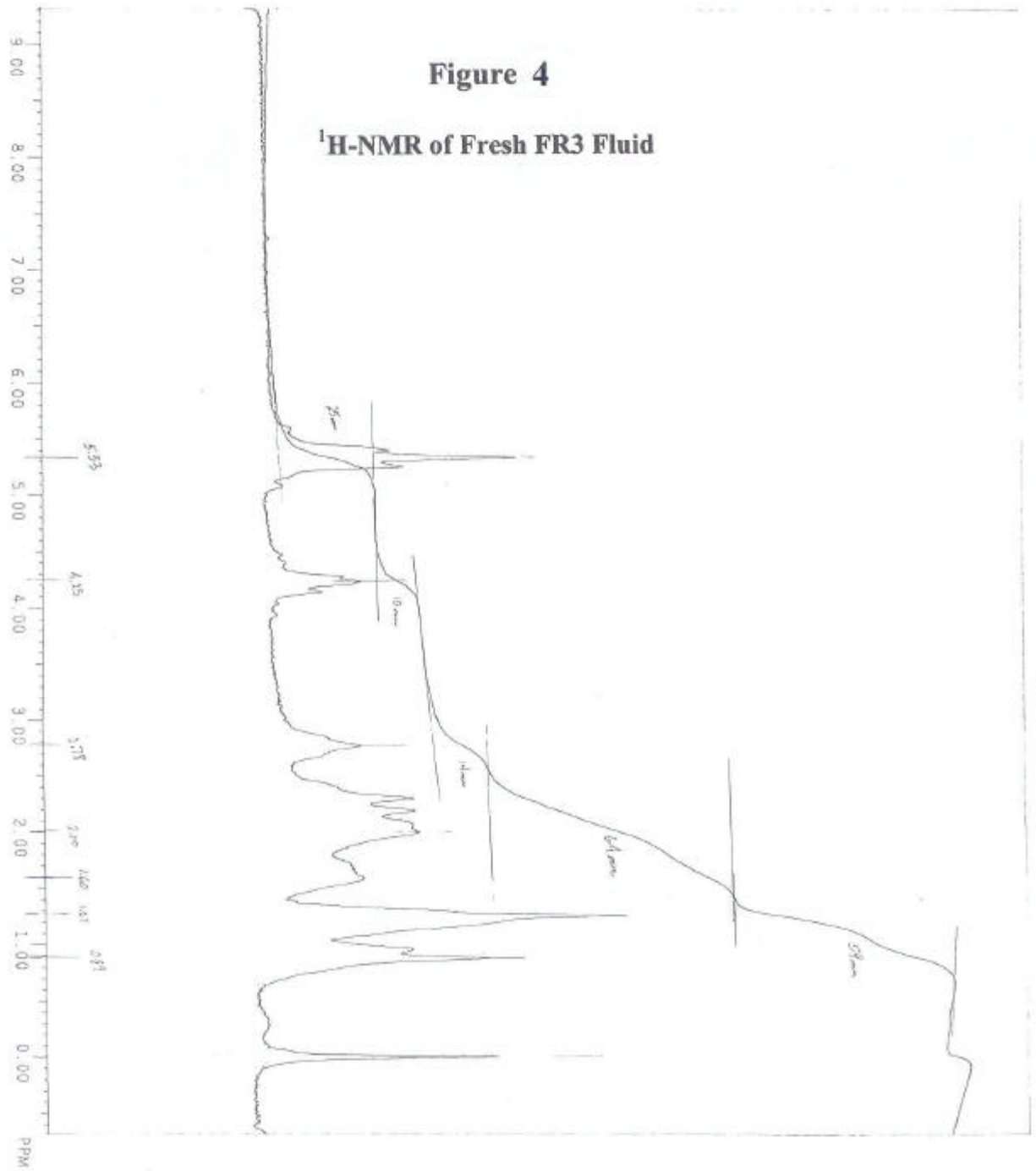


Figure 3

FTIR Spectra of Mineral Oil Aged Papers

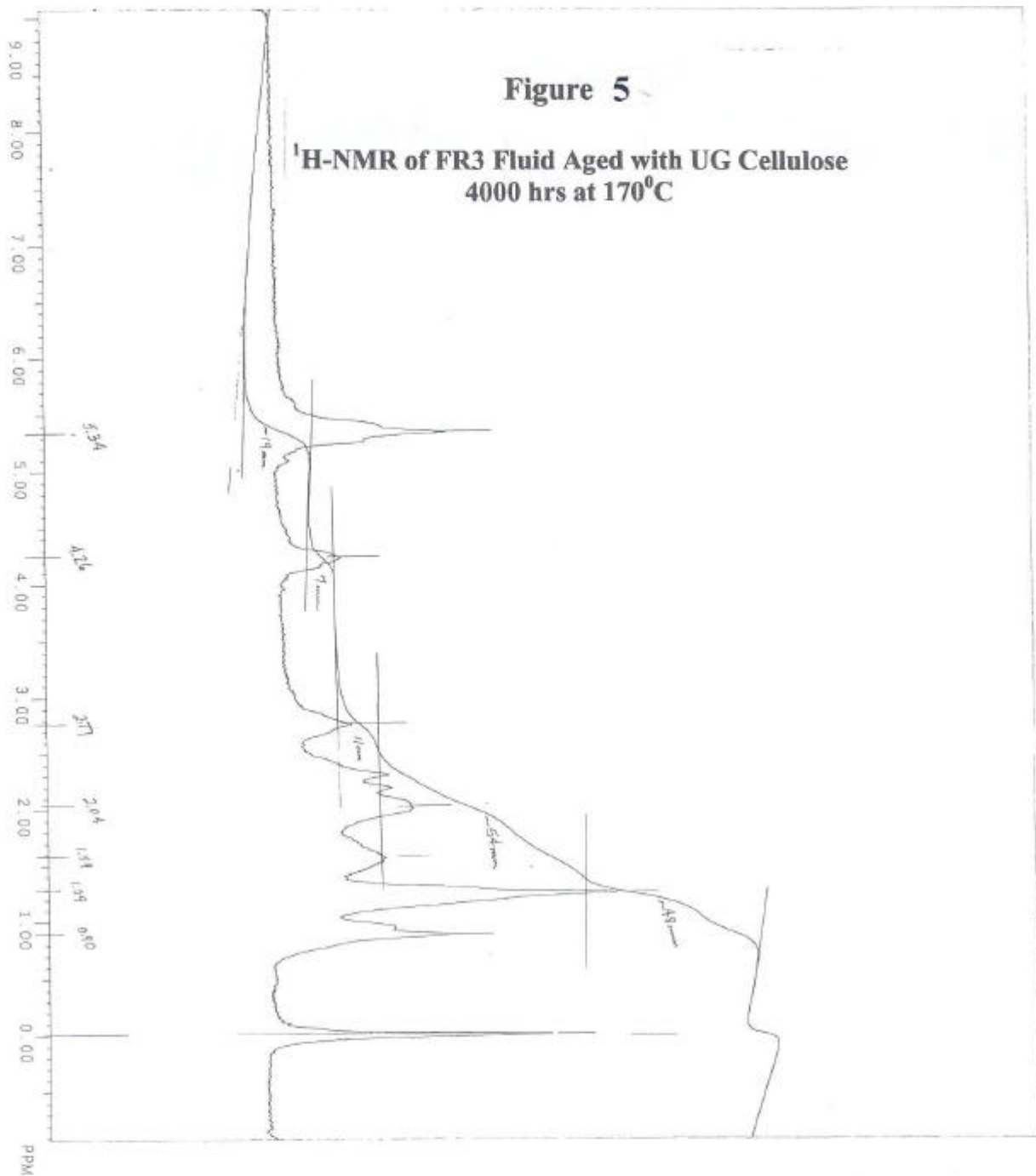




¹H-NMR
fresh FR-3 Fluid
No Aging 31.101
Spectrum taken
3/22/01 K. Rapp
D-Galvanform/TMS
Amplitude Co

Figure 5

¹H-NMR of FR3 Fluid Aged with UG Cellulose
4000 hrs at 170°C



¹H-NMR
FR-3 Fluid Aged
with UG Cellulose
for 4000 hrs @ 170°C
Spectrum taken
3/22/01 K. Kopp.
D-Chloroform / TMS
Amplitude Co
(Bomb # 25)