Natural Ester FR3 Insulating Liquid - Very Paper Friendly

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***Abstract*- Envirotemp™ FR3™ fluid is a renewable, bio-based natural ester (vegetable oil) dielectric coolant for the use in distribution- and power transformers. Because of the exceptionally high flash/fire points of approximately 330/360 °C, the readily biodegradation and the very small CO_2 footprint this fluid is used more and more worldwide. As the dielectric fluid is always in direct contact with the insulation paper the complex interaction between paper and fluid should be understood very well. Comparisons were made between mineral oil and the natural ester FR3™ fluid as dielectric fluid.**

I. Introduction

Ageing of insulating paper depends mostly on the temperature, but the moisture and oxygen contents of the system are also important criteria. When using mineral oil, the ageing process is also accelerated by production of corrosive short chain acids like formic and acetic acid. Above all, if left unchecked within the transformer, moisture will help to destroy the solid insulation system. This paper shows the results of the investigation done by different levels of water content and by increased temperature.

II. The Moisture System between Insulating Liquid and Paper

Moisture is the natural enemy of a paper insulation system that causes degradation and influences the end of life. Moisture can come from the outside – free breathing system – or is released during the paper ageing. The presence of moisture accelerates paper aging. Both, electrical and mechanical strength will be reduced. Water can be present in the insulation system paper/insulating liquid in

- dissolved form,
- bounded to foreign atoms and -molecules, which come from the aging process and
- as free water.

Basically, cellulose and the insulating liquids behave diametrically in terms of water absorption. Cellulose is hydrophilic and when temperature increases, the water absorption decreases. The insulating fluids are mostly hydrophobic, which means that if the temperature increases, the water solubility increases at the same time. According to [1], the thermal decomposition of the paper is proportional to the water content. An increased humidity in the transformer reduces the life expectancy significantly [2]. To compare the behavior of mineral oil and natural ester FR3™ fluid in the paper/insulating fluid/water system, tests were done as follows:

1. Without adding water
2. Adding 1 % water by wt of the solid insulation.
3. Adding 1,5 % water by wt of the solid insulation.

The transformer materials tested were:

a. Pressboard 2 mm (2,438 g δ = ± 0,1062 g)
b. Four layers of paper-wrapped copper conductors (Kraft paper, 0.08 mm x 11.2 mm, 0,2805 g δ = ± 0,0257 g) Copper conductor (0.18 mm x 6 mm)
c. Mineral oil Nynas Nytro 4000x (14 ml)
d. Natural Ester Envirotemp™ FR3™ Fluid (14 ml)

Before testing, pressboard and the paper-wrapped copper conductors were dried under vacuum (1300 Pa) at 105 °C for 24 hours. Before drying, the materials had the following initial moisture:

a. Pressboard: 3,61 %, δ = ± 0,45 %
b. Paper (Kraft paper): 3,95 %, δ = ± 0,75%

As next step the solid samples were impregnated with mineral oil and natural ester liquid. Due to the higher viscosity of the natural ester compared to the mineral oil, a slower intake of the liquid in the solid insulating material was expected. The basis for the absorption of the insulating liquid in the capillaries of the solid insulation is the Hagen-Poiseuillesche law [3], which is well applicable for Reynolds numbers up to 2000 (1).

$$dV = \frac{\pi * r^4}{8 * \eta * l} * (p_1 - p_2) * dt \quad (1)$$

With (2)

$$V = r^2 * \pi * l \quad (2)$$

you get the differential equation (3)

$$r^2 * \pi * dl = \frac{\pi * r^4}{8 * \eta * l} * (p_1 - p_2) * dt \quad (3)$$

and by substituting the initial conditions t = 0, l = 0 the equation (4).

$$t = \frac{l^2 * 8 * \eta}{r^2 * (p_1 - p_2)} \quad (4)$$

Because of the adhesive intermolecular forces, the surface tension at the capillary edges must be taken into account, which causes an additional pressure, resulting in the following corrected pressure term (5).

$$p = (p_1 + p_k - p_2) \quad (5)$$

Reference [4] describes the correction value p_k as follows (6):

$$p_k = \frac{2 * \sigma_T * cos\theta}{r} \quad (6)$$

If the surface tension determined by the tensiometer and the capillary height (h) are known, the contact angle (θ) can be calculated by formula (7).

$$\theta = \cos^{-1}\left(\frac{h * r * g * \rho}{2 * \sigma_T}\right) \quad (7)$$

The impregnation was carried out at 80 °C for 20 hours under vacuum (1300 Pa). The following assumptions were made for the calculation of the impregnation time:

- ✓ Pore radius: Because of microscopic measurement on pressboard, the radius was assumed as 2,7 x 10^{-6} m.
- ✓ The pore radius for pressboard was also used for paper.
- ✓ As the paper insulation consists of four layers, the time to impregnate the thickness of one layer was simply multiplied by four. The phase transitions between the individual layers were not taken into account.
- ✓ The insulating liquids were placed in the vacuum drying oven together with the dried samples. As the liquid didn't come from outside, the pressure difference between final vacuum and ambient pressure was not included in the calculation, the pressure term consists exclusively of the capillary pressure.

Table I shows the calculated insulation impregnation time. For FR3™ fluid it is approximately three to four times higher compared to Nynas Nytro 4000X. However, practical tests indicate a difference of the impregnation rate in the two times lower for natural esters.

TABLE I
CALCULATION OF IMPREGNATION TIMES

Insulating liquid	Density [kg/m³][80 °C]	Surface tension [mN/m] [80 °C] Tensiometer	cos(θ)	p_k [Pa] Papier Pressboard	Viscosity [mm²/s]	t [s] Papier	t [s] Pressboard
Nynas Nytro 4000X	821	23,0	0,913	$3,16*10^4$	3,3	0,01	0,4
FR3™ Fluid	880	29,1	0,773	$3,39*10^4$	12,0	0,04	1,4

Preparing and treatment of the samples after impregnation

The impregnated samples were placed in headspace vials (Figure 1, after taken sample for water determination), then the appropriate amount of water was added by microliter syringe. The headspace vials were filled up with the respective insulating liquid and closed. For the distribution and homogenization of the doped water, these headspace vials were placed in an ultrasonic bath (Struers Metason 120, 70 W) and sonicated for 15 minutes.


Figure 1: Headspace Vials

The samples thus prepared were stored in a drying oven for a period of 168 hours to equilibrate at 80 °C. To prevent any possible exchange of moisture through the septum, the headspace vials were stored in a horizontal position, so that the septum was completely surrounded by liquid. The headspace bottles were rolled from time to time.

After storage in the oven, the moisture content of the insulating liquid was the first measurement. For this purpose, the insulating liquid was taken from the headspace vial by syringe. The water content determination was carried out by Karl Fischer titration. This is also in practice the method of choice to infer from the moisture of the insulating liquid to the moisture of the solid insulation, as it is practically the only method that can be performed on the device in operation.

Results of the moisture test

Figure 2 shows the total water content absorption in the insulating fluid. For the mineral oil the level is very low and a dependency from the total water content cannot be seen. The results of the natural ester FR3™ fluid are completely different. The level of absorbed water is much higher and the dependency of the amount of doped water can be seen very well.

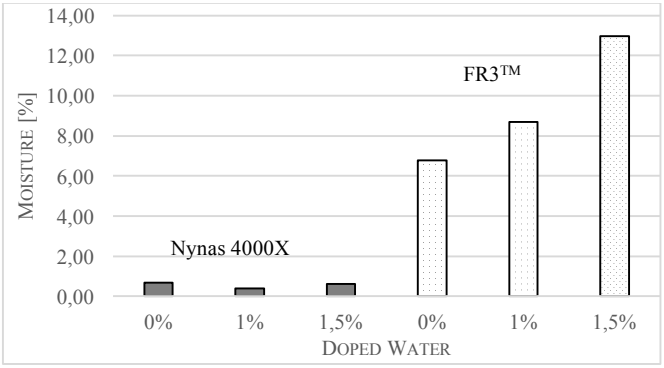

Figure 2: Water content of the insulating liquids after treatment

The results were also used for modelling the transport of the water in the solid samples. Fick's second law (8) was used as diffusion equation [5]. The diffusion equation is a differential equation second-order with respect to location and first-order with respect to time. For solving them you need three boundary conditions.

$$\frac{\partial p}{\partial t} - \boldsymbol{D} * \frac{\partial^2 p}{\partial z^2} = \mathbf{0} \tag{8}$$

For getting the parameter *D* the first Fick's (9) law is useful [7]. After converting the equation, *D* can be calculated by (10). F. Musai describes in [6] that the main reason for the deviations between model and reality lies in the inaccuracy of the diffusion coefficient. In this case, it was experimentally determined and fits very well with [1].

$$\dot{n} = -D * \frac{dc}{dx} \tag{9}$$

$$D = \frac{\dot{n} * d}{2 * c_1} \tag{10}$$

After solving the differential equations, you get for example the results for pressboard [8] by adding 1,5 % water of the solid insulation shown by Figure 3 and Figure 4. Comparing both figures, the results show that under the completely same condition natural ester FR3™ fluid absorbs much more water than mineral oil and keeps cellulose paper and pressboard dry. This helps to extend the lifetime of transformers.

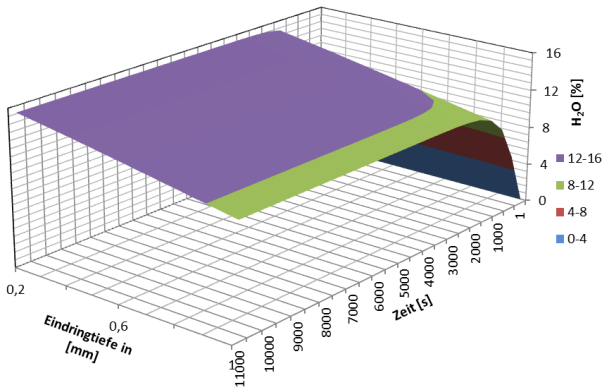

Figure 3: Nynas 4000X, 1.5% - moisture in pressboard – envelope

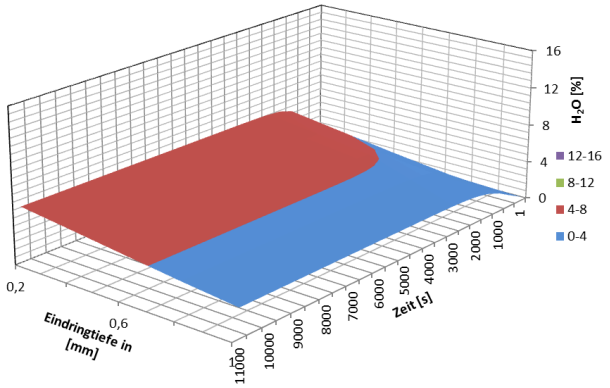

Figure 4: FR3™, 1,5% – moisture in pressboard – envelope

III. Interaction with the Solid Insulation (Paper) in the Course of an Aging Test

The aging of the insulating fluids took place at Graz University of Technology - Institute for High Voltage Technology and System Management. The insulating fluids (mineral oil, FR3™ fluid) were mixed with common transformer materials in the usual ratios used in transformers as well as pure, new liquid samples, and were stored sealed at 140 °C for 14 days.

Furan production due to aging

Besides methanol, furans are currently the only markers that can be used to monitor the state of the solid-state insulation paper when the transformer is energized. Several empirical formulas offer the possibility to deduce the furan concentration in the insulating liquid (currently only for mineral oil) by using the degree of polymerization (DP) of the cellulose. Even if the determined DP values are being assessed with appropriate caution, they are just indicative values. High attention should be paid to the fact that only an average DP value can be obtained with this method and that the minimum DP value for a safe operation of the transformer is unknown.

Figure 5 shows that under the aging conditions of the Graz study the content of 2-FAL which stems from the decomposition of the paper is more than three times higher by using mineral oil compared to using the natural ester FR3™ fluid. If the natural ester is very much degraded the detection by HPCL can be influenced showing a to high value of furanic compounds [9].

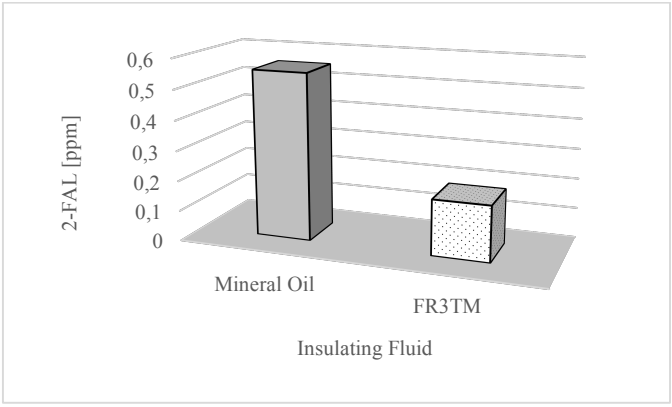

Figure 5: Furan production because of treatment

Alteration of the total acid number due to aging

Due to the thermal aging, it was expected that the total acid number of those samples containing the proportionate transformer materials would increase compared to the blanks (same test conditions, but without transformer materials), however the opposite happened.

Table II shows the deviation of the total acid number compared to the starting value. The mineral oil samples stayed nearly constant. And the total acid number of the natural ester FR3™ fluid with transformer materials compared with the blank sample decreased by approximately 30 to 40 % - an indication that transesterification or esterification may have taken place [10], [11]. In this case, the hydroxyl groups of the cellulose are esterified by fatty acids that were already formed through hydrolysis and became triggered by the high temperature of aging, thus, the acids were consumed. By hydrolytic cleavage of the esters, originating from the insulating liquid, fatty acids can be replenished. Thus water plays two different roles. On the one hand, water acts as a reaction catalyst, which promotes degradation of the cellulose. On the other hand, water is consumed as a reactant with the ester liquid, which produces fatty acids. Finally, the fatty acids react to form new generated ester linkages that offer a layer over the cellulose and protects the cellulose from further chemical attack.

TABLE II
TOTAL ACID NUMBER – DEVIATION FROM THE STARTING VALUE [%]

	Blank	With transformer materials
Nynas Nytro 4000X	+688	+675
FR3™ Fluid	+13	-22

Modifications in IR spectrum due to the aging test

Infrared spectroscopy can be used for both qualitative and quantitative analysis. Otherwise, the vibration is not infrared active [12]. The particularly useful bands for the structure elucidation of the insulating liquids are in the range of 4000 to 700 cm^{-1} wavenumbers. Figure 6 and Figure 8 shows the IR spectrum of the liquids before treatment (ageing). Figure 7 and Figure 9 shows the IR spectrum after treatment. The red line stems

from the sample without transformer materials and the black one represents the sample with them. The mineral oil blank after ageing without transformer materials showed a large peak at wavenumber 1740 cm^{-1} (Figure 7, red line). This indicates that during ageing carboxylic acids were formed. The Natural ester FR3™ fluid did not show this effect.

As the peak of the mineral oil with transformer materials after ageing is much smaller (black line, Figure 7) there was some interactions between the transformer materials – almost likely the paper with mineral oil.

The new peak at wavenumber 2800 – 2900 cm^{-1} could be an indication of the interaction and change. Degradation of the paper is indicated by the significant development of furans as shown in Figure 5 and even the CO_2 peak at wavenumber 2337 cm^{-1} [13] in Figure 7.

As the total number of acid with and without transformer materials stayed constant, new acids must be formed.

For the natural ester, infrared indicated changes in the carbonyl wavenumber region between 1700 – 1800 cm^{-1} per Figure 9. The changes in the absorptions in the carbonyl region are still under study.

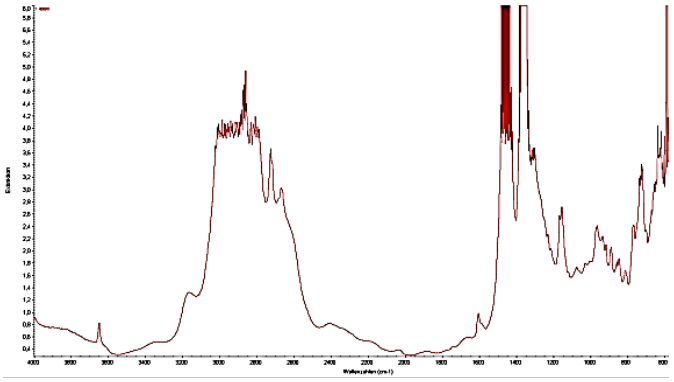

Figure 6: FTIR Spectrum - Nynas Transformer Oil – Nytro 4000X Before Ageing

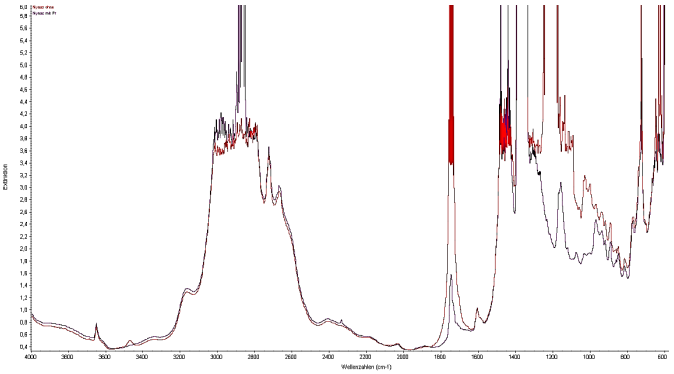

Figure 7: FTIR Spectrum - Nynas Transformer Oil Nytro 4000X – Modification after treatment (ageing)

It could be that changes in the carboxylic acids due to utilization by the esterification mechanism versus generation of new acids due to hydrolysis is most likely impossible to discern by infrared or any method since the acids are most likely the same. However, a net reduction in new acids shown by depletion of water while at the same time a reduction of the acids as measured by the acid value determination offers some hint that esterification of paper may have taken place. Some further explanation of the cellulose, transesterification mechanism is described in [14].

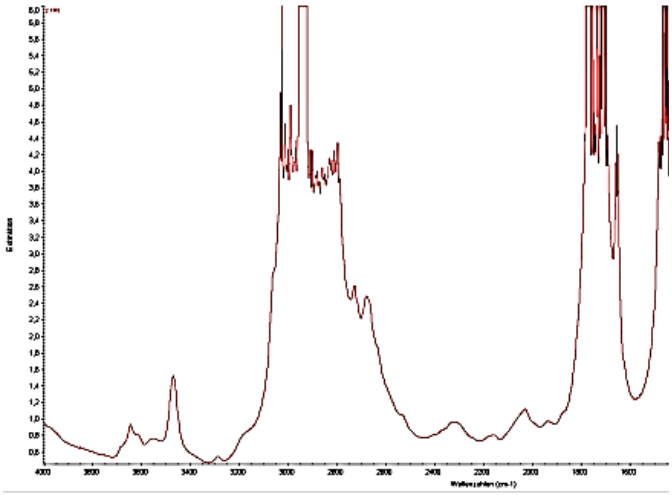

Figure 8: FTIR Spectrum - Natural Ester – Envirotemp™ FR3™ Before Ageing

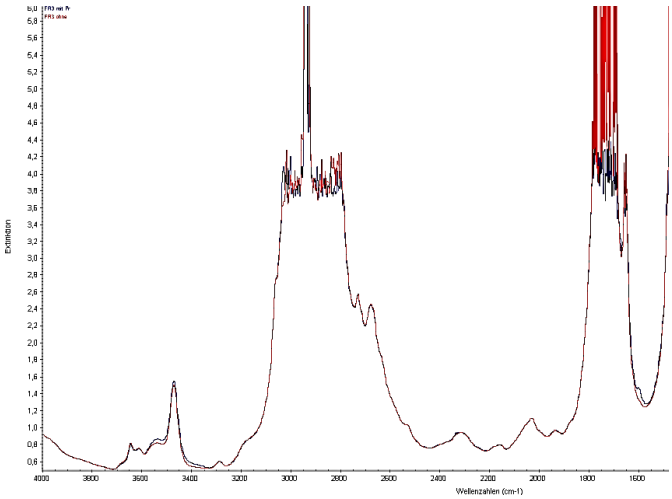

Figure 9: FTIR Spectrum - Natural Ester Envirotemp™ FR3™ - Modification after treatment (ageing)

IV. CONCLUSION

The investigations show that the natural ester FR3™ fluid can absorb and utilize more water than mineral oil. This helps to keep the cellulose dry which is very important for extending the life of transformer paper and pressboard cellulose. If hydrolysis of the natural ester happens, long chain acids are formed. They are hardly dissociated and for this reason not aggressive. At higher temperatures, the carboxylic acids can combine with the hydroxyl groups of the cellulose to form a new ester. The new esterified cellulose becomes protected from further attack, thus extending the life of the solid insulation which is known to impact the life of the transformer

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