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WATER SATURATION LIMITS AND MOISTURE EQUILIBRIUM DIAGRAMS OF ALTERNATIVE INSULATION MATERIALS

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Abstract: In recent years one can observe a higher interest in alternative dielectric materials for power transformers. These are for example natural and synthetic esters or aramid fiber based solid insulation materials. In this paper moisture saturation curves of various insulation oils are presented up to a temperature of 140°C, together with the sorption isotherms of Nomex® paper. These lead to adjusted equilibrium charts for moisture diagnosis of transformers with unconventional insulation systems.

1 INTRODUCTION

Classically the insulation system of a power transformer is built from cellulose material for solid insulation and mineral oil as liquid dielectric and coolant. As the generally very stable properties of mineral oil sometimes are not acceptable for a specific application, there is a constant search for additional alternative materials. For example the fire point is often below 145°C, which could be a problem in fire sensitive areas. Also recently the water polluting potential is considered more often. This is why for example ester fluids and alternative solid insulating materials like Nomex® are being researched – even in the light of higher costs.

The basic characterization of these materials in an insulation system is critical for setting the design rules and maintenance guidelines for equipment using these materials. Only then the materials could be used optimally and their specific characteristics could be beneficial to the equipment. Also the condition monitoring and diagnostics for the purpose of asset management of liquid-immersed power transformers recently play a more important role.

Moisture content in insulation is critical for aging processes and dielectric performance. Moisture is a significant factor accelerating the aging processes in solid cellulose insulation. Knowledge of moisture content in the solid insulation can be used to assess the condition of insulation system and be part of planned maintenance.

In an operating transformer the assessment of the moisture content in the solid insulation cannot be made easily without destruction of the insulation system as the solid insulation is not accessible. The data can only be obtained by measuring the water content of the transformer liquid at a given temperature while assuming thermodynamic equilibrium between solid and liquid insulation materials. The results are then applied to equilibrium curves such as those developed by Oommen or Fabre-Pichon. These curves are valid only for a specific liquid and solid material combination. In case of the new materials these charts are not appropriate.

This contribution will focus on the experimental determination of water solubility and sorption curves of liquid and solid insulating material. It is possible to bring this data into mathematical models. To create the moisture equilibrium curves it is assumed that the relative humidity of the oil and relative humidity of the preparation atmosphere lead to the same absolute moisture content in the solid insulation. Thus it is possible to combine the moisture isotherms of liquid and the solid material sorption curves into moisture equilibrium curves. The paper will present and discuss various moisture equilibrium diagrams of liquid/solid combinations.

Finally these diagrams are validated for different material combinations in case of thermal equilibrium by testing them against a well-known moisture content in the solid insulation in a sealed test cell. With help of a mathematical model it is possible to calculate the deviations in the sorption curves resulting from the inaccuracy of the measurement equipment and give a estimated uncertainty of the new equilibrium curves.

2 DEFINITIONS AND EXPERIMENTAL SETUP

2.1 Definition of water content and its determination

Water content of a material can be described in different ways. The first is water content by weight, which is often called absolute moisture. Because oils cannot dissolve much water, a convenient unit is ppm, which translates to µg water in one gram of oil. Cellulose can absorb much more water and therefore percent by weight is used that is based on the mass of a dry sample. The other concept of describing moisture content is based on water saturation. The vapor pressure compared to the partial pressure at saturation is called relative moisture content (RH). Sometimes this expression is called water activity in the context of liquids and solids. This is a simplification, because a correct definition would be water potential, which is a function of partial pressure, temperature and molar concentration. For reason of simplicity the term water activity is used as synonym for relative moisture content. It should be noted that the values are temperature dependent.

Absolute moisture content can be measured by coulometric Karl-Fischer titration. Oil samples are injected directly into the measurement cell with a syringe. Samples of solid insulation are heated in vials in an oven at 170°C and the water vapor is transferred by dry air with a tubing system into the reaction cell. The lowest reasonable detection limit for the available equipment is 10µg of water. Higher amounts lead to better results. For measurement of liquids the relative standard deviation is 1% for water standards of 105ppm (ca. 100µg water) for many measurements. The absolute error is 1µg. For very low water contents, like in mineral oil, the error can be considerably higher. For solids relative standard deviation is below 1%.

Relative moisture can be measured with capacitive sensors and the unit is percent. They consist of a capacitor with a very hygroscopic dielectric where water ingress is reflected in a change of permittivity and thus capacity. It is sufficient to measure the latter and from this the relative moisture can be determined. These sensors can be calibrated with a defined atmosphere (e.g. the air over saturated salt solutions in a closed container). These sensors work in gases as well as liquids. The specified absolute accuracy is +/- 2% RH, but a better performance with < +/-1% RH was noticed just after calibration.

2.2 Preparation of the samples

Most of the samples were prepared in a climate chamber which could heat up to 100°C. The relative moisture can be controlled up to 100% RH, although at high temperature the maximum was 45% RH. The starting point of the preparation was dry pressboard and oil. Generally it was avoided to make large temperature or humidity changes in the climate chamber from preparation step to preparation step so that the equilibration time between the chamber atmosphere and the material could be as short as possible. The solid material was conditioned for at least 24h in the defined atmosphere.

3 EXPERIMENTS

3.1 Water saturation limits of insulating liquids

The water saturation limit is calculated for a specific temperature. For a known relative humidity, which is smaller than 100% saturation, the absolute water content is measured in ppm. This value is extrapolated linearly to 100%. To obtain the lowest possible spread of the data values, it was found that the relative humidity should be as high as possible. This reduces the measurement error which would be multiplied many times for small relative humidities. A linear increase in water content is assumed proportional to the relative humidity. In Figure 1 this behavior is represented for several oils at 60°C. One can conclude that the linear extrapolation can be made without significant errors.

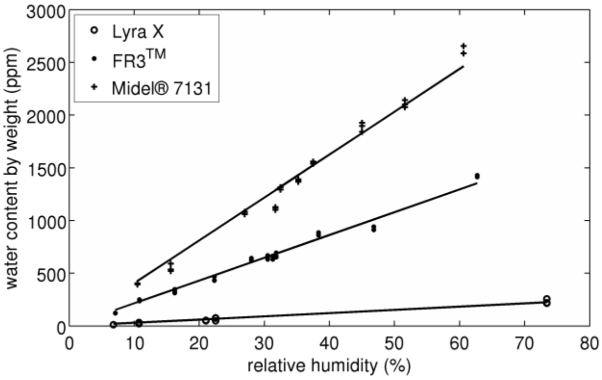

Figure 1: Isotherms of insulating liquids at 60°C

Because the water absorption and thus the saturation curves of the insulating liquids are dependent on the temperature, several samples were analyzed at different temperatures. The investigations for temperatures to 140°C were new. They are necessary because esters are also suitable for use at a higher temperature range. The samples up to 100°C were heated and moistened in a climate chamber. For temperatures above 100°C they were heated in a sealed container on a hot plate and moistened by adding a calculated amount of water. It was ensured that the temperature value was kept constant for a long time. The relative humidity of the oil was determined with a capacitive sensor until a constant value of the moisture had set. On moistening of the oils, there were problems starting at a temperature above 100°C. The boiling point of the oil was reduced by the addition of water. At a relative humidity of more than 30%, there was a bubbling-effect at higher temperatures. This resulted in larger variations of the saturation values at temperatures of more than 100°C.

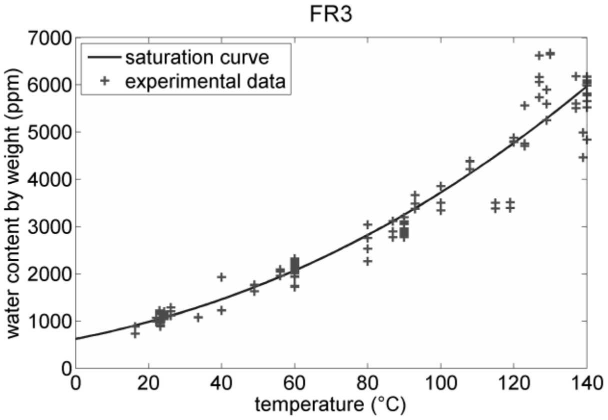

Figure 2: Water saturation curve for FR3™

Table 1: Water saturation limits of oils (ppm)

Oil temp. °C	20	40	60	100	120	140
FR3	983	1461	2072	3722	4771	5970
Midel7131	1941	2752	3742	6265	7794	9494
Lyra X	56	117	225	671	n/a	n/a

Table 2: Water saturation parameters

Oil	Parameter a	Parameter b	Avg. deviation
FR3	$4.900 \cdot 10^5$	1821	8.6%
Midel 7131	$4.586 \cdot 10^5$	1602	10.3%
Lyra X	$6.013 \cdot 10^6$	3396	11%

Figure 1 and 2 show the saturation curves for two ester fluids. With the experimental data a mathematical description can be found as seen in equation (1) [1]. By using a Matlab-fit with 95% confidence interval the parameters of FR3™, Midel®7131 and a naphthenic mineral oil were determined. For the options of the fit the “robust: LAR” (least absolute residuals) was set. This means that data points which have a strong deviation from the curve are considered weaker. The calculated parameters for the different oils are shown in table 2. The average deviation is calculated by averaging the relative deviation of each data point from the fitted curve.

$$W_S(T) = a \cdot e^{(-b/T)} \qquad (1)$$

In formula (1) W_s is the water saturation limit in ppm for a given absolute temperature *T* in Kelvin. The parameters *a* and *b* are material parameters.

The saturation values for FR3™ and Midel® 7131 are in the expected range – the synthetic ester can dissolve roughly the double amount of water than the natural ester. It can be seen that in the higher temperature ranges over 100°C the curve still follows an exponential slope, but the scatter of the data points is getting bigger.

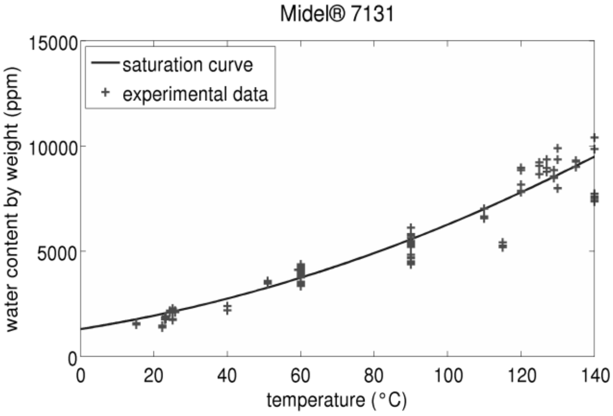

Figure 3: Water saturation curve for Midel® 7131

3.2 Sorption isotherms of solid insulating material

Dried samples of 1mm thick high density (HD) pressboard from Krempel and Nomex® paper were conditioned in the climate chamber for 24 hours.

The relative moisture content of the atmosphere was then slightly elevated each day up to the possible maximum. From each sample the water content was determined by Karl-Fischer Titration in relation to its dry mass. As the titrator is connected to an oven for solid samples, the optimal heating temperature was found to be 170°C for Nomex® paper as well as the HD pressboard.

Different materials can have a different shape for their sorption isotherms. Materials like paper and pressboard typically have an S-shaped curve [2]. In order to get a mathematical model a curve has to be found, which makes most sense to fit. In literature the Antoine function (2) has been introduced for these kinds of isotherms [4, 5].

$$f(RH/100) = \frac{C \cdot (RH/100)^{(\frac{A}{B})}}{1 + (C-1) \cdot (RH/100)^{A \cdot B \cdot (RH/100)}} \cdot D \qquad (2)$$

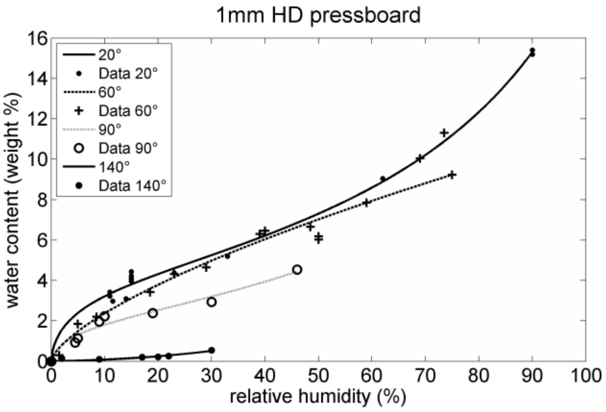

Figure 4: Absorption isotherm for 1mm HD pressboard

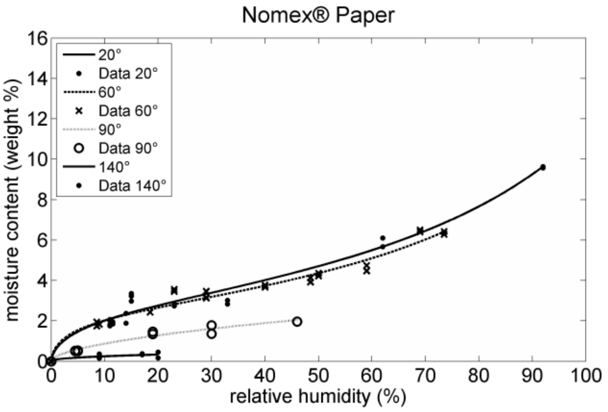

Figure 5: Absorption isotherm for Nomex paper

Table 3: Parameters for fitting the sorption isotherms of solid material

HD Pressboard 1mm					
	A	***B***	***C***	***D***	***Deviat.***
20°C	0.09861	0.1619	0.007038	19.80	6.3%
60°C	0.08298	0.1227	0.018890	12.94	10.1%
90°C	0.06369	0.0847	0.001205	20.69	11.1%
140°C	0.37580	0.1832	0.001599	98.95	32.8%
Nomex® Paper					
20°C	0.0427	0.0705	0.0017	11.50	14.7%
60°C	1.8610	3.2130	0.1751	33.38	6.3 %
90°C	0.4956	0.8869	1.0000	3.152	9.7%
140°C	0.1398	0.3230	0.9116	0.667	27,7%

In this formula *A*, *B*, *C*, *D* are material parameters and *RH* is the value of relative humidity in percent. This function can take three different slopes. If *A*=*B*, then a straight line is described. For *A*<*B* an S-shape and for *A*>*B* a mathematical saturation function will result. All parameters have to be positive and *C* should be smaller than 1. Parameter *D* resembles the moisture content at 100% relative humidity. In table 3 an overview of the determined parameters will be given. Generally Nomex® absorbed less water than cellulosic high density pressboard for sheets of 1mm thickness (Figure 3 and 4). As a rule of thumb the aramid fiber absorbs 50% less water than the cellulosic counterpart. Thin sheets have a higher water content than a thicker pressboard at the same boundary conditions.

3.3 Construction of the moisture equilibrium diagrams [3]

In order to create the moisture equilibrium diagrams (ED), it is assumed that the relative humidity of the oil and relative humidity of the preparation atmosphere lead to the same absolute moisture content in the solid insulation. Thus it is possible to combine the moisture isotherms of oil and the solid material sorption curves into moisture equilibrium diagrams. Together with the formula of the saturation curves and the formula of the sorption curves it is possible to create a mathematical description for the moisture equilibrium diagrams – formula (3).

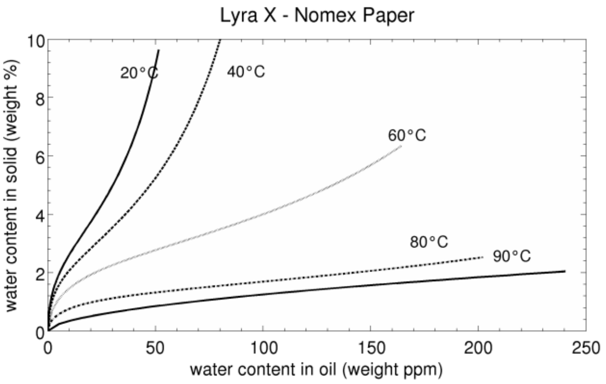

Figure 6: ED. for mineral oil and Nomex® paper

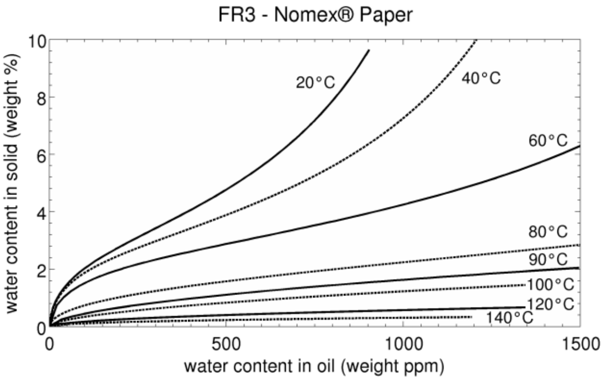

Figure 7: ED. for FR3 and Nomex® paper

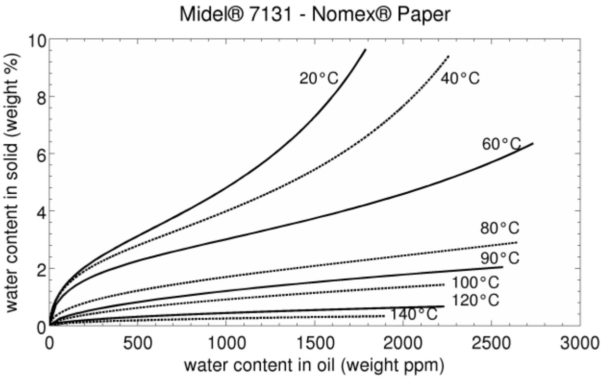

Figure 8: ED. for Midel 7131 and Nomex® paper

$$g(W,T) = \frac{C \cdot \left(\frac{W}{a\cdot e^{-b/T}}\right)^{\left(\frac{A}{B}\right)}}{1+(C-1)\cdot\left(\frac{W}{a\cdot e^{-b/T}}\right)^{A\cdot B\cdot\left(\frac{W}{a\cdot e^{-b/T}}\right)}} \cdot D \tag{3}$$

The parameters *a* and *b* are known from the saturation curves for oil and the parameters *A*, *B*, *C* and *D* are known from the sorption curves. The parameter *W* stands for the measured water content in oil in ppm and *T* is the absolute temperature the sample was taken.

The sorption diagrams were measured at temperature of 20°C, 60°C, 90°C and 140°C. The curves at 40°C, 80°C, 100°C and 120°C were determined by a shape-preserving interpolation in Matlab.

3.4 Validation

The generated moisture equilibrium diagrams were checked for their validity by experiments with well-known moisture content in solid and liquid insulation. For this purpose, various samples were prepared with an oil-solid combination. At various temperatures, oil samples were taken to determine the water content by titration. In addition, the moisture content of the solid samples was determined to confirm the values derived from the equilibrium diagrams.

To obtain a tolerance for the deviations of equilibrium diagrams, the average deviations of the saturation and the sorption diagrams were used. As the differences depend on many parameters, it is not possible to determine an overall standard deviation for the individual curves. The deviations must be calculated separately for each point. The calculation of the possible values is illustrated by formula (3). The average deviations of the sorption curves have an impact on the parameter *D*. Also the parameter *a* of the saturation curves has to be multiplied with the average relative deviation of the measurement points. This results in a tolerance range by which the accuracy of the moisture equilibrium diagrams can be established. For example for a given temperature and water content in the oil, it is now possible to find a lower and upper limit around the expected result from the equilibrium diagram.

The following table 4 shows the measured values of different oil/solid combinations with different moisture contents at various temperatures. This shows very good results and is a confirmation for the curves..

Table 4: Validation of the equilibrium diagrams

Validation of mineral oil with HD pressboard					
T [°C]	***Water cont. in oil measured [ppm]***	***Water content in solid measured***	***Water content. derived from diagrams***		
			Equilibrium diagram	***Lower limit***	***Upper limit***
22	22.5	6.22%	5.47%	4.84%	6.22%
60	87	6.02%	6.00%	5.00%	7.17%
95	22.7	3.89%	3.61%	2.98%	4.39%
Validation of Midel® 7131 with Nomex® paper					
20	781.7	3.57%	3.78%	3.05%	4.64%
60	1149.9	2.76%	3.35%	2.97%	3.78%
Validation of FR3™ with Nomex® paper					
25	405.3	3.15%	3.56%	2.90%	4.30%
60	711.2	3.84%	3.52%	3.15%	3.94%
95	330.7	0.98%	0.88%	0.76%	1.01%

4 CONCLUSION

This contribution described the experiments how to determine saturation curves and sorption isotherms. The results obtained confirm the documented properties of the insulating oils and show examples of characteristics of alternative insulation materials including Nomex® aramid paper and ester fluids. An extension for temperatures up to 140°C was also made. Then the moisture equilibrium diagrams were constructed and described by a formula. Additionally it was possible to calculate the uncertainty in the equilibrium diagram for a given point resulting from deviations of the saturation curves and sorption isotherms.

Finally the equilibrium curves were checked for their validity in thermodynamic and kinetic equilibrium. The values show that even under controlled conditions inaccuracies from the description of the liquid and solid materials lead to theoretical uncertainties in the estimation of the water content of the solid insulation. In worst case of very wet insulation this can be about 1% of weight. In case of dry material and higher temperatures the accuracy gets better.

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