

Thermally Accelerated Aging of Insulation Paper for Transformers with Different Insulating Liquids

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Supplementary Materials

In the following additional information about the measuring devices as well as the optical change of the insulating material is presented. Furthermore, the correlation of the aging markers for the different systems and fluids is presented in figures.

S1 Additional information measuring devices

In the following subsections, the measuring devices as well as the method of measurement are discussed in more detail.

S1.1. Degree of Polymerization

In this investigation, the determination of the DP value of the paper samples was carried out in the external accredited laboratory *Analysen Service GmbH – Umwelt- und Öllabor Leipzig* in Leipzig, Germany. For this purpose, the aged paper samples for DP measurement were divided and weighed in form of samples of 9 g and then put into sealable LDPE bags with respective labeling. Thereafter, all paper samples were sent to the laboratory and tested.

The determination of the DP value of insulating paper follows the standard IEC 60450. It specifies how the tests of paper samples proceed in order to obtain reproducible and accurate results. To determine the DP value, the paper sample is immersed in the watery solvent of copper ethylenediamine hydroxide $\text{Cu}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2(\text{OH})_2$ with the concentration of 1 mol/l. Subsequently, the specific viscosity η_s of the paper immersed solution is measured. From the result of the specific viscosity, the intrinsic viscosity η of the solution is derived, from that, the DP value is finally calculated [74].

S1.2. Moisture

The moisture content of insulating oil is determined by the coulometric method called *Karl-Fischer*-titration. The *TitroLine 7500 KF trace* offered by the company *SI Analytics GmbH* [77] is used for the coulometric measurement of the absolute moisture content. The measurement is carried out automatically according to the standard DIN 51777 [78]. The used solvent is *Hydranal Coulomat AG-H* produced from the company *Sigma-Aldrich Chemie GmbH*. For the measurement of moisture content, a 5 ml plastic syringe was used to extract the sample of the insulating liquid out of the hermetically sealed aluminum bottle. During this process, 5 ml of the insulating liquid was filled into the syringe slowly and carefully to avoid bubbles, and additional trapped air in the syringe was removed. The syringe was then weighed by a digital precision scale. The weight of the syringe was measured again after 1 ml of the insulating liquid was injected into the glass titration vessel through an airtight septum so that the difference value is the weight of this 1 ml sample. The solvent in the vessel was well mixed during the whole measurement using a magnetic stirrer.

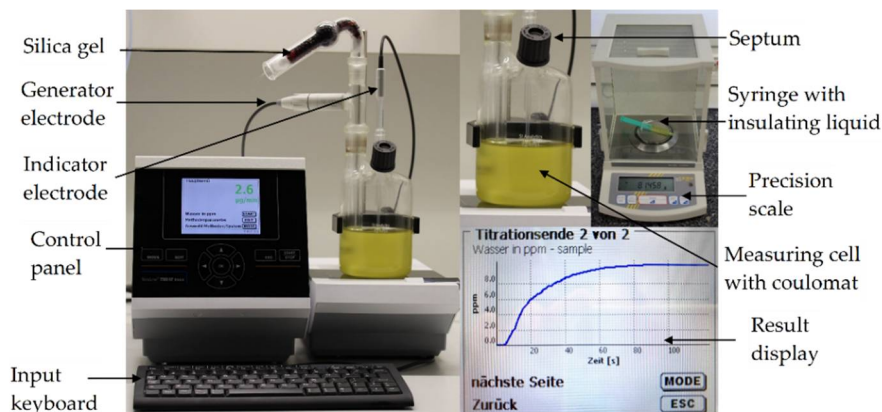


Figure S1. Measuring device for determining the water content, the detail of titration cell, weighing of the insulating liquid sample and a measurement curve.

After entering the weight of the 1 ml sample of the insulating liquid in *TitroLine 7500 KF trace* program, the analysis of the moisture content began. The measurement ends automatically and the result will be displayed digitally in ppm on the screen. The measurement curve can also be viewed on the device to confirm the validity of the measurement. The measurement was performed five times and the mean of the results was calculated to avoid deviations. Figure S1 shows the measuring device and its functions.

S1.3. Dissolved Gas Analysis

Dissolved gas analysis (DGA) is one of the most important tools for assessing the condition of high voltage equipment such as transformers with oil-paper insulation based on the standard IEC 60599 [47]. It is used to detect the fault of the equipment at an early stage based on the quotients of analyzed gas concentrations. Failures lead to the degradation of insulating materials, which release gases in the form of free gases or dissolved in the insulating liquid. For the analysis of the aged insulating oil samples, the device for gas-in-oil analysis *TOGA GC*, offered by the company *Energy Support GmbH*, is used. It is a gas chromatograph where the measurement is carried out using a flame ionization detector and a thermal conductivity detector. Apart from that, a vacuum degassing system is adopted for the extraction of the dissolved gases from the insulating liquid, which can realize the automatic degassing. Furthermore, the entire system is controlled by the *TOGA GC* software with a computer which is coupled to this system via a serial port [79]. To measure the gas content of insulating oils, the oil sample was first taken out of the aluminum bottle in accordance with the standard IEC 60475 by a 50 ml glass syringe connected with a PTFE hose via a two-way valve [34]. Figure S2 shows the example of a 50 ml syringe.

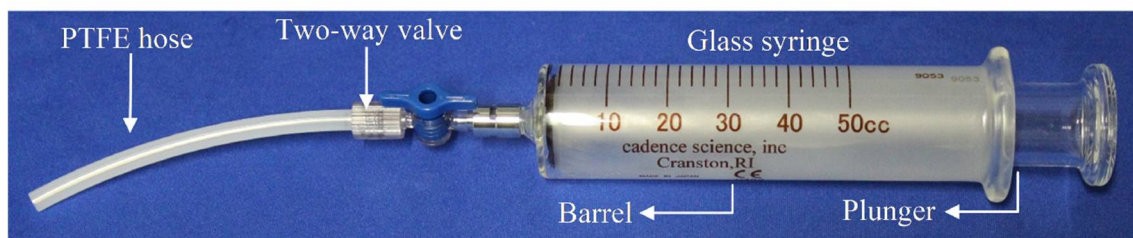


Figure S2. 50 ml glass syringe with a connected PTFE hose via a two-way valve.

The glass syringe was previously rinsed and wetted with the oil sample to remove possible impurities and achieve better tightness of the syringe. After extracting the liquid sample, the syringe was held vertically to let the bubbles move to the front of the syringe

and the plunger was pulled slowly to remove the bubbles out of the syringe. After sampling, the glass syringe was connected to the vacuum degassing system and the oil sample was then analyzed immediately in order to prevent falsification by longer storage time. The release of the gases from the insulating oil was initially carried out in the vacuum degassing system, into which the sample was injected. A vacuum pump degassed the oil sample, wherein the extracted gases were moved into a vacuum chamber and separated from the air via solenoid valves. The carrier gas argon, which is regarded as the mobile phase, transferred the released gases into the separation columns, where the different gases were separated. On the inner wall of the 30 m \times 0.32 mm dimensioned capillary column, a thin film exists, which is considered as the stationary phase. Finally, the various gases were detected by two detectors, the flame ionization detector (FID) and the thermal conductivity detector (TCD). Due to their different properties, the gases reach the detectors after different retention times, which refer to the time required for the gases from the injection to the leaving of the separation columns [79].

In principle, the detectors generate an electrical voltage when a substance flows in. The voltage depending on the time, due to the detection of individual fractions, are recognized as so-called peaks. The flame ionization detector (FID) is a scientific instrument with a high sensitivity. It can detect almost all organic compounds. The operation of FID is based on the detection of ions which are generated during the combustion of organic compounds in a hydrogen flame. Ions are detected by means of a metal collector which is biased with a high DC voltage. The current across this collector is thus proportional to the rate of ionization which in turn depends on the concentration of organic species in the sample gas. FID can detect the fault gases including CH_4 , C_2H_2 , C_2H_4 , C_2H_6 , C_3H_6 and C_3H_8 as well as CO and CO_2 . However, for the detection of the inorganic gases CO and CO_2 , a so-called methanizer in *TOGA GC* must be used, which converts these two elements into methane via hydrogenation at a temperature of 300 $^\circ\text{C}$ with the help of the connected hydrogen supply [79]. The analysis of the gases was accomplished in the connected computer. The software *TOGA GC* automatically detects the peaks in the voltage curves, assigned these to the respective components, and finally determined the absolute concentration of these gas components. Figure S3 shows the setup of the measuring device for the analysis of dissolved gases in the insulating liquid.



Figure S3. DGA system for the detection of dissolved gases in the insulating liquid.

S1.4. Dissipation Factor $\tan \delta$ and Relative Permittivity ϵ_r

The dielectric dissipation factor $\tan \delta$ and the relative permittivity ϵ_r are good indicators to assess the dielectric properties of insulating materials. The determination of these parameters is carried out with the device *DTL C* produced by the company *BAUR GmbH* based on the standard IEC 60247 [80], which states that the insulating liquid can subject to the electrical stress of 1 kV/mm. In terms of [81], the measurement of the dissipation factor ranges from 4 to $1 \cdot 10^{-6}$ with the resolution of $1 \cdot 10^{-6}$ while the relative permittivity is

measured in the range of 1 to 30 with the resolution of $1 \cdot 10^{-2}$. The test temperature can be set from 11 to 110 °C with the resolution of 0.1 °C.

It is obvious from Figure S4 that the test cell of this device is made up of an external high-voltage electrode and an inner measuring electrode. The measuring errors can be avoided through the guard ring because additional influences such as leakage currents on the interface between the insulating oil and the air would affect the test results. The measuring process of the dissipation factor and the relative permittivity took place in principle fully automatically. Before the measurement, the filling glass tube and the test cell were rinsed two times with a new insulating liquid of the same type as the sample and one time with the sample to avoid influences of contaminants and possible sample residues from previous measurements. After emptying the test cell, the measured oil sample was poured into the filling glass, flowing through the cell and final to the deaeration glass tube. For the investigation in this study, a test voltage of 2000 V AC at a frequency of 50 Hz was specified.

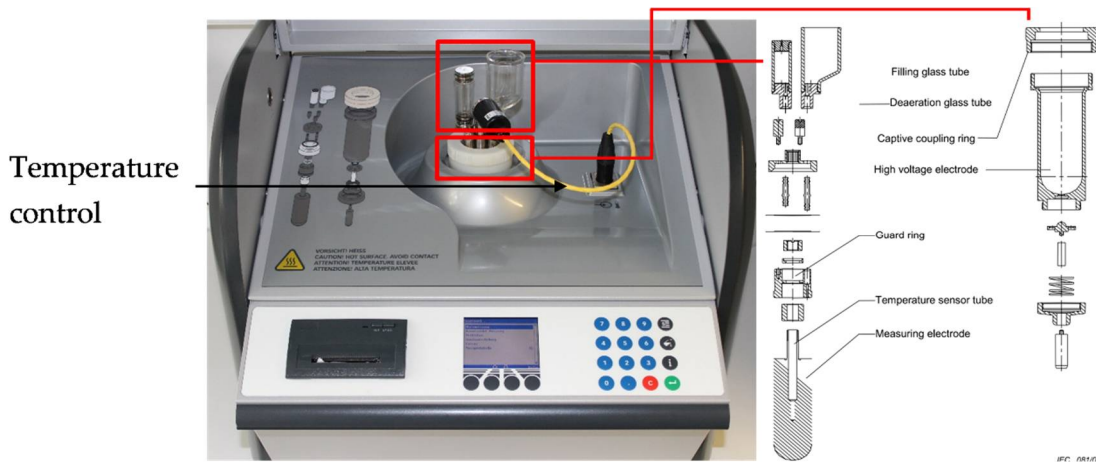


Figure S4. Device for determining the dissipation factor $\tan \delta$ and relative permittivity ϵ_r .

S1.5. Breakdown Voltage

According to IEC 60156 and VDE 0370-5 [53], the breakdown voltage is a characteristic value for the suitability of oil to withstand electrical stress. The measurement of the breakdown voltage by means of the *Breakdown Analyzer BA100* from *b2 electronics GmbH* thus primarily shows the degree of contamination and water content in the sample.

The fully automatic determination of the breakdown voltage was carried out in a standardized test vessel with a volume of approx. 300 ml. This test vessel contains two VDE spherical calotte with a distance of $2.5 \text{ mm} \pm 0.05 \text{ mm}$, which are completely surrounded by the insulating liquid during measurement. The homogeneity of the electrical field between this type of electrodes is $\eta = 0.97$, where η is called *Schwaiger's utilization factor* and refers to the proportion of the inhomogeneous arrangement to the homogeneous structure. At the beginning of the measurement, a five-minute waiting allows any gas bubbles to escape. An AC voltage was applied between the electrodes and increased stepwise by 2 kV/s. After the breakdown, a waiting time of two minutes elapses before another measurement starts. In the meantime, the oil sample was mixed by a magnetic stirrer. A visible electric spark across the electrodes occurred at the moment of the breakdown of the sample and the voltage at this time is recorded and displayed. The effective values of breakdown voltage are determined in six successive tests and the output will be their mean value with standard deviation. In addition, the maximum output voltage of the BA100 is 100 kV and the measured voltages are given with an accuracy of $\pm 1 \text{ kV}$ [82]. Figure S5 shows the setup of the measuring device for determining the breakdown voltage of the insulating liquid.

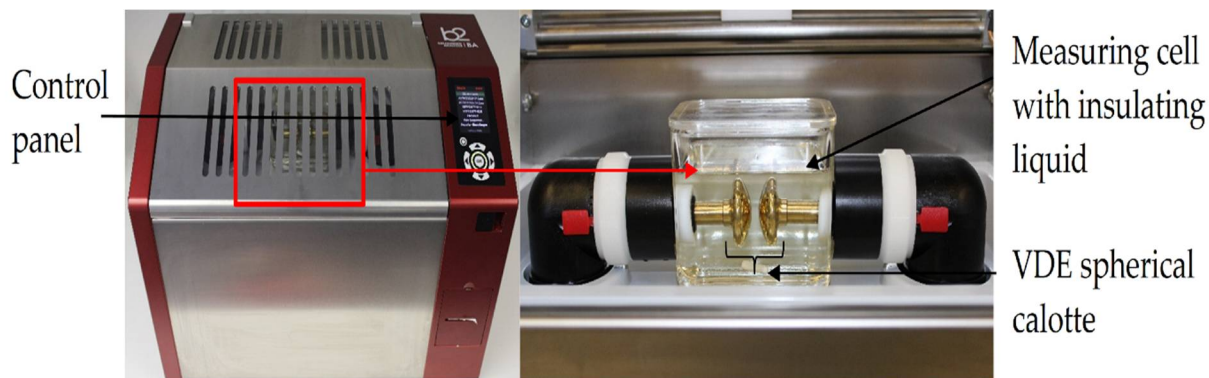


Figure S5. Device for determining the breakdown voltage U_D of the insulating liquid.

S1.6. Interfacial Tension

The determination of interfacial tension between water and oil samples in this study was carried out by the tensiometer *Sigma 702ET* supplied from the company *Biolin Scientific* in accordance with the standard ASTM D971-12 [56]. This device is based on the *Du Noüy* ring method and can measure the maximum interfacial tension of 1000 mN/m with a resolution of 0.01 mN/m. The 0.185 mm thick ring is made up of platinum with a radius of 9.545 mm [83]. Before the measurement, it should be noted that the test vessel, the density probe, and the *Du Noüy* ring must be thoroughly cleaned before each step because the interfacial tension is greatly affected by contaminants. This was fulfilled by means of 2-propanol, acetone, and distilled water. Additionally, the *Du Noüy* ring must be flamed briefly with a butane gas flame to clean the residual on the ring. Moreover, the distilled water with a density of 1.00 g/cm³ was selected as a liquid of higher density, since the insulating liquid samples have lower density values.

At the beginning of the measurement, the balance was first calibrated with a calibration weight and a glass density probe measuring the density of distilled water. After the calibration, the density of the liquid sample (about 20 ml) was determined also by the glass density probe following the instructions on the screen. The density probe with known volume was hung on the balance hook and immersed into the liquid sample to be measured. The force, which is needed to hold the probe at a constant depth in the oil, was then recorded. The software in the device automatically calculated the density of the sample based on the *Archimedes* principle [83].

Before determining the interfacial tension, the surface tension of the distilled water (about 40 ml) was first measured by the *Du Noüy* ring hung on the hook, whose value has to be in the range of 71-73 mN/m. Moreover, the sample vessel must be cleaned and rinsed thoroughly again, and a new sample of the water has to be added into the vessel. After this process, the *Du Noüy* ring, remained in the distilled water and the liquid sample (about 25 ml), has to be carefully introduced to the water surface. When the measurement started, the ring was pulled from the water into the oil sample until the maximum of the tensile force was reached, which was realized by lowering the horizontal platform (sample table) at a constant speed. Figure S6 shows the setup of the measuring device for determining the interfacial tension of the insulating liquid.

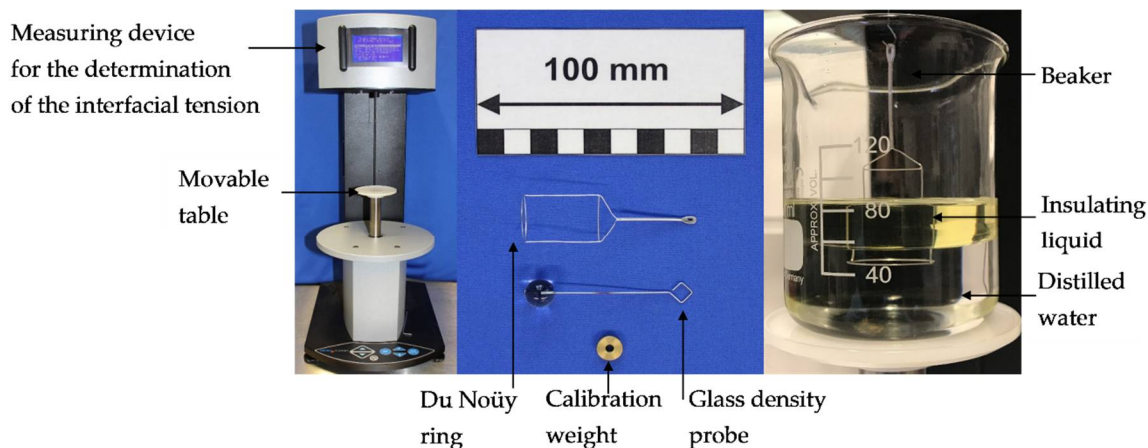


Figure S6. Device for determining the interfacial tension σ of the insulating liquid.

S1.7. Acidity

The determination of the acidity in this study was completed by the potentiometric titration with the *TitroLine 7000* from the company *SI Analytics GmbH* in terms of the standard IEC 62021-1 and IEC 62021-3 [59,60]. Figure S7 shows the device for determining the acid number. This device essentially consists of an analysis computer, a combination electrode (single-rod measuring cell) containing a glass electrode (measuring electrode) and a reference electrode which is filled with a reference electrolyte of potassium chloride (KCL) in deionized water at the concentration recommended by the electrode manufacturer [59], a burette and a magnetic stirrer. Before the measurement, a multi-point calibration of the pH values was performed by putting the pH-glass immersed successively in three buffer solutions with the pH values of 4.00, 7.00, and 10.01 (Figure S7) according to the instructions on the screen, and the results were saved in the device [86]. The first part of the measurement is the determination of the blank value of the titration using the solvent of 2-propanol with a high concentration of 99.9 % (isopropanol, IPA). 20 ml of the solvent was poured into a 50 ml clean beaker with a magnetic stirrer, which was then put on the platform of the *TitroLine 7000*. After getting a desirable blank value according to IEC 62021, which was entered into the program, the determination of the acidity can begin. 5 g of the liquid sample was filled into another clean glass beaker with a magnetic stirrer and weighed by a digital precision scale and then mixed with 20 ml of 99.9 % 2-propanol. For the precision of the results, the acidity value of the oil sample was usually measured three times and calculated according to the criterion in IEC 62021-1 to ensure that the values are in the specified range, or the measurement should be repeated.

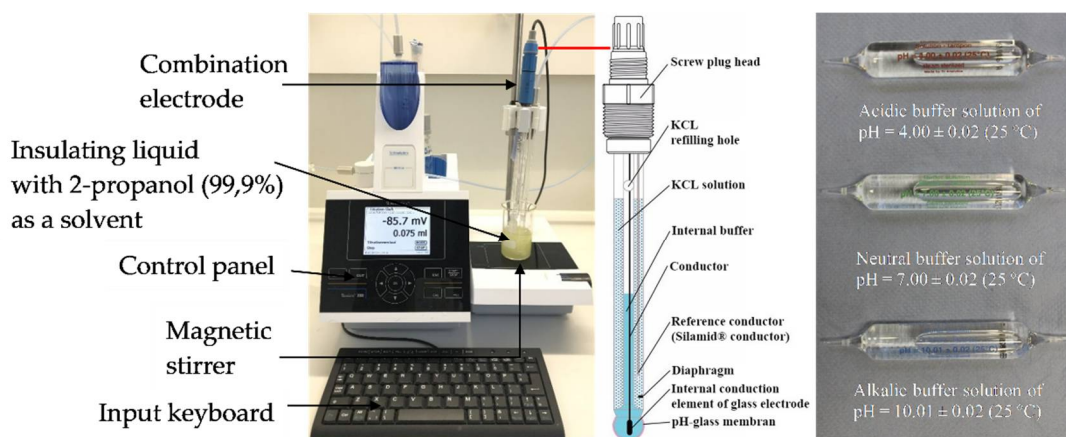


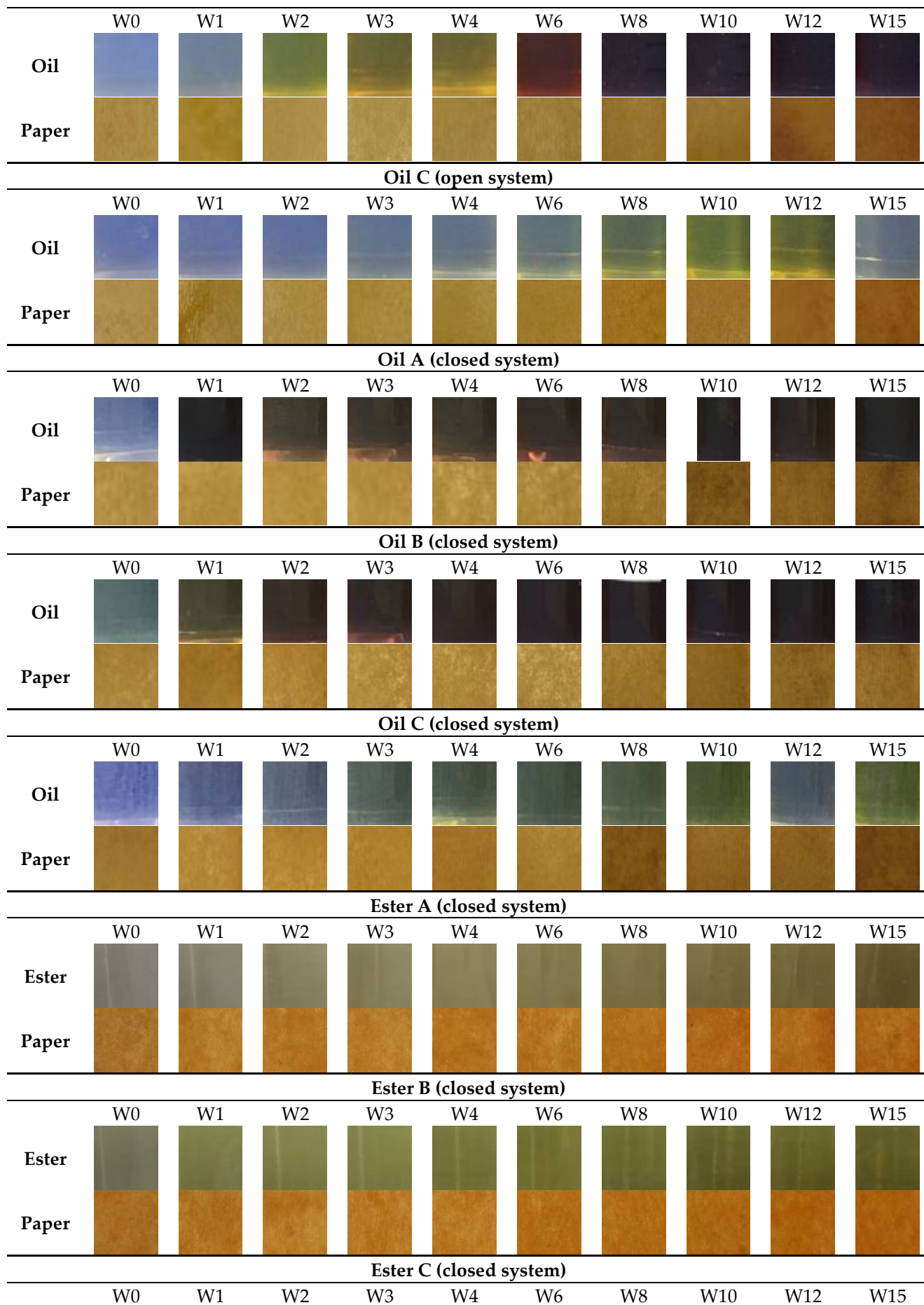
Figure S7. Device for determining the acid value of the insulating liquid.

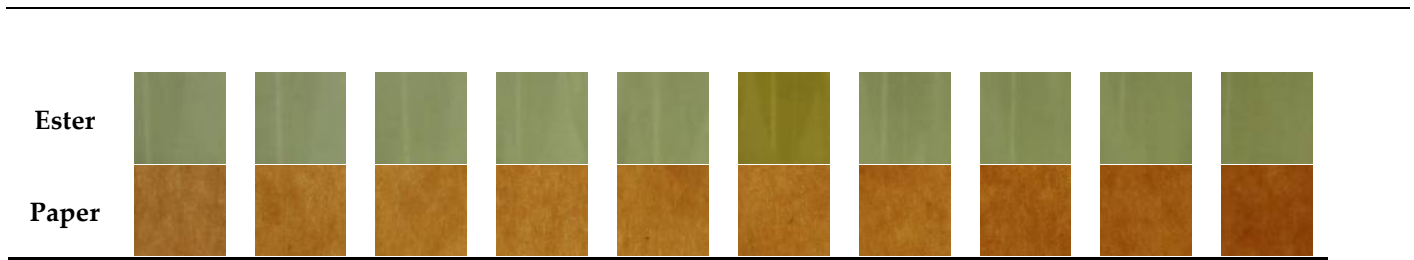
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S1.9. Inhibitor Content

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Figure 1 displays two rows of color swatches illustrating the color changes in oil and paper over time. The top row, labeled "Oil A (open system)", shows 10 swatches (W0 to W15) with a color gradient from light blue (W0) to dark brown (W15). The bottom row, labeled "Oil B (open system)", shows 10 swatches (W0 to W15) with a color gradient from light yellow (W0) to dark brown (W15). The labels "Oil" and "Paper" are positioned to the left of the respective rows.





S3 Correlation of the aging markers

The correlations presented below have the following color coding for the pearson correlation coefficient r .



	Moisture	Breakdown	Acid	IFT	DP	Viscosity 10°C	tan δ 25°C	CO	CO ₂	CO ₂ /CO	ε _r 25°C
Moisture											
Oil A	1.00	0.35	0.64	-0.68	-0.71	0.85	0.63	0.58	0.37	-0.54	0.74
Oil B	1.00	-0.81	0.71	-0.77	-0.63	0.84	0.68	0.80	-0.20	-0.77	0.80
Oil C	1.00	-0.28	0.73	-0.76	-0.58	0.79	0.66	0.62	-0.06	-0.72	0.63
Breakdown											
Oil A		1.00	0.24	-0.37	-0.48	0.57	0.17	0.28	0.20	-0.19	0.64
Oil B		1.00	-0.30	0.51	0.46	-0.62	-0.35	-0.55	0.06	0.49	-0.52
Oil C		1.00	0.02	0.23	-0.12	-0.06	-0.20	0.25	0.50	-0.12	-0.17
Acid											
Oil A			1.00	-0.85	-0.95	0.72	0.83	0.81	0.48	-0.94	0.86
Oil B			1.00	-0.91	-0.85	0.82	0.78	0.86	-0.14	-0.89	0.80
Oil C			1.00	-0.94	-0.78	0.89	0.79	0.69	-0.15	-0.90	0.77
IFT											
Oil A				1.00	0.92	-0.60	-0.93	-0.98	-0.84	0.89	-0.77
Oil B				1.00	0.93	-0.92	-0.84	-0.97	0.09	0.96	-0.86
Oil C				1.00	0.73	-0.91	-0.85	-0.57	0.34	0.86	-0.83
DP											
Oil A					1.00	-0.77	-0.84	-0.88	-0.59	0.93	-0.94
Oil B					1.00	-0.79	-0.67	-0.89	-0.19	0.81	-0.70
Oil C					1.00	-0.77	-0.35	-0.62	-0.15	0.85	-0.33
Viscosity 10°C											
Oil A						1.00	0.58	0.46	0.15	0.71	0.87
Oil B						1.00	0.94	0.87	-0.29	-0.92	0.98
Oil C						1.00	0.78	0.79	-0.01	-0.94	0.77
tan δ 25°C											
Oil A							1.00	0.91	0.79	-0.61	0.65
Oil B							1.00	0.79	-0.36	-0.86	0.96
Oil C							1.00	0.52	-0.44	-0.73	1.00
CO											
Oil A								1.00	0.88	-0.80	0.70
Oil B								1.00	0.06	-0.89	0.79
Oil C								1.00	0.52	-0.84	0.53
CO₂											
Oil A									1.00	0.52	0.38
Oil B									1.00	0.36	-0.43
Oil C									1.00	-0.08	-0.42
CO₂/CO											
Oil A										1.00	-0.83
Oil B										1.00	-0.91
Oil C										1.00	-0.72
ε_r 25°C											
Oil A											1.00
Oil B											1.00
Oil C											1.00

Figure S9. Pearson correlation coefficients r for the open system with Oil A, B and C.

	Moisture	Breakdown	Acid	IFT	DP	Viscosity 10°C	tan δ 25°C	CO	CO ₂	CO ₂ /CO	ε _r 25°C
Moisture											
Oil A	1.00	0.35	0.64	-0.68	-0.71	0.85	0.63	0.58	0.37	-0.54	0.74
Oil B	1.00	-0.81	0.71	-0.77	-0.63	0.84	0.68	0.80	-0.20	-0.77	0.80
Oil C	1.00	-0.28	0.73	-0.76	-0.58	0.79	0.66	0.62	-0.06	-0.72	0.63
Breakdown											
Oil A		1.00	0.24	-0.37	-0.48	0.57	0.17	0.28	0.20	-0.19	0.64
Oil B		1.00	-0.30	0.51	0.46	-0.62	-0.35	-0.55	0.06	0.49	-0.52
Oil C		1.00	0.02	0.23	-0.12	-0.06	-0.20	0.25	0.50	-0.12	-0.17
Acid											
Oil A			1.00	-0.85	-0.95	0.72	0.83	0.81	0.48	-0.94	0.86
Oil B			1.00	-0.91	-0.85	0.82	0.78	0.86	-0.14	-0.89	0.80
Oil C			1.00	-0.94	-0.78	0.89	0.79	0.69	-0.15	-0.90	0.77
IFT											
Oil A				1.00	0.92	-0.60	-0.93	-0.98	-0.84	0.89	-0.77
Oil B				1.00	0.93	-0.92	-0.84	-0.97	0.09	0.96	-0.86
Oil C				1.00	0.73	-0.91	-0.85	-0.57	0.34	0.86	-0.83
DP											
Oil A					1.00	-0.77	-0.84	-0.88	-0.59	0.93	-0.94
Oil B					1.00	-0.79	-0.67	-0.89	-0.19	0.81	-0.70
Oil C					1.00	-0.77	-0.35	-0.62	-0.15	0.85	-0.33
Viscosity 10°C											
Oil A						1.00	0.58	0.46	0.15	0.71	0.87
Oil B						1.00	0.94	0.87	-0.29	-0.92	0.98
Oil C						1.00	0.78	0.79	-0.01	-0.94	0.77
tan δ 25°C											
Oil A							1.00	0.91	0.79	-0.61	0.65
Oil B							1.00	0.79	-0.36	-0.86	0.96
Oil C							1.00	0.52	-0.44	-0.73	1.00
CO											
Oil A								1.00	0.88	-0.80	0.70
Oil B								1.00	0.06	-0.89	0.79
Oil C								1.00	0.52	-0.84	0.53
CO₂											
Oil A									1.00	0.52	0.38
Oil B									1.00	0.36	-0.43
Oil C									1.00	-0.08	-0.42
CO₂/CO											
Oil A										1.00	-0.83
Oil B										1.00	-0.91
Oil C										1.00	-0.72
ε_r 25°C											
Oil A											1.00
Oil B											1.00
Oil C											1.00

Figure S10. Pearson correlation coefficients r for the closed system with Oil A, B and C.

	Moisture	Breakdown	Acid	IFT	DP	Viscosity 10°C	tan δ 25°C	CO	CO ₂	CO ₂ /CO	ε _r 25°C
Moisture											
Oil A	1.00	0.35	0.64	-0.68	-0.71	0.85	0.63	0.58	0.37	-0.54	0.74
Oil B	1.00	-0.81	0.71	-0.77	-0.63	0.84	0.68	0.80	-0.20	-0.77	0.80
Oil C	1.00	-0.28	0.73	-0.76	-0.58	0.79	0.66	0.62	-0.06	-0.72	0.63
Breakdown											
Oil A		1.00	0.24	-0.37	-0.48	0.57	0.17	0.28	0.20	-0.19	0.64
Oil B		1.00	-0.30	0.51	0.46	-0.62	-0.35	-0.55	0.06	0.49	-0.52
Oil C		1.00	0.02	0.23	-0.12	-0.06	-0.20	0.25	0.50	-0.12	-0.17
Acid											
Oil A			1.00	-0.85	-0.95	0.72	0.83	0.81	0.48	-0.94	0.86
Oil B			1.00	-0.91	-0.85	0.82	0.78	0.86	-0.14	-0.89	0.80
Oil C			1.00	-0.94	-0.78	0.89	0.79	0.69	-0.15	-0.90	0.77
IFT											
Oil A				1.00	0.92	-0.60	-0.93	-0.98	-0.84	0.89	-0.77
Oil B				1.00	0.93	-0.92	-0.84	-0.97	0.09	0.96	-0.86
Oil C				1.00	0.73	-0.91	-0.85	-0.57	0.34	0.86	-0.83
DP											
Oil A					1.00	-0.77	-0.84	-0.88	-0.59	0.93	-0.94
Oil B					1.00	-0.79	-0.67	-0.89	-0.19	0.81	-0.70
Oil C					1.00	-0.77	-0.35	-0.62	-0.15	0.85	-0.33
Viscosity 10°C											
Oil A						1.00	0.58	0.46	0.15	0.71	0.87
Oil B						1.00	0.94	0.87	-0.29	-0.92	0.98
Oil C						1.00	0.78	0.79	-0.01	-0.94	0.77
tan δ 25°C											
Oil A							1.00	0.91	0.79	-0.61	0.65
Oil B							1.00	0.79	-0.36	-0.86	0.96
Oil C							1.00	0.52	-0.44	-0.73	1.00
CO											
Oil A								1.00	0.88	-0.80	0.70
Oil B								1.00	0.06	-0.89	0.79
Oil C								1.00	0.52	-0.84	0.53
CO₂											
Oil A									1.00	0.52	0.38
Oil B									1.00	0.36	-0.43
Oil C									1.00	-0.08	-0.42
CO₂/CO											
Oil A										1.00	-0.83
Oil B										1.00	-0.91
Oil C										1.00	-0.72
ε_r 25°C											
Oil A											1.00
Oil B											1.00
Oil C											1.00

Figure S11. Pearson correlation coefficients r for the closed system with Ester A, B and C.