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Thermal Ageing of Dry Cellulose Paper Impregnated with Different Insulating Liquids—Comparative Studies of Materials Properties

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Abstract: Natural and synthetic esters are increasingly being chosen instead of mineral oil for environmental and fire safety reasons. However, their use in power transformers is limited due to insufficiently well-understood ageing processes affecting their properties and the properties of cellulosic materials impregnated with them. The research results presented in many scientific papers prove that the use of esters slows the ageing process of cellulosic materials. This article presents the results of research aimed at answering the question of whether the effect of slowing the ageing process will also occur in the case of insulation with very low initial moisture. The answer to this question will allow us to better understand the role of water in the ageing process of the transformer's insulation system. The thermal ageing process was carried out at a temperature of 150 °C in closed systems. The degree of cellulose polymerisation was taken as a measure of the degree of paper ageing. Great attention was paid to measuring the water content in both paper and electro-insulating liquids at various stages of their ageing. Furthermore, measurements of the properties of electro-insulating liquids were made, which are considered markers of ageing. The test results obtained indicate that in the case of a dry insulation system, corresponding to the initial moisture of the new units, the type of liquid used to impregnate the cellulosic material does not significantly affect its depolymerisation process. However, in the case of paper impregnated with natural esters, a lower dynamic of moisture increase in insulation was observed.

Keywords: power transformer; cellulose insulation; mineral oil; synthetic ester; natural ester; ageing; degree of polymerisation; neutralisation value; water content

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1. Introduction

Petroleum-based mineral oils have been used in power transformers since 1887 [1]. However, the insulating system based on mineral oil-impregnated cellulosic materials has been used in power transformers on a large scale since the 1920s [2]. The popularity of cellulose and mineral oil is mainly due to their good physicochemical properties and also to the availability of raw materials for their production, which makes these materials relatively inexpensive. Almost a hundred years of use of insulation based on cellulosic materials and mineral oil allowed for sufficient knowledge of the properties of such insulation under its operating conditions. Therefore, these materials are most often chosen for transformers of strategic importance for the electric power system. These devices include primarily generator step-up transformers in power plants and transformers connecting high-voltage lines, called grid transformers.

Currently, alternatives to mineral oil are mainly synthetic and natural esters [3,4]. These liquids are increasingly used in low- and medium-voltage distribution transformers and occasionally in grid and step-up transformers. The greatest advantage of these liquids, compared to mineral oil, is their good fire properties, including high flash and fire points [5,6]. Furthermore, synthetic and natural esters are considered environmentally friendly liquids due to their biodegradability [4,7].

The limitation in their use, especially in transformers strategic for the operation of the electric power system, is the insufficient and well-understood ageing processes affecting the properties of liquids and cellulosic materials impregnated with them. Therefore, research is necessary to answer the question of how the properties of electro-insulating liquids and materials impregnated with them change as a result of various types of exposure [8].

One of the parameters that very well describes the phenomenon of the degradation of solid materials used in power transformers is the degree of polymerisation of cellulose. For new insulation, the degree of polymerisation of the cellulose is usually between 1000 and 1300. During the insulation drying process in the transformer production stage, the polymerisation degree value can decrease by a dozen percent compared to the initial value [9,10]. During the operation of the transformer, the degree of polymerisation of cellulose gradually decreases, and the dynamics of this process mainly depends on the temperature and degree of moisture of the insulating system [11,12]. In turn, the increase in the water content in the insulation system is highly dependent on the oxidation processes of cellulosic materials [13,14]. Figure 1 shows one of several oxidation reactions of the cellulose molecule $(C_6H_{10}O_5)_n$, leading to an increase in moisture in the transformer insulation system. Water molecules are formed as a result of the reaction of oxygen with secondary hydroxyl groups located at the second and third carbon atoms in the β-D-glucose residue.

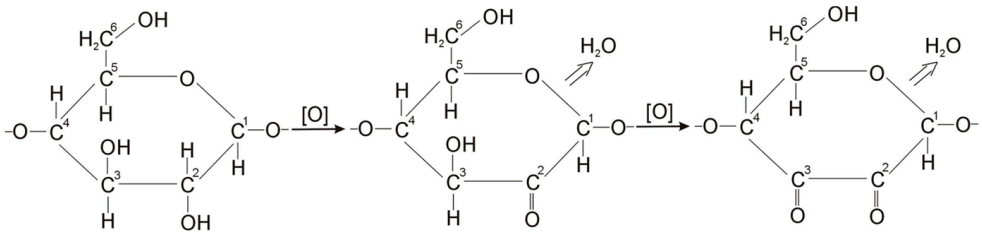


Figure 1. Oxidation reactions of cellulose molecules that lead to an increase in water content in the transformer's insulation system.

Therefore, the water in the transformer insulation system is both a product of cellulose oxidation and a catalyst in the cellulose depolymerisation process. The factor that can significantly change the dynamics of cellulose depolymerisation is the type of liquid with which the cellulosic material is impregnated. This is primarily due to the different solubilities of water in electro-insulating liquids. The different solubilities of water in liquid dielectrics are related to their different polarities. This is because of the presence of ester bonds in their structure. This enables the formation of hydrogen bonds between the oxygen atom belonging to the ester molecule and the hydrogen atoms belonging to the water molecule [7,15].

As the temperature of the insulating system increases, the water migrates from the cellulosic materials, whose hygroscopicity decreases, to the electro-insulating liquid, whose solubility of the water increases [16]. In particular, in the case of insulation systems with synthetic esters and natural esters, the water content in the solid insulation decreases, which can significantly slow the ageing process of the insulation. This can be proven by the test results of two twin hermetically sealed distribution transformers with a rated power of 200 kVA and a rated voltage of 10/0.4 kV presented in [17]. One of the transformers used mineral oil, while the other was filled with natural esters. These transformers had been operating in the power system for seven years with a similar load profile, with the natural ester-insulated transformer periodically being loaded more heavily than the mineral oil-insulated transformer. The tests carried out on paper insulation showed an approximately 42% higher value of the degree of cellulose polymerisation in the case of a transformer filled with natural esters compared to a transformer insulated with mineral oil. Moreover, the authors of [17] also found a much lower level of water content in the insulation of high-voltage windings of a transformer insulated with natural esters (avg. 0.67%) compared to a transformer insulated with mineral oil (avg. 1.73%).

In addition, a number of studies conducted in various research centres confirmed a slower ageing process of cellulosic materials impregnated with esters compared to cellulosic materials impregnated with mineral oil. The authors of [18] pointed to a slower cellulose depolymerisation process and a decrease in tensile strength in the case of paper impregnated with esters from palm oil compared to mineral-oil-impregnated cellulosic materials. After 1008 h of ageing at 120 °C in a closed system, the decrease in the degree of polymerisation in the case of paper impregnated with natural esters and mineral oil was 49% and 62%, respectively.

The authors of [19] also showed that the ageing dynamics of cellulose insulation impregnated with natural esters from sunflower oil are lower compared to those of paper impregnated with mineral oil. However, these authors noticed that the difference in the ageing dynamics of paper impregnated with natural esters changes with increasing temperature.

According to the authors of [20], the phenomena that slow the ageing process of ester-impregnated cellulose insulation are mainly related to the impact of water. One of the previously mentioned phenomena is the migration of water from cellulosic materials to an ester. Another phenomenon is the hydrolysis process of natural ester, which reduces the water content of the insulation and causes the formation of long-chain fatty acids. Hydrolysis of a triglyceride consumes three water molecules and generates one molecule of glycerol and three long-chain fatty acids [20,21]. These acids combine with cellulose molecules through a process called transesterification [19,20,22,23]. The authors of [19] indicated that these long-chain fatty acids attached to cellulose may constitute a barrier to water penetration, which may be another explanation for the slowdown in the ageing process of ester-impregnated cellulosic materials.

The main goal of the research conducted as part of this work was to obtain an answer to the question of whether the effect of slowing the ageing process of cellulosic materials will also occur in the case of insulation with very low initial moisture, corresponding to new transformers. Furthermore, the aim of the work was to assess the properties of electro-insulating liquids at various stages of insulation ageing.

2. Materials and Methods

The purpose of this research was to compare the ageing dynamics of cellulose paper impregnated with three different electro-insulating liquids. Furthermore, this research included the analysis of the changes in the properties of electro-insulating liquids during the ageing process. This research was divided into four main stages: Stage I included the preparation of three sets of samples. Each set consisted of five bottles containing paper samples impregnated with mineral oil, synthetic ester, or natural ester. This stage mainly included the drying of the materials and the selection of the appropriate weight ratio from liquid to paper. Stage II was related to the ageing of materials in a heating chamber at a temperature of 150 °C. Stage III consisted of conditioning the samples in a heating chamber at 50 °C for 168 h. Stage IV included the testing of selected properties of both paper and electro-insulating liquids. Material properties that are considered markers of ageing were selected for this investigation.

To study the dynamics of ageing of cellulose paper depending on the type of liquid used for its impregnation, Nytro 10 XN inhibited mineral oil by Nynas (Stockholm, Sweden), Midel 7131 synthetic ester by M&I Materials (Stretford, UK), and Cargill's natural ester made of soy FR3 (Cargill, Wayzata, MN, USA) were used. Table 1 compares the properties of these liquids that are most important from the point of view of the conducted research. These properties are provided by their manufacturers in their catalogue cards. In addition, transformer insulation crepe paper type Kraft was used in the tests in the form of tapes cut to the appropriate length. The basis weight of paper was 145 g/m^2. The width of the paper tapes used was 30 mm.

Table 1. Comparison of the properties of electro-insulating liquids based on the data available in product data sheets [24–26].

Property	Mineral Oil	Synthetic Ester	Natural Ester
Water content, ppm	<20	50	4–50
Neutralisation value, $mgKOH/g_{oil}$	<0.01	0.02	0.01–0.05
Interfacial tension at 25 °C, mN/m	49	-	-
Dissipation factor at 90 °C -	<0.001	<0.008	0.01–0.03
Resistivity at 90 °C, GΩ·m	-	>20	-
Kinematic viscosity at 40 °C, mm^2/s (cSt)	7.6	29	32–34

Before starting the investigation, the materials had to be properly prepared. Liquids that radically differ in their water solubility were selected for testing. Therefore, to limit the impact of water on the ageing process resulting from its migration from cellulose insulation to electro-insulating liquids in the heating and ageing of the materials, it was necessary to dry them. It was assumed that the water content in the paper insulation before the ageing process began should not exceed 0.5% [27,28], while the relative humidity of the electro-insulating liquids should be below 5%, which, according to the standard IEC 60422 [29], corresponds to dry insulation.

Initial tests of the water content in the samples of electro-insulating liquids showed their moisture content exceeded 5% relative saturation; therefore, they were subjected to a drying process. Drying was carried out using a 3A molecular sieve, which had previously been regenerated at a temperature of 260 °C for 5 h. The molecular sieve was then placed in bottles filled with electro-insulating liquids for a period of 21 days. In the next step, the liquids were degassed in a vacuum chamber at a temperature of 50 °C and a pressure of 0.16 mbar. The degassing time was 24 h. After the process of drying and degassing the electro-insulating liquids, their relative saturation did not exceed 1%.

The paper samples were prepared for testing in the form of 100 cm long and 3 cm wide tapes. The cut tapes were wrapped in rolls whose average weight was 4.58 g. A total of 60 such paper rolls were prepared and then subjected to the drying process. This process was carried out at a temperature of 90 ± 5 °C and a pressure of approximately 0.16 mbar. The drying time was 16 h.

To compare the ageing dynamics of cellulosic materials impregnated with various electro-insulating liquids, 15 bottles of 5 were prepared for each type of liquid. The sample numbering is presented in Table 2.

Each bottle contained four rolls of dried paper and a strip of copper (13.9 g), which served as a catalyst in the ageing process of the materials. The bottles were then filled with liquids (225 mL), leaving an air cushion due to the expected increase in liquid volume resulting from their thermal expansion. The weight ratio of the materials corresponded to the weight ratio of these materials in the selected distribution transformer with a rated power of 40 MVA.

In the next step, the paper was impregnated using a vacuum chamber in which bottles with the tested materials were placed. Samples were impregnated for 24 h at a 0.16 mbar vacuum and a temperature of 50 °C. Then, all the bottles were closed, and the sample impregnation and conditioning process continued in a heat chamber at 40 °C for 168 h.

Then, the samples marked 1, 6, and 10 were removed from the heat chamber. The remaining samples were aged at 150 °C for 24, 72, 168, and 336 h, according to Table 2. After ageing, all the samples were conditioned for 7 days at 50 °C. Then, tests of the selected properties of paper and electro-insulating liquids began.

Table 2. Numbering of samples and their ageing times.

Sample Number	Kind of Liquid	Ageing Time, h
1	Natural ester	0
2	Natural ester	24
3	Natural ester	72
4	Natural ester	168
5	Natural ester	336
6	Mineral oil	0
7	Mineral oil	24
8	Mineral oil	72
9	Mineral oil	168
10	Mineral oil	336
11	Synthetic ester	0
12	Synthetic ester	24
13	Synthetic ester	72
14	Synthetic ester	168
15	Synthetic ester	336

The degree of cellulose polymerisation was taken as a measure of the degree of ageing of paper. This is the most important parameter of the cellulosic material, which corresponds to its mechanical strength. In addition, the water content in the paper was also tested, which, in turn, affected its dielectric properties and the dielectric properties of the electro-insulating liquid.

Measurements of the average viscometric degree of polymerisation (DP) were made according to IEC 60450 [30]. DP measurements were carried out in three stages. First, the shredded paper was dissolving in the bis (etylenodiamine) copper (II hydroxide solution) reagent under a nitrogen atmosphere. To speed up the paper dissolution process, mechanical shaking of the dissolved sample was used. In the second stage, the specific viscosity was determined using a Ubbelohde viscometer in a water bath at a temperature of 20 °C. In the last step, the average degree of cellulose polymerisation was calculated according to the guidelines contained in IEC 60450 [30].

Water content measurements of both paper and the electro-insulating liquids were performed using the Karl Fischer coulometric method according to the IEC 60814 standard [31]. For paper tests, water extraction was carried out using methanol. All measurements were performed using a titrator 831 KF by Metrohm (Herisau, Switzerland) and the following chemical reagents: HYDRANAL Coulomat Oil as a catholyte, HYDRANAL Coulomat CG as an anolyte, n-heksan for cellulose degreasing, HYDRANAL Water Standard 1.0, and Hydranal Water Standard in Oil to verify the correct operation of the device for measuring the water content.

In addition to the water content, electro-insulating liquids were visually assessed, and spectrophotometric measurements were carried out in the visible light (VIS) range. In addition, their neutralisation value, interfacial tension, kinematic viscosity, dissipation factor, and resistivity were also tested. These properties best describe the degree of ageing of the electro-insulating liquids selected for this research.

Absorption measurements in the VIS range were carried out using a Jasco V570 spectrophotometer (Jasco, Tokyo, Japan). A cuvette with an optical path length of 10 mm was used for these tests.

To measure the neutralisation value of electro-insulating liquids, the colorimetric titration method was used. p-Naphthalobenzeine was used as an indicator of the change in colour. A digital burette Titrette 25 mL by BRAND (Wertheim, Germany) was used for the titration. An alcoholic potassium hydroxide solution (0.1 mol/L) was used to neutralise the acids contained in the tested liquids.

Interfacial tension measurements were performed according to IEC 62961 [32]. The Sigma 702 ET tensiometer from Biolin Scientific (Gothenburg, Sweden) was used in this study. The Du Noüy ring method was used for the measurements. This test involves

measuring the force exerted on the ring when it passes through the water-insulating liquid interfacial zone.

The measurement of the kinematic viscosity of the electro-insulating liquids was performed according to the ISO 3104 standard [33]. The measurement system included a water bath, in which the temperature was maintained at 20 °C. An Ubbelohde viscometer was immersed in the water bath and was used to measure the flow time of the tested liquid through the capillary. The kinematic viscosity of the liquid was calculated on the basis of the viscometer constant and the liquid flow time.

Measurements of the dissipation factor and volume resistivity of electro-insulating liquids were carried out according to the IEC 60247 standard [34]. Tests of the dissipation factor and volume resistivity were performed in the same three-electrode system at a temperature of 50 °C. In the case of the dissipation factor, alternating voltage was used. The electric field intensity was equal to 0.07 kV/mm. In turn, the volume resistivity was calculated on the basis of the measured resistance and electrical capacity of a three-electrode system. The resistance was measured with a direct voltage applied for a time of 60 s. The electric field intensity was equal to 250 V/mm.

3. Results

3.1. Results of the Paper Properties Tests

3.1.1. Degree of Polymerisation of Cellulose

The main aim of this study was to compare the ageing dynamics of dry cellulose paper impregnated with three different electro-insulating liquids, such as natural ester, mineral oil, and synthetic ester. The degree of cellulose polymerisation, which corresponds to the mechanical strength of the paper, was taken as a measure of the degree of paper ageing. Figure 2 shows the results of the test of the viscosity degree of polymerisation of cellulose.

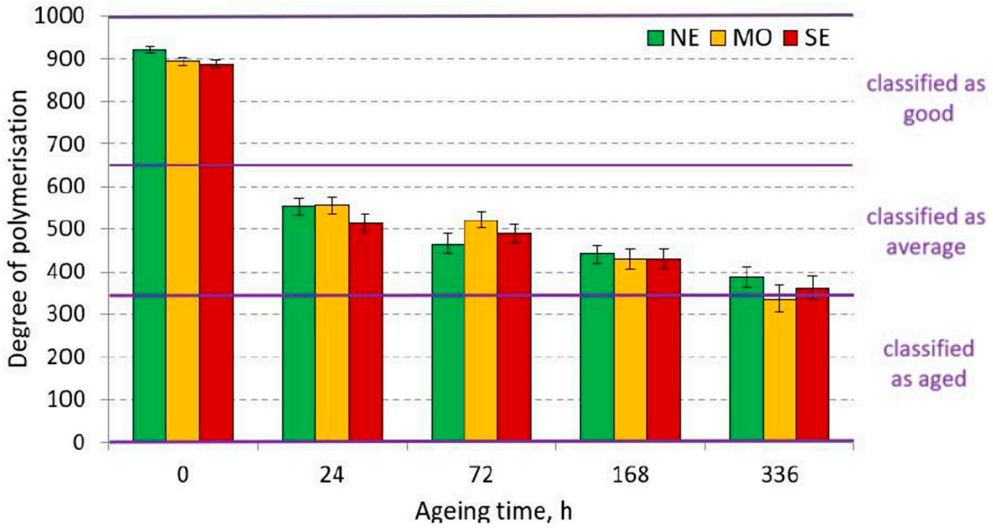


Figure 2. Change in the degree of polymerisation of cellulose over the ageing time of paper samples impregnated with natural ester (NE), mineral oil (MO), and synthetic ester (SE); the expanded uncertainties calculated for the coverage factor, k = 2, are marked in the form of bars.

The degree of polymerisation was tested for new paper, before ageing, and for papers aged in various liquids at 150 °C for 24, 72, 168, and 336 h. The degree of polymerisation of three unaged paper samples impregnated with natural ester, mineral oil, and synthetic ester was similar, and its average value was 901. According to the classification presented in the IEC 60450 standard [30], cellulosic material with this degree of polymerisation should be classified as "good". The obtained value of the degree of polymerisation is in the upper part of the range, covering the materials classified as "good".

The ageing process of paper impregnated with various liquids at 150 °C caused significant degradation of all samples. A particularly high rate of cellulose depolymerisation occurred in the first 24 h of ageing. After this time, the average value of the degree of cellulose polymerisation for papers impregnated with various electro-insulating liquids was 541, which indicates a 40% decrease in the degree of polymerisation compared to the initial value. Cellulose with this degree of polymerisation, according to the IEC 60450 standard [30], can be classified as "medium".

During the next 13 days of ageing, the cellulose depolymerisation process was much slower and linear. On the basis of the degree of polymerisation of cellulose in individual stages of ageing, it should be stated that this process was similar for all paper samples, regardless of the type of liquid with which they were impregnated. After the ageing process was completed, the average value of the degree of polymerisation for the samples aged in various liquids was equal to 362. This is a value at the border of materials classified according to the standard [30] as "medium" and "aged". According to the data presented in [35], a decrease in the degree of polymerisation of cellulose to this value corresponds to a reduction in the tensile strength and tear resistance of the paper to approximately 50% and 15%, respectively.

For the assumed experiment conditions, i.e., for a low initial material moisture, there was no influence of the type of liquid on the ageing dynamics of the paper. The differences obtained in the results of the degree of cellulose polymerisation for the samples impregnated with various liquids at subsequent stages of their ageing were similar to those obtained for unaged samples.

3.1.2. Water Content of Paper

Figure 3 shows the results of the water content measurements in paper samples impregnated with various liquids, performed before the start of the ageing process and in its various stages. To compare the influence of the type of liquid on the ageing dynamics, it was necessary to eliminate or limit the influence of the presence of water in the materials on this process. Before ageing the paper samples impregnated with various liquids, their moisture levels were checked using the Karl Fischer method. The initial water content of all the samples was low and did not exceed 0.35% by weight. Insulation with this low water content is considered dry.

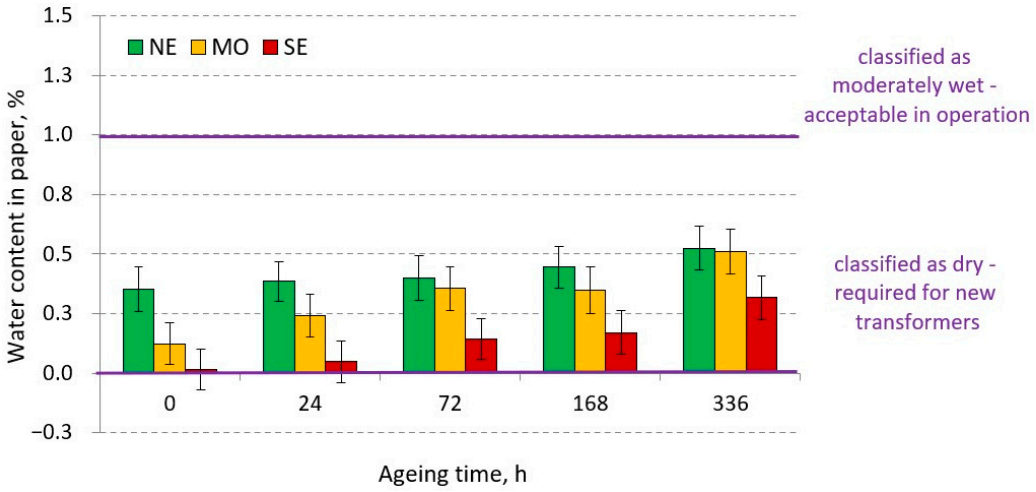


Figure 3. Change in the water content of the paper samples impregnated with natural ester (NE), mineral oil (MO), and synthetic ester (SE) over their ageing time; the expanded uncertainties calculated for the coverage factor, k = 2, are marked in the form of bars.

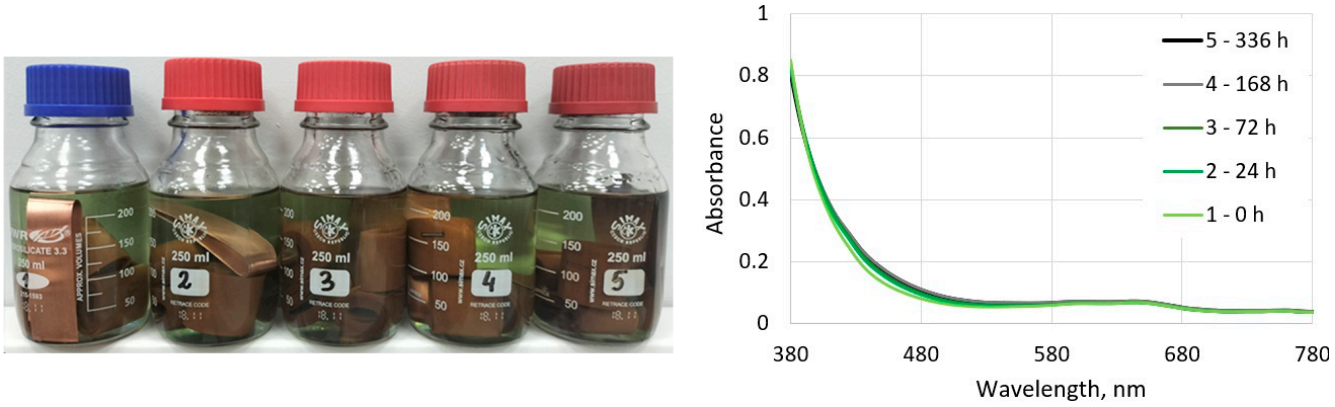
As a result of the ageing process, a slight increase in water content was observed in all paper samples, regardless of the type of liquid used for impregnation. After 14 days of ageing, the water content of all the samples was still at a low level, allowing for the tested

paper samples to be classified as dry insulation. A slight increase in the water content of the paper was caused by the cellulose oxidation process, an example of which is shown in Figure 1. The highest dynamics of the increase of water in paper during ageing occurred in the case of the material impregnated with mineral oil, which can be explained by the much lower solubility of water in this liquid compared to both esters.

3.2. Test Results on the Properties of Electro-Insulating Liquids

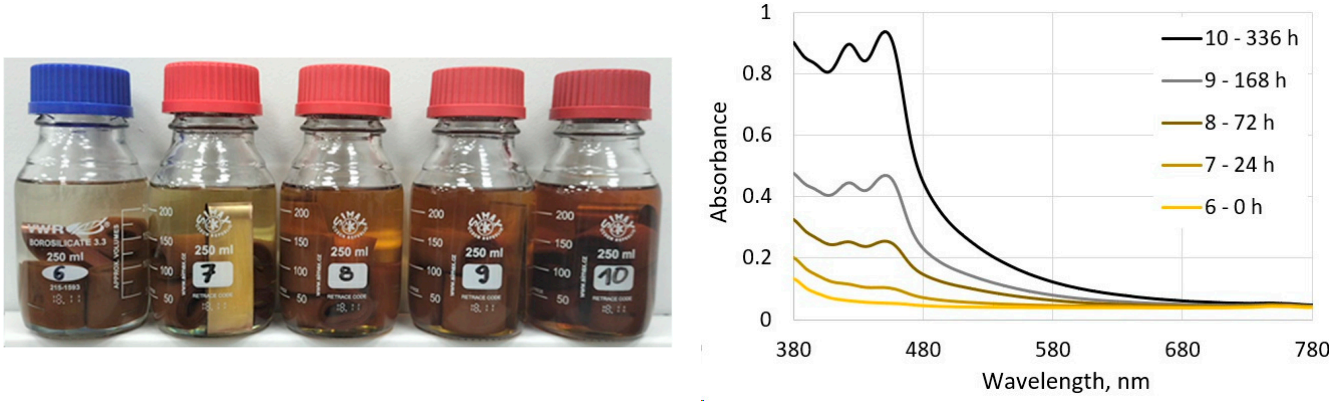
3.2.1. Visual and Spectrophotometric Assessments of the Ageing Degree of Electro-Insulating Liquids

Figures 4a, 5a and 6a show the paper samples impregnated with natural ester, mineral oil, and synthetic ester at various stages of ageing, respectively. Bottles with blue caps contained samples that had not been subjected to the ageing process. In turn, Figures 4b, 5b and 6b present the results of spectrophotometric tests in the VIS range of natural ester, mineral oil, and synthetic ester, respectively.



(**a**) (**b**)

Figure 4. (**a**) Paper samples impregnated with natural ester—sample 1 unaged; samples 2 to 5 successively aged for 24, 72, 168, and 336 h, respectively; (**b**) the absorbance spectra of natural esters measured at different stages of ageing.



(**a**) (**b**)

Figure 5. (**a**) Paper samples impregnated with mineral oil—sample 6 unaged; samples 7 to 10 successively aged for 24, 72, 168, and 336 h, respectively; (**b**) the absorbance spectra of mineral oil measured at different stages of ageing.

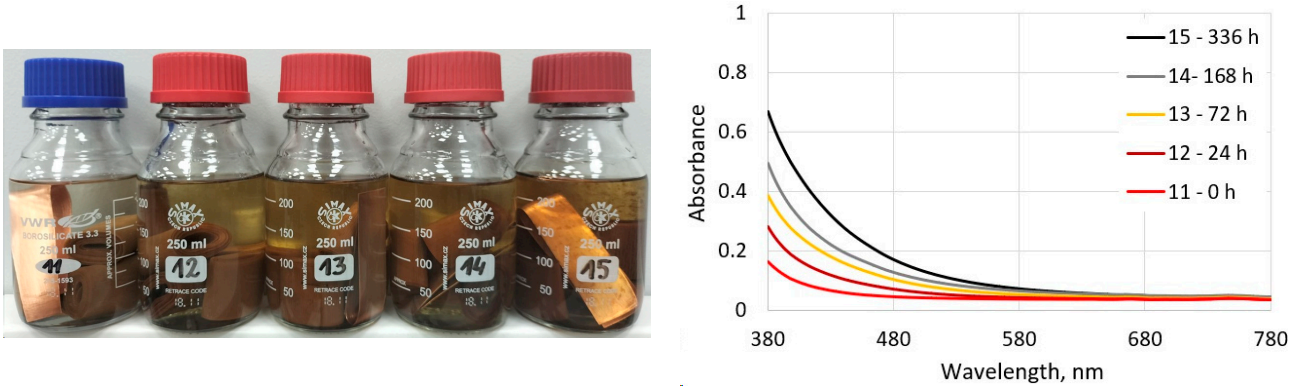


Figure 6. (**a**) Paper samples impregnated with synthetic ester—sample 11 unaged; samples 12 to 15 successively aged for 24, 72, 168, and 336 h, respectively; (**b**) the absorbance spectra of synthetic esters measured at different stages of ageing.

Taking the colour of a given liquid as an indicator of the degree of its ageing, it can be concluded that, in the case of natural ester, this process was the least intense among the tested liquids. Visually distinguishing an unaged natural ester sample from aged samples is very difficult. The colours of all the liquids are similar. Only the quantitative assessment of absorbance in the VIS range measured using a spectrophotometer allowed the samples to be ranked from the least to the most ageing. The difference in absorbance values at a wavelength of 400 nm between the sample aged for 336 h and the unaged sample for natural ester, mineral oil, and synthetic ester is 0.024, 0.737, and 0.382, respectively. These values correspond to the visual assessment of the degree of ageing of the liquid.

3.2.2. Neutralisation Value

Figure 7 shows the results of the measurements of the neutralisation values of the liquids tested at subsequent stages of their ageing. For all the tested liquids, an increase in the neutralisation value is visible, mainly due to their oxidation and hydrolysis processes. In the case of inhibited mineral oil, the increase in the neutralisation value is linear, whereas in the case of both esters, the dynamics of the increase in the neutralisation value in the second week of ageing is much greater, and the changes in the neutralisation value during ageing are exponential. The neutralisation value of the natural ester after 14 days of ageing increased to 0.28 mgKOH/g and was higher than that of the least aged mineral oil by 0.22 mgKOH/g.

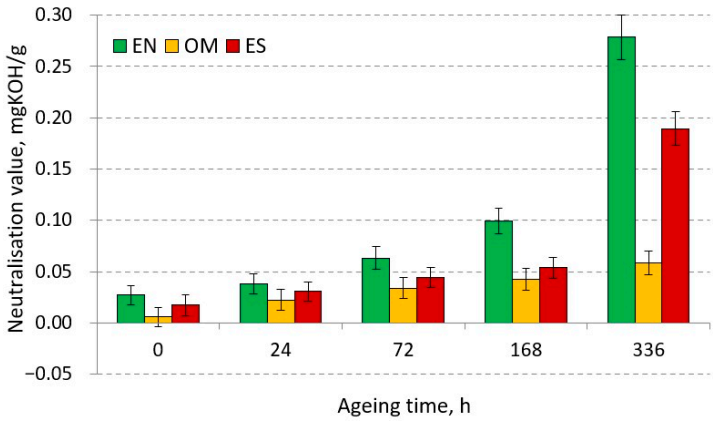


Figure 7. Change in the neutralisation value of natural ester (NE), mineral oil (MO), and synthetic ester (SE) over their ageing time; the expanded uncertainties calculated for the coverage factor, k = 2, are marked in the form of bars.

According to the limit values given in the standards IEC 62975 [36], IEC 60422 [29], and IEC 61203 [37], for all the liquids tested, the neutralisation values measured after 336 h of ageing indicate their good condition.

The greatest increase in the neutralisation value was observed in the case of natural esters, which is caused by its oxidation and hydrolysis processes that lead to the formation of long-chain fatty acids, which is described in Section 4. On the basis of the presented results, it can be concluded that in the case of mineral oil and synthetic esters, changes in their colour are accompanied by an increase in the neutralisation value, while in the case of the natural esters, despite a large increase in their neutralisation value, no significant changes in the colour of this liquid were observed.

3.2.3. Interfacial Tension

Figure 8 shows the results of the interfacial tension measurements of the liquids tested at subsequent stages of their ageing. The test results obtained indicate a gradual decrease in interfacial tension in the case of mineral oil. The greatest dynamics of changes occurs during the initial stage of ageing. For the assumed experimental conditions, there was no effect of insulation ageing on the decrease in the level of interfacial tension between the synthetic ester and the natural ester. Interfacial tension is considered a marker of mineral oil ageing; however, its application to natural and synthetic esters is challenging due to the polar molecular structure of the ester group [38].

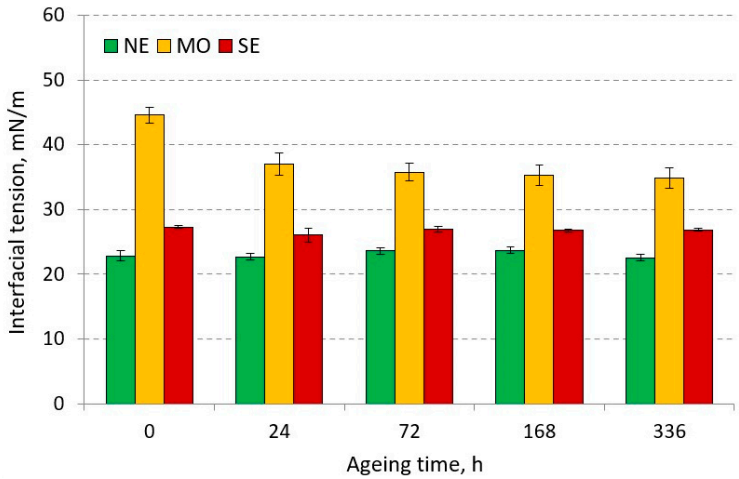


Figure 8. Change in the interfacial tension of natural ester (NE), mineral oil (MO), and synthetic ester (SE) over their ageing time; the expanded uncertainties calculated for the coverage factor, k = 2, are marked in the form of bars.

In the case of natural esters and mineral oil, the interfacial tension values measured in individual ageing stages related to the limit values given in IEC 62975 [36] and IEC 60422 [29], respectively, indicate the good condition of the liquid. IEC 61203 [37] does not indicate the limit values of interfacial tension for synthetic esters.

The decrease in the interfacial tension of mineral oil was caused by the formation of polar products of the decomposition of the oil and paper insulation. A sharp drop in interfacial tension occurred during the first stage of ageing. As a result of the presence of ageing inhibitors in the oil, the decrease in interfacial tension was not significant, and the final value indicates a good condition of the oil.

3.2.4. Kinematic Viscosity

Figure 9 shows the results of the viscosity measurements of the liquids tested during various stages of insulation ageing. Viscosity tests were carried out for a liquid temperature of 20 °C. This is the value for which the kinematic viscosity of esters is approximately four times higher than the viscosity of mineral oil. Kinematic viscosity can be an indicator of

the degree of ageing of the natural ester, and the oxidation of natural ester liquids tends to increase the viscosity. For none of the liquids tested, there was no effect of ageing on the change in the liquid viscosity.

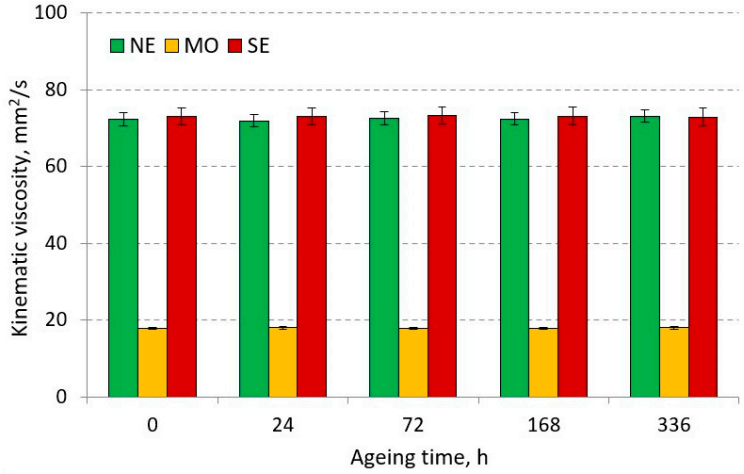


Figure 9. Change in the kinematic viscosity of natural ester (NE), mineral oil (MO), and synthetic ester (SE) over their ageing time; the expanded uncertainties calculated for the coverage factor, k = 2, are marked in the form of bars.

Ageing was carried out in a closed system without oxygen. This is the reason why no viscosity changes were observed, especially in the case of the natural ester. The manufacturers of this kind of insulating liquids have emphasised that they are not recommended for breathing units because their surfaces may polymerise with continuous exposure to the air. This can increase ester viscosity, initiate gelling, and reduce cooling capabilities [38].

3.2.5. Water Content of Electro-Insulating Liquids

Before starting the water content measurement, all the samples were conditioned for 7 days at 50 °C to achieve a moisture equilibrium between the tested electro-insulating liquid and the paper. Figure 10 shows the results of measurements of the water content of the electro-insulating liquids after subsequent stages of insulation ageing. The water content was measured using the Karl Fischer coulometric method.

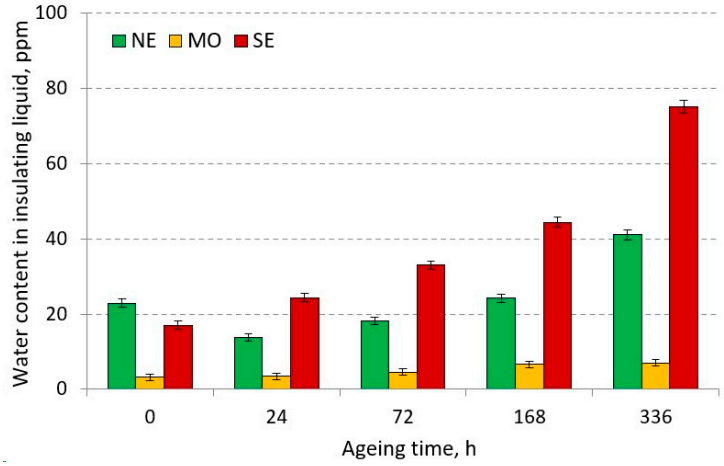


Figure 10. Change in the water content in natural ester (NE), mineral oil (MO), and synthetic ester (SE) over their ageing time; the expanded uncertainties calculated for the coverage factor, k = 2, are marked in the form of bars.

The water content of all types of tested liquids increased with the ageing time. The highest increases in water content are visible in the case of the synthetic ester and natural

ester. This is due to the much higher solubility of water in these liquids compared to that of mineral oil. Using Formula (1), the saturation limit S of the liquids tested was calculated:

$$logS = \mathrm{A} - \frac{\mathrm{B}}{T} \quad (1)$$

The specific coefficients A and B of different insulating liquids taken from [16] were used for the calculations. For a temperature of 50 °C, the water saturation limits of the synthetic ester, mineral oil, and natural ester are as follows: 2739 ppm, 155 ppm, and 1437 ppm [16].

In terms of the influence of the water content of the liquids on the dielectric properties and, in particular, electrical strength, it is reasonable to compare the relative water saturation of the tested liquids. The relative saturation of liquids at various stages of their ageing (Figure 11) was calculated by dividing the results of the water content presented in Figure 10 by their water saturation limit calculated for a temperature of 50 °C.

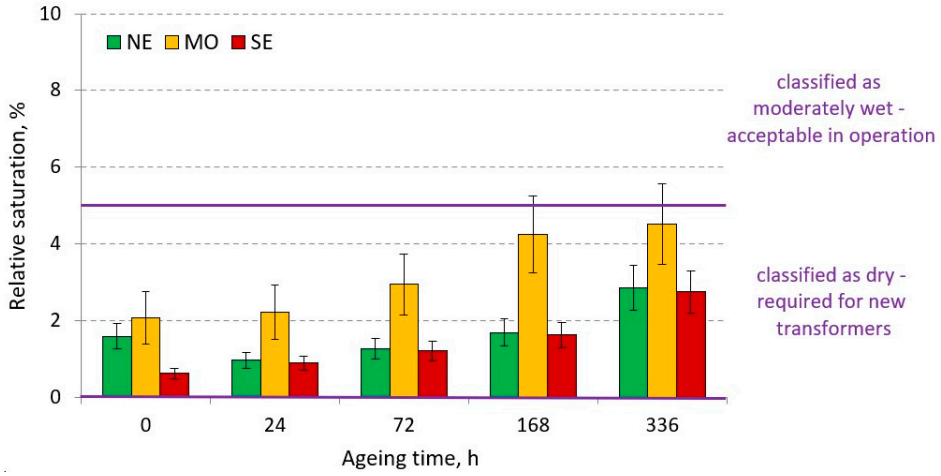


Figure 11. Change in the relative saturation of natural ester (NE), mineral oil (MO), and synthetic ester (SE) over their ageing time; the expanded uncertainties calculated for the coverage factor, k = 2, are marked in the form of bars.

The relative saturation of all the liquids before ageing started was very low, at about 2%. At subsequent stages of insulation ageing, the relative saturation of the tested liquids gradually increased. The highest values of relative saturation were observed for mineral oil, which is related to its low water solubility. The relative saturation of esters at subsequent stages of ageing is similar. It should be noted that, for all the liquids, the relative water saturation level did not exceed 5%, which, according to the standard [29], allows them to be classified as "dry". In this range, moisture has a slight impact on the electrical strength of electro-insulating liquids [39].

3.2.6. Dissipation Factor, Dielectric Permittivity, and Volume Resistivity

Table 3 presents the results of the dissipation factor (tgδ), dielectric permittivity (ε_r), and volume resistivity (ρ) of the tested liquids in subsequent stages of their ageing. These properties were determined using a three-electrode measuring capacitor with a capacity of C_0 = 60 pF, according to the measurement procedures presented in Section 2. All measurements were carried out at a liquid temperature of 50 °C.

On the basis of the obtained test results, there was no effect of liquid ageing on their electrical permittivity. In most cases, an increase in the dissipation factor and a decrease in the volume resistivity of the tested liquids were observed with the insulation ageing time. This is due to the appearance of polar ageing products that affect the dielectric properties. Mineral oil had the best dielectric properties in all stages of insulation ageing, while synthetic esters had the worst.

Table 3. The results of the measurement of the dissipation factor (tanδ), capacitance (C), relative permittivity (ε_r), resistance (R), and volume resistivity (ρ) at a temperature of 50 °C.

Sample Number	Kind of Liquid	Ageing Time, h	tanδ, %	C, pF	ε_r, -	R, GΩ	ρ, GΩ m
1	NE	0	0.49	183.1	3.1	7.0	47.59
2	NE	24	0.57	183.5	3.1	6.1	41.49
3	NE	72	0.37	184.4	3.1	7.4	50.10
4	NE	168	0.71	184.7	3.1	5.2	34.98
5	NE	336	0.46	184.2	3.1	5.9	39.73
6	MO	0	0.07	129.8	2.2	362.0	2454
7	MO	24	0.01	129.9	2.2	485.0	3288
8	MO	72	0.01	129.9	2.2	364.0	2467
9	MO	168	0.02	129.9	2.2	370.0	2508
10	MO	336	0.08	129.9	2.2	194.6	1319
11	SE	0	0.24	189.9	3.2	12.0	81.63
12	SE	24	1.41	189.4	3.2	4.2	28.34
13	SE	72	1.30	189.4	3.2	4.7	32.07
14	SE	168	1.89	189.2	3.2	5.5	37.08
15	SE	336	2.53	189.1	3.2	3.7	25.02

4. Discussion

Figures 3 and 10 show the water content of paper insulation and electro-insulating liquids at various stages of their ageing. Both figures show a clear increase in the humidity levels of both paper and liquid with the time of ageing. However, to compare the dynamics of the increase in water content, it is necessary to calculate the total amount of water present in both paper and liquid insulation at each stage of ageing. Figure 12 shows the relationship between the total water content present in both paper and the electro-insulation liquids, calculated based on the data in Figures 3 and 10 and based on the weight of the individual materials. The water content of both paper and the electro-insulating liquids was measured after conditioning the samples at a temperature of 50 °C. The purpose of conditioning the samples was to achieve a moisture equilibrium between the materials.

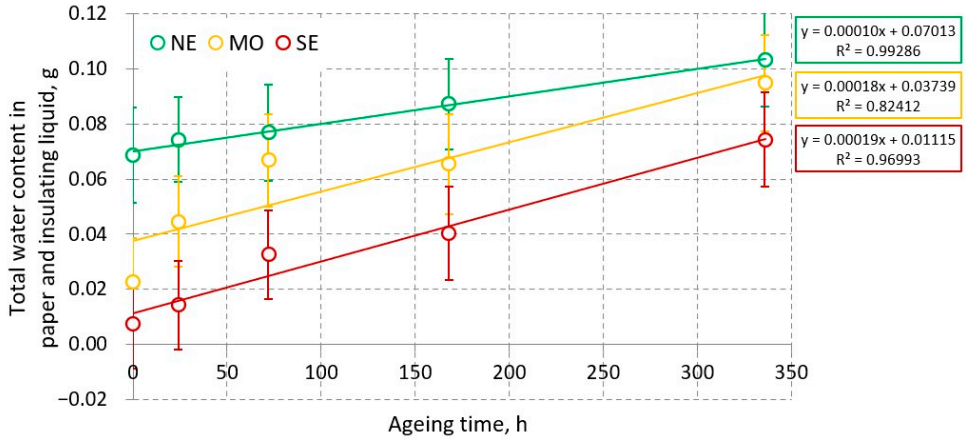


Figure 12. Change in total water content in insulation consisting of paper samples and different liquids over their ageing times; the expanded uncertainties calculated for the coverage factor, k = 2, are marked in the form of bars.

The total water content in the insulation before the ageing process began was very low in all cases, but not equal. Obtaining exactly the same water content in the system is a very difficult task, especially in the situation of very low moisture levels in the prepared materials. The analysis of the results presented in Figure 12 shows that, regardless of the type of liquid used to impregnate the paper, a successive increase in the water content in the insulation was observed. The increase in water content is described by a linear relationship.

The most valuable conclusions came from comparing the dynamics of water growth. In the case of mineral oil and synthetic esters, similar dynamics of water content increase are observed. The slopes of the linear functions that describe the increase in water content in both systems are the same. However, the dynamics of the increase in water content in the insulation consisting of paper and natural ester are much smaller.

The results obtained are not consistent with the research results presented in [8]. The authors of this work presented results showing a greater dynamics of the increase in water content in cellulosic materials impregnated with ester liquids. The discrepancies in the dynamics of the increase in water content may result from the fact that the ageing conditions were different in both cases. These differences include different initial moisture levels, different weight ratios of cellulosic material to liquid, and different ageing temperatures. Furthermore, the results of the water content of the cellulosic materials presented in [8] were determined using the DFR (Dielectric Frequency Response) method, while the test results presented in this article were determined based on the Karl Fischer standardised method. In the case of the DFR method, the obtained results could have been influenced by polar insulation decomposition products, as indicated by the high value of the neutralisation value of the natural ester [8].

The explanation for the lower dynamics of the increase in water content in the system consisting of paper and natural ester is as follows: The ageing of the materials was carried out in a closed system. An air headspace was left above the liquid surface. The oxygen contained in the system was reacting with the cellulosic material. As a result of this reaction, the water content slightly increased in all tested insulation systems. The water present in the natural ester leads to the hydrolysis of the ester groups, resulting in the formation of long-chain fatty acids, which raise the neutralisation value of the ester. This process reduces the water content in the insulation.

The increase in the neutralisation value of the natural ester with its ageing time was also confirmed by the authors of [8,40]. It should be noted that the long-chain fatty acids formed in esters are weak and do not damage the insulation system. However, the oxidation of esters produces short-chain fatty acids that react strongly with other transformer materials and promote the development of oxidation products [41].

The research results presented in this paper confirm a significantly greater increase in the neutralisation value of natural and synthetic esters compared to mineral oil [42]. The test results presented in [42] also confirm a greater increase in the dissipation factor in the case of synthetic esters compared to natural esters and mineral oil. It is justified to continue research in this area in order to identify the reason for the significantly higher values of the dissipation factor in the case of the synthetic ester.

Through analysing the degree of polymerisation of cellulosic materials impregnated with various liquids, we can conclude that the degradation process of these materials was similar for the assumed ageing conditions. These conclusions are consistent with the observations of the authors of [43]. The test results presented in this work showed slight differences in the degree of polymerisation of cellulosic materials impregnated with mineral oil and natural and synthetic esters aged in a closed system. However, it should be emphasised that the ageing process described in this article and in [43] was carried out for dried insulation, characterised by a very low level of moisture. In the case of a high water content in the insulation, the factors that determine the slowdown of the ageing process are the high solubility of water in esters, the hydrolysis of esters, leading to the formation of long-chain fatty acids, and the combination of these acids with cellulose molecules in the so-called transesterification process. This is confirmed by the results presented in [8,22].

5. Conclusions

The limitation in the use of liquids alternatively to mineral oil, such as natural and synthetic esters, especially in power transformers strategic for the operation of the electric power system is the insufficiently well-understood ageing processes that affect the properties of the liquids and cellulosic materials impregnated with them.

Comparing the research results obtained from various scientific centres is very difficult due to the multitude of factors that influence ageing processes. Many literature reports show that, in the case of natural and synthetic esters characterised by their high water solubility, the ageing dynamics of cellulosic materials are lower compared to the case of using mineral oil as a liquid dielectric.

However, the test results presented in this work show that in the case of well-dried insulation, as should be the case for new power transformers, in which the water content of the cellulose insulation is approximately 0.5%, the ageing dynamics of cellulosic materials are similar, as evidenced by the test results on the degree of polymerisation of cellulose. Furthermore, the analysis of the moisture content of the aged insulation led to the conclusion that the dynamics of the increase in water content in the case of cellulose insulation impregnated with natural ester is lower than in the case of mineral oil and synthetic ester. The reason for this is the hydrolysis process of the natural ester, in which the triglyceride reacts with water, leading to the formation of glycerol and long-chain fatty acids. This reaction is responsible for the reduction of water in the insulation as well as the increase in the acid number of the ester, which was confirmed by the obtained test results.

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References

1. El-Harbawi, M.; Al-Mubaddel, F. Risk of Fire and Explosion in Electrical Substations Due to the Formation of Flammable Mixtures. *Sci. Rep.* **2020**, *10*, 6295. [CrossRef]
2. Prevost, T.A.; Oommen, T.V. Cellulose insulation in oil-filled power transformers: Part I—History and development. *IEEE Electr. Insul. Mag.* **2006**, *22*, 28–35. [CrossRef]
3. Rozga, P.; Beroual, A.; Przybylek, P.; Jaroszewski, M.; Strzelecki, K. A Review on Synthetic Ester Liquids for Transformer Applications. *Energies* **2020**, *13*, 6429. [CrossRef]
4. García, B.; Ortiz, A.; Renedo, C.; García, D.F.; Montero, A. Use Performance and Management of Biodegradable Fluids as Transformer Insulation. *Energies* **2021**, *14*, 6357. [CrossRef]
5. Dombek, G.; Gielniak, J. Fire safety and electrical properties of mixtures of synthetic ester/mineral oil and synthetic ester/natural ester. *IEEE Trans. Dielectr. Electr. Insul.* **2018**, *25*, 1846–1852. [CrossRef]
6. Przybylek, P. Determination of Mineral Oil Concentration in the Mixture with Synthetic Ester Using Near-Infrared Spectroscopy. *Energies* **2023**, *16*, 6381. [CrossRef]
7. Martin, R.; Athanassatou, H.; Duart, J.C.; Perrier, C.; Sitar, I.; Walker, J.; Claiborne, C.; Boche, T.; Cherry, D.; Darwin, A.; et al. *Experiences in Service with New Insulating Liquids*; Cigré Technical Brochure 436; International Council on Large Electric Systems (CIGRE): Paris, France, 2010.
8. Meira, M.; Álvarez, R.E.; Verucchi, C.J.; Catalano, L.J.; Ruschetti, C.R. Thermal Aging Analysis of Mineral Oil and Natural Ester Immersed Windings. In Proceedings of the IEEE Electrical Insulation Conference (EIC), Knoxville, TN, USA, 22 June–3 July 2020. [CrossRef]
9. Przybylek, P.; Gielniak, J. The Use of Methanol Vapour for Effective Drying of Cellulose Insulation. *Energies* **2023**, *16*, 4465. [CrossRef]
10. Lundgaard, L.E.; Hansen, W.; Linhjell, D.; Painter, T.J. Ageing of Oil-impregnated Paper in Power Transformers. *IEEE Trans. Power Deliv.* **2004**, *19*, 230–239. [CrossRef]
11. Emsley, A.M.; Xiao, X.; Heywood, R.J.; Ali, M. Degradation of cellulosic insulation in power transformers. Part 3: Effects of oxygen and water on aging in oil. *IEE Proc. Sci. Meas. Technol.* **2000**, *147*, 115–119. [CrossRef]
12. Lawson, W.G.; Simmons, M.A.; Gale, P.S. Thermal Ageing of Cellulose Paper Insulation. *IEEE Trans. Electr. Insul.* **1977**, *EI-12*, 61–66. [CrossRef]
13. Prosiński, S. *Chemia Drewna*, 2nd ed.; Państwowe Wydawnictwo Rolnicze i Leśne: Warsaw, Poland, 1984; pp. 154–196.
14. Bródka, B.; Mościcka-Grzesiak, H. Budowa i struktura celulozy w aspekcie procesów degradacji izolacji papierowo-olejowej. *Przegląd Elektrotech.* **2006**, *1k/2006*, 53–56.
15. Przybyłek, P. Rozpuszczalność wody w estrze syntetycznym oraz mieszaninie estru z olejem mineralnym w aspekcie suszenia izolacji celulozowej. *Przegląd Elektrotech.* **2016**, *10*, 92–95. [CrossRef]
16. Przybylek, P. Water saturation limit of insulating liquids and hygroscopicity of cellulose in aspect of moisture determination in oil-paper insulation. *IEEE Trans. Dielectr. Electr. Insul.* **2016**, *23*, 1886–1893. [CrossRef]

17. Zhao, Y.; Qian, Y.; Wei, B.; Wang, R.; Rapp, K.J.; Xu, Y. In-Service Ageing Comparison Study of Natural Ester and Mineral Oil Filled Distribution Transformers. In Proceedings of the IEEE International Conference on Dielectric Liquids (ICDL), Rome, Italy, 23–27 June 2019. [CrossRef]
18. Suwarno; Ritonga, A. Effects of Thermal Aging on the Characteristics of Kraft Paper in Various Liquid Insulating Materials. In Proceedings of the International Symposium on Electrical Insulating Materials (ISEIM), Tokyo, Japan, 13–17 September 2020.
19. Yang, L.; Liao, R.; Caixin, S.; Zhu, M. Influence of vegetable oil on the thermal aging of transformer paper and its mechanism. *IEEE Trans. Dielectr. Electr. Insul.* **2021**, *18*, 692–700. [CrossRef]
20. Frimpong, G.K.; Oommen, T.V.; Asano, R. A Survey of Aging Characteristics of Cellulose Insulation in Natural Ester and Mineral Oil. *IEEE Electr. Insul. Mag.* **2011**, *27*, 36–48. [CrossRef]
21. Garcia, B.; Garcia, T.; Primo, V.; Burgos, J.C.; Urquiza, D. Studying the Loss of Life of Natural-Ester-Filled Transformer Insulation: Impact of Moisture on the Aging Rate of Paper. *IEEE Electr. Insul. Mag.* **2017**, *33*, 15–23. [CrossRef]
22. Chauvelon, G.; Saulnier, L.; Buleon, A.; Thibault, J.F.; Gourson, C.; Benhaddou, R.; Granet, R.; Krausz, P. Acidic Activation of Cellulose and Its Esterification by Long-Chain Fatty Acid. *J. Appl. Polym. Sci.* **1999**, *72*, 1933–1940. [CrossRef]
23. Rapp, K.J.; McShane, C.P.; Luksich, J. Interaction Mechanisms of Natural Ester Dielectric Fluid and Kraft Paper. In Proceedings of the IEEE International Conference on Dielectric Liquids (ICDL), Coimbra, Portugal, 26 June–1 July 2005. [CrossRef]
24. NYTRO® 10XN Product Data Sheet by NYNAS. Available online: https://www.nynas.com/en/products/transformer-oils/products/nytro-10xn/ (accessed on 13 December 2023).
25. MIDEL 7131 Product Data Sheet by M&I MATERIALS. Available online: https://www.midel.com/app/uploads/2023/11/MIDEL-7131-Product-Brochure.pdf (accessed on 13 December 2023).
26. FR3® Fluid Product Data Sheet by CARGILL. Available online: https://www.cargill.com/bioindustrial/doc/1432243645220/fr3-most-proven-natural-ester.pdf (accessed on 13 December 2023).
27. Cybulski, M.; Przybylek, P. The application of a molecular sieve for drying the insulation system of a power transformer in terms of improving its operational reliability. *Eksploat. Niezawodn. Maint. Reliab.* **2022**, *24*, 502–509. [CrossRef]
28. Oommen, T.V.; Prevost, T.A. Cellulose Insulation in Oil-Filled Power Transformers: Part II Maintaining Insulation Integrity and Life. *IEEE Electr. Insul. Mag.* **2006**, *22*, 5–14. [CrossRef]
29. *IEC 60422*; Mineral Insulating Oils in Electrical Equipment, Supervision and Maintenance Guidance. International Electrotechnical Commission (IEC): Geneva, Switzerland, 2013.
30. *IEC 60450*; Measurement of the Average Viscometric Degree of Polymerization of New and Aged Cellulosic Electrically Insulating Materials. International Electrotechnical Commission (IEC): Geneva, Switzerland, 2004.
31. *IEC 60814*; Insulating Liquids—Oil-Impregnated Paper and Pressboard—Determination of Water by Automatic Coulometric Karl Fischer Titration. International Electrotechnical Commission (IEC): Geneva, Switzerland, 1997.
32. *IEC 62961*; Insulating Liquids—Test Methods for the Determination of Interfacial Tension of Insulating Liquids—Determination with the Ring Method. International Electrotechnical Commission (IEC): Geneva, Switzerland, 2018.
33. *ISO 3104*; Petroleum Products—Transparent and Opaque Liquids—Determination of Kinematic Viscosity and Calculation of Dynamic Viscosity. ISO: Geneva, Switzerland, 2020.
34. *IEC 60247*; Insulating Liquids—Measurement of Relative Permittivity, Dielectric Dissipation Factor (tan d) and d.c. Resistivity. International Electrotechnical Commission (IEC): Geneva, Switzerland, 2008.
35. Lundgaard, L.E.; Allan, D.; Atanasowa-Höhlein, I.; Clavreul, R.; Dahlund, M.O.; Gasser, H.P.; Heywood, R.; Krause, C.; Lessard, M.C.; Saha, T.K.; et al. *Ageing of Cellulose in Mineral-Oil Insulated Transformers*; Cigré Technical Brochure 323; International Council on Large Electric Systems (CIGRE): Paris, France, 2007.
36. *IEC 62975*; Natural Esters—Guidelines for Maintenance and Use in Electrical Equipment. International Electrotechnical Commission (IEC): Geneva, Switzerland, 2021.
37. *IEC 61203*; Synthetic Organic Esters for Electrical Purposes—Guide for Maintenance of Transformer Esters in Equipment. International Electrotechnical Commission (IEC): Geneva, Switzerland, 1992.
38. Rao, U.M.; Fofana, I.; N'cho, J.S. On Some Imperative IEEE Standards for Usage of Natural Ester Liquids in Transformers. *IEEE Access* **2020**, *8*, 45446–145456. [CrossRef]
39. Atanasova-Höhlein, I.; Končan-Gradnik, M.; Gradnik, T.; Čuček, B.; Przybylek, P.; Siodla, K.; Brede Liland, K.; Senja, L.; Qiang, L. Experience with Capacitive On-Line Sensors for Moisture Evaluation in Transformer Insulation. *IEEE Electr. Insul. Mag.* **2019**, *35*, 18–26. [CrossRef]
40. Rao, U.M.; Sood, Y.R.; Jarial, R.K. Oxidation Stability Enhancement of a Blend of Mineral and Synthetic Ester Oils. *IEEE Electr. Insul. Mag.* **2016**, *32*, 43–47. [CrossRef]
41. Kouassi, K.; Fofana, I.; Cissé, L.; Hadjadj, Y.; Yapi, K.; Diby, K. Impact of Low Molecular Weight Acids on Oil Impregnated Paper Insulation Degradation. *Energies* **2018**, *11*, 1465. [CrossRef]

42. Jeanneton, A.; Perrier, C.; Beroual, A. Thermal Aging Study of Alternative Liquids for Oil-Paper High-Voltage Insulation in Current Transformers. In Proceedings of the IEEE International Conference on Dielectric Liquids (ICDL), Sevilla, Spain, 29 May–2 June 2022. [CrossRef]
43. Münster, T.; Werle, P.; Hämel, K.; Preusel, J. Thermally Accelerated Aging of Insulation Paper for Transformers with Different Insulating Liquids. *Energies* **2021**, *14*, 3036. [CrossRef]