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Article



Performance of Natural Ester as a Transformer Oil in Moisture-Rich Environments

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Abstract: Interest has risen among utilities in using natural ester (NE) insulating oils in transformers as a substitute for conventional mineral oil. However, present understanding on aging behaviour of NE-paper composite insulation system and knowledge on application of existing condition monitoring tools for NE-based insulation are inadequate. This limits the cost effective and reliable field applications of NE insulating oil. To pave the way the application of NE-based insulation in transformers, a systematic study has been performed to compare the aging behaviour of transformer grade pressboard (PB) impregnated in NE and conventional mineral oil. Applicability of a number of chemical and physical parameters, including acidity value, dielectric dissipation factor (DDF), viscosity, and colour for assessing the quality of NE insulating oil is also discussed in this paper. Comparisons are made based on the limiting values provided in the related IEEE Standard and properties of mineral oil under similar aging conditions.

Keywords: acidity; ageing; colour; dielectric dissipation factor (DDF); hydrolysis; natural ester (NE); mineral oil; oxidation; viscosity

1. Introduction

A transformer is an expensive, indispensable, and strategically-important equipment of any electric power system. Almost all of the large power transformers in power delivery systems around the world are still being insulated with mineral-based insulating oil and cellulosic paper-based solid insulation material [1,2]. Low fire point is a major disadvantage associated with typical mineral insulating oils, which increases the risk of subsequent fire in case of a transformer failure. Moreover, the transformers using mineral oil could cause severe environmental damage during an uncontrolled oil spill due to poor biodegradable characteristics of mineral oil [3,4]. Therefore, in order to improve the environmental sustainability and fire safety, there is an increasing demand for NE-based insulating liquids, which have a higher fire point and excellent biodegradable characteristics [4,5]. However, their application is still limited to sealed-type transformers due to higher oxidation susceptibility of NEs. Moreover, the knowledge and understanding on aging behaviour of NE-paper insulation systems and applicability of existing condition monitoring techniques for NE-paper insulation systems are still inadequate to widely use NEs in power transformers.

NEs possess completely different chemical compositions and physical properties compared to conventional mineral oil. Thus, it is essential to understand the impact of these differences on aging behaviour of NE-paper composite systems and methods utilized for assessing the degree of degradation of NE insulating oil, such as acidity value, DDF, viscosity, and colour. Particularly, investigation of aging behaviour of moderately wet NE-paper insulation system is of paramount significance because

even in a well-sealed transformer, moisture in the paper insulation can increase up to 2%–3% over time. In general, pressboards are used as spacers, barriers, and clamping rings in a transformer and they can highly influence the mechanical strength of the transformer's winding structure. Pressboard aging can significantly reduce the withstand capability of winding against mechanical impacts (due to the loss of clamping pressure). In this way, the aging of pressboard insulation has a profound influence on transformer lifetime. This paper was aimed at providing an aging behaviour comparison between moderately wet pressboards impregnated in NE and those impregnated in mineral oil.

In this study, extensive controlled aging experiments of different oil-paper insulation systems are conducted. PB insulation with about 2% of moisture content are put into two different sealed containers, one containing one type of commercially available sunflower oil-based NE, and another containing mineral insulating oil. This arrangement is intended to compare the aging behaviour of moderately wet PB insulation in NE with than in mineral oil. Moreover, impacts of changing physicochemical properties of the NE over aging on PB insulation and its cooling and insulation properties are also investigated by considering mineral oil as the benchmark.

This paper is organized as follows. Sections 2 and 3 explain the experimental setup adopted in this study and kinetic of degradation of paper insulation, respectively. Sections 4 and 5 analyse the experimental results, followed by conclusions in Section 6.

2. Experimental Setup

2.1. Materials

High-density pressboard (PB) insulation $(1.2 \text{ g} \cdot \text{cm}^{-3})$ with a textured surface and thickness of 1.5 mm, Shell Diala mineral oil (MIN), and sunflower oil-based NE insulating oil (NEA) were utilized in this study.

2.2. Sample Preparation and Aging Experiment Setup

A set of disc-shaped PB specimens with diameter of 100 mm were prepared. Firstly, PB specimens were dried in two different sealed chambers under a very high vacuum level (<1 kPa) at 65 °C for 24 h. The temperature was then increased to 95 °C and the drying process was continued for another 24 h. The temperature was then reduced to 40 °C and degassed oil (mineral or NEA) was infused into the chambers while they are kept in vacuum condition (refer to Figure 1a). According to [6], 110 mm thick PB block is fully impregnated with natural ester in a period of 200 h at 60 °C. Therefore, the containers were kept in a temperature-controllable oven for 168 h at 60 °C, which is more than enough for a complete impregnation. Dry oil-impregnated PB samples were then inserted into two different humidity control chambers (refer to Figure 1b).

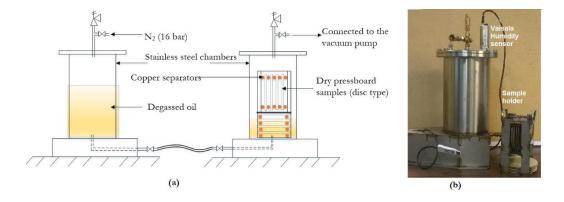


Figure 1. (a) Oil impregnation; (b) Moisture conditioning chamber, and sample holder.

The humidity inside the chambers was controlled at a constant level of 11% using saturated salt solutions prepared using lithium chloride (LiCl). In each of the chambers, a total of 20 pieces of PB specimens were arranged in a horizontal and a vertical stack. PB specimens are separated by small copper bars to allow moisture diffusion through both surfaces. This moisture conditioning process was performed over 28 days at 50 °C. The above moisture conditioning process intended to increase the moisture content of PB to about 2%–2.5% based on the Fessler equation and Jeffries' data [7] and it does not influence the DDF of oil. After completing the moisture condition process, PB specimens, degassed oil (mineral oil/NEA), and copper bars were accommodated in two different stainless steel chambers; in such a way that the mass ratio between oil, PB, and copper was maintained at 10:1:1.

Both chambers were hermetically sealed and headspaces of the chambers were filled with dry nitrogen. Then chambers were placed inside an oven for aging. Aging of PB specimens was carried out at 120 °C. Aging was stopped after 28, 35, 48, 62, 73, and 84 days and oil and PB samples were taken for analysis. Before the sampling, aging chambers were kept at room temperature for seven days. The initial condition of oil-PB insulation system is provided in Table 1. To obtain oil sample from the steel aging chamber, an oil resist plastic tube was connected to the drain valve of the aging chamber. Oil sample was then taken into a 100 mL amber glass bottle. In oil sample collection, we have observed that the ageing chamber's drain valve has been completely blocked after some time of usage due to NE oil oxidation. Therefore, the NE oil sample after 1752 h and 1984 h were collected by opening the top lid of the aging chamber. This can be conducted since the dissolved gases were not collected for analysis in this paper.

Table 1. Initial condition of oil (mineral/NE) impregnated PB insulation.

Impregnated Oil	Moisture Content (%)	DP	
Mineral	2.2	1305	
NEA	2.4	1307	

3. Kinetic Degradation of Cellulose Insulation

Emsley and Stevens [8] have found that most of the published aging data on cellulose paper materials were shown to be in good agreement with the pseudo-zero rate kinetic model developed by Ekenstam in 1936 for linear polymer degradation. As shown in Equation (1) the rate of reaction k of the pseudo-zero model is constant throughout the aging process and it is assumed to be proportional to the number of unbroken polymer chain bonds available in the system.

$$\frac{1}{DP_t} - \frac{1}{DP_0} = kt \tag{1}$$

where DP_0 and DP_t represent the average degree of polymerization at the initial time (t = 0) and at any time t, respectively. Emsley [8] has characterized the temperature dependence of reaction rate using the Arrhenius relationship as shown in:

$$k = A \times e^{\left(\frac{-E_a}{RT}\right)} \tag{2}$$

where E_a is the activation energy of degradation reaction in J·mol⁻¹, *T* is temperature in Kelvin, *R* is the gas constant (8.314 J·mol⁻¹·K⁻¹), and *A* is a pre-exponential factor in h⁻¹. From their investigations, Lundgaard *et al.* [9] and Emsley [8] claimed that the activation energy for degradation reaction of Kraft paper is about 114 kJ·mol⁻¹ and 111 kJ·mol⁻¹, respectively, and it does not depend on the condition of the reaction environment. This has been recently confirmed by the activation energy value of 106 kJ·mol⁻¹ obtained in an aging study performed under different moisture and oxygen conditions [10]. Factor (*A*) in Equation (2) shows great dependence on the availability of reactants,

such as moisture, low molecular acids in cellulose (paper/pressboard), and dissolved oxygen in oil. Combining the above Equations (1) and (2), the expected lifetime of the cellulose insulation at a given temperature can be calculated as:

$$expected \ life(year) = \frac{\frac{1}{DP_{end}} - \frac{1}{DP_{start}}}{A \times 24 \times 365} \times e^{\frac{E_a}{RT}}$$
(3)

4. Comparison of Aging of Pressboard (PB)

4.1. Decrease in Degree of Polymerization (DP) of Pressboard (PB) Insulation

In this study, the average viscometric degree of polymerization of new and aged pressboard insulation is measured according to the test method defined in [11]. After the PB specimen has been cleaned, a considerable portion of PB specimen is stripped off to provide enough sample size for the DP analysis. Samples from two different PB specimens from the same batch are collected and their DP values are measured and the average is reported.

Figure 2a compares the decrease in DP value of PB aged in both mineral and NEA oils. One notable fact that can be seen in Figure 2a is that the measured average DP of PB insulation decreases rapidly at the beginning and then it declines at a relatively lower rate regardless of the types of oils used in the oil-PB insulation system. This is due to typical structural features of cellulose. The long chain cellulose polymers in new PB insulation [12] may contain weak links in the middle, which naturally occurs in every 500 glucose monomer units [8]. These weak links can be sliced easily under thermal stresses, and it would account for fast initial drops in DP [8]. Further, amorphous regions of cellulose degrades more rapidly than the crystalline regions, which would also support the rapid initial aging [8]. This may be because the majority of water and acid produced during aging sits in the amorphous regions [13] due to their greater permeability. On the other hand, greater existence of crystalline regions does not allow water and acid penetration into the inner PB structure [9].

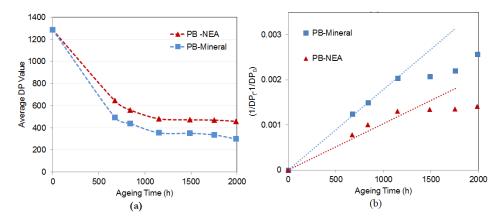


Figure 2. (a) Decrease of DP values of PB impregnated with mineral oil and NE, and (b) $1/DP_{t-1}/DP_0$ *versus* aging time of PB.

Figure 2a clearly indicates that reduction in DP of PB insulation in the NEA is substantially lower than that of mineral oil throughout the aging process in spite of the fact that initial moisture content of PB samples aged in both mineral and NEA oils is nearly same. Moreover, degradation of PB in the NEA (*i.e.*, decrease of DP value) is negligibly small during the last 824 h and its DP is 100 to 150 higher than the DP of PB aged in mineral oil over the whole aging period. This confirms that NE insulating oil shows resistance to ageing of cellulose paper insulation. This behaviour is comparable to aging experimental results presented in [14,15]. As it is proposed in [14], one could assume that pressboard insulation aged in the NEA has reached a levelling-off degree of polymerization (LODP). However,

this might not be an appropriate interpretation because LODP of cellulose paper insulation occurs when DP value reaches about 200 mainly due to slower aging rate of the crystalline domains.

In present study, aging of PB mainly occurs via hydrolysis and pyrolysis reactions since the aging experiment has been conducted in minimum oxygen environment. As the aging temperature has been maintained at a constant level throughout the experiment, the observed difference in aging of PB in the mineral and NEA oil is caused by different rate of hydrolysis reaction. Thus, one could conclude that NEA retards the hydrolysis reaction in PB giving higher DP values to PB in NEA over time. This is caused by high moisture solubility [16] and hydrolytic degradation of NE itself. As a result, the interaction between water and PB is reduced and, consequently, the hydrolysis reaction in PB in NE is delayed.

Figure 2b shows that reaction rate of PB degradation in both mineral and NEA decreases after 1152 h. This effect is more substantial for PB aged in NEA. This is mainly caused by the reduction of moisture content in PB insulation, as shown in Figure 3. Moreover, the increase of moisture solubility of oil over aging further reduces the interaction between water and PB. In the case of PB aged in mineral oil, its DP is close to LODP and this may also be a reason for decreasing the aging rate of PB in mineral oil.

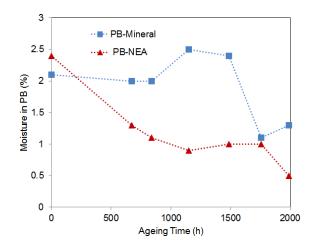


Figure 3. Change of moisture in PB over aging.

As suggested in [9], this study considered the reaction rate of the PB insulation aged in mineral oil and NE in the first 1152 h as the reaction rates correspond to their initial moisture contents. The calculated k values for PB aged in mineral oil and NEA are 18×10^{-7} h⁻¹ and 10×10^{-7} h⁻¹, respectively. Since oil does not alter the bond energy of cellulose molecules, this study assumes that E_a for degradation of PB is 111 kJ·mol⁻¹ in both types of oils. Using Equations (2) and (3) the life expectancy of PB insulation in the mineral oil and NEA for corresponding initial moisture content have been calculated. The results are compared with the IEEE life expectancy curve [17] for dry paper insulation as illustrated in Figure 4. It is clear that life expectancy of PB in mineral oil at a standard temperature of 110 °C decreases by a factor of 27 due to the increase of moisture to about 2.2%, whilst that of PB with 2.4% moisture in NE is reduced only by a factor of 15.

According to the research works conducted by Coulibaly *et al.* [18], it has been found that pressboard and paper have quite similar aging behaviours under similar condition in mineral and NE oils. Therefore, the results obtained for pressboard insulation in this paper can also be beneficial to understand the aging behaviour of paper insulation under similar conditions.

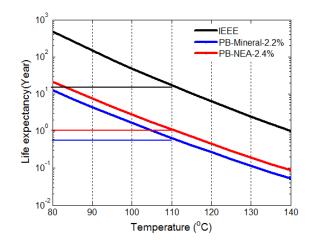


Figure 4. Comparison of life expectancy curve.

4.2. Correlation between Furfural and Pressboard PBAging

Thermal degradation of cellulose paper insulation used in electrical equipment, such as transformers, yields a class of furanic compounds including 2-furfural aldehyde (2-FAL), 2-acetylfuran (2-ACF), 2-furoic acid, 5-methyl-2-furfural (5-MEF), 2-furfurylalcohol (2-FOL), and 5-hydroxymethyl-2-furfural (5-HMF) [19–22]. These furanic compounds are partly dissolved in oil. Thus, this study has analysed the five main types of furanic compounds dissolved in oil in order to identify their correlation with aging conditions of PB insulation. The concentrations of these furanic compounds in oil has been identified and quantified by using high-performance liquid chromatography techniques according to ASTM D5837-99.

As shown in Figure 5, the highest amount of furanic compound detected in both types of oil is 2-FAL, which is a more stable compound at 120 °C than 5-HMF and 2-FOL. Additionally, its amount gradually increases with aging. In all similar aging conditions the 2-FAL concentration detected in mineral oil is much higher than that in NE.

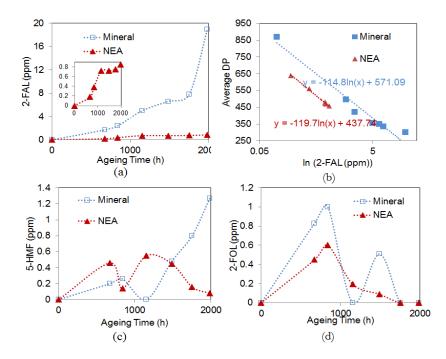


Figure 5. Furanic compounds in oil over aging (**a**) 2-FAL; (**b**) relationship between 2-FAL and DP; (**c**) 5-HMF; and (**d**) 2-FOL.

This observation is consistent with experimental results given in [14,23] where 2-FAL has been detected in very low concentration when the PB is aged in NE. This study hypothesizes that this behaviour is caused by two factors. The first is that DP of PB aged in NE has not reached a level below 400 and, typically, 2-FAL is largely produced when DP value falls below 400. In addition, 2-FAL can be lost due to thermal and hydrolytic decomposition and it is more pronounced in acidic environments [24]. As such, 2-FAL could be less stable in NE due to a comparably high quantity of oxidation inhibitors used in NE insulating oil or due to a significant increase in acidity of NE over thermal aging.

Figure 5b indicates that ln(2-FAL) and DP of PB aged in both types of oils has nearly linear relationship. Relationship corresponds to mineral oil gives DP value of 491, 386, and 347 for 2-FAL concentration of 2, 5, and 7 ppm, respectively. If one uses the relationship obtained by Pablo [25], it gives DP of 551, 386 and 310 for similar concentration of 2-FAL confirming the consistent of our results in this DP region. However, established relationships show dependence on oil type. This means that the existing 2-FAL based interpretation schemes developed for mineral oil-paper insulation systems based on absolute values and the rate of change may not be directly used for NE-based insulation systems.

As seen in Figure 5c,d, one can claim that 5-HMF is the second highest furanic compounds detected in both types of oils in most of the cases. This is mainly because hydrolysis of PB mainly occurs via formation of 5-HMF. Moreover, production of furanic compounds due to degradation of PB insulation in decreasing order is 2-FAL > 5-HMF > 2-FOL [26]. In the case of 677 h and 840 h aged mineral and NEA oil samples, the concentration of 2-FOL is larger than that of 5-HMF and also it is noted that 2-FOL concentration becomes zero at the last stage of aging. This is due to the fact that 2-FOL is less stable compared to 2-FAL and 5-HMF.

5. Aging of Oil

5.1. Viscosity

Oxidation of insulating oils produces large molecular weight compounds leading to the increase of oil viscosity. This study measures the change of viscosity of both mineral and NE insulating oils over thermal aging using method prescribed in ASTM D445.

It can be seen in Figure 6 that viscosity of both types of oils remains almost constant throughout the aging process. It indicates that no severe oxidative degradation has occurred in both types of oils. These results agree with the aging setup (refer to Section 2) because the aging experiment has been conducted in a sealed environment with minimum oxygen. However, NE oil used in this study should essentially hydrolyse because initial moisture content of PB in the aging chamber with NE is 2.4%. Thus, one could hypothesize that hydrolytic degradation of NE insulating oils does not have a significant influence on their viscosity.

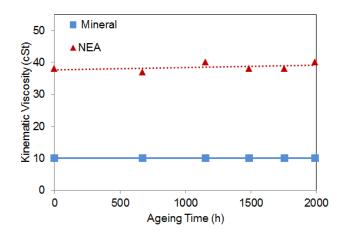


Figure 6. Change of viscosity of oil over aging.

5.2. Acidity

This study investigates the applicability of neutralization number (acidity) for determining the quality of NE insulating oils. The method prescribed in ASTMD 974 has been utilized to determine the acidity level of new and aged oil samples. Figure 7 shows that acidity of both types of oils increases with aging time. This behaviour is more significance in NEA such that acidity of the aged NEA oil samples at 1752 h (4.55 mgKOH/g) and 1984 h (6.2 mgKOH/g) is 76 and 43 times greater than that of mineral oil samples.

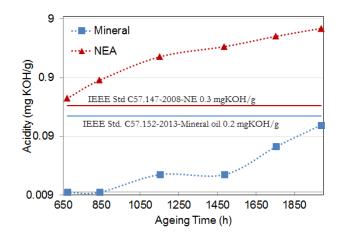


Figure 7. Change of acidity over aging.

It is generally accepted that oxidation of insulating oil and degradation of cellulose insulation in transformers results in increasing the acidity level of oil [27]. However, in this study we cannot expect oxidative degradation of oil because the aging experiment has been conducted under a nitrogen cushion. This is confirmed by the viscosity measurement results presented in Figure 6.

Therefore, this study ascribes the large increase of acidity values of NEA oil to hydrolytic degradation, because the reaction between NE and water mainly yields free fatty acids. Moisture solubility of all types of oil exponentially increases with temperature causing migration of moisture from pressboard to oil at high temperature levels. This behaviour enhances the hydrolysis reaction in NE oil. Moreover, this is an autocatalytic reaction, because free fatty acid molecules themselves accelerate the hydrolysis reaction. Thus, in this study, one could mention that the rapid increase of acidity of NEA oil is solely due to hydrolytic degradation.

It can be observed from Figure 7 that acidity of mineral oil is less than the limiting value (0.2 mgKOH/g) given in [28] throughout the aging process. Thus, one could say that even after 1984 h of ageing mineral insulating oil is in good condition for further use as an insulating liquid. On the other hand, it clearly shows that acidity of NEA has increased beyond acceptable limiting values (0.3 mgKOH/g) after 672 h of ageing and moreover, the acidity of NEA oil after 1752 h and 1984 h aging is 15 and 20 times higher than the acceptable level, respectively. According to the guidelines provided in [29], NE oil used in this experiment at all recorded aging conditions is categorized as unsuitable oil for further use.

However, this study has observed that the aging rate of PB insulation in NEA oil in the last 824 h is negligibly small (refer to Figure 2) in spite of fact that acidity of NEA oil is very high during this period. It confirms that acid produced by hydrolytic degradation of NEs is not detrimental to paper insulation. It could be possibly due to the fact that hydrolysis of NEs mainly yield long-chain fatty acids and they do not dissociate into H+ as low molecular carboxyl acids. Acidic corrosion of copper and steel materials in transformers is also governed by the H+ ions in the system. Therefore, one can hypothesize that acids produced in NEs do not cause extra corrosion in copper conductors and core steel. This hypothesis is confirmed by the fact that copper conductors and the steel sample holder used

in this study have not shown any sign of corrosion even after 1984 h of aging with NEA oil. Thus, this study proposes to measure the low molecular acids content, in addition to measuring the total acidity value for diagnostic purposes of in-service aged NE insulating oil.

5.3. Change of Dielectric Dissipation Factor (DDF)

This study analyses the variation of DDF of mineral and NE insulating oils over thermal aging. All measurements have been conducted in a standard three electrodes test cell at 50 Vrms using commercially available equipment (IDA 200). It is worthwhile to mention, at the beginning none of the oil samples considered in this study were saturated with water. Thereby, one could assume that there is no influence of moisture on the measured DDF of oil [30].

Temperature dependence of DDF of insulating oil is solely characterized by its conductivity. Thus, it can also be represented using an Arrhenius-type equation governed by the activation energy. Consequently, activation energy can be calculated by multiplying the gradient of the log (DDF) *vs.* reciprocal of the absolute temperature and Boltzmann constant.

Figure 8 shows that the activation energy of NEA varies within the range of 0.37 eV and 0.45 eV during aging, whilst that of mineral oil is in the range of 0.36 eV and 0.47 eV. The average activation value of both oils is 0.41 eV, which is used to normalize the standard set limit of the DDF to 55 $^{\circ}$ C.

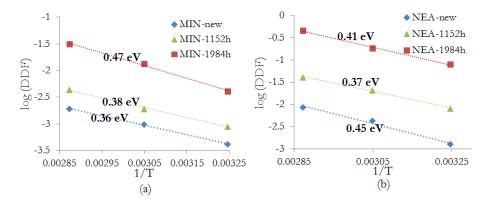


Figure 8. Temperature dependence of (a) DDF mineral oil and (b) NE.

Figure 9 represents the DDF of mineral and NE oil corresponding to oil temperature of 55 °C. It clearly shows that the DDF of both types of oil exponentially increases with aging time. Moreover, this behaviour is paramount significance in NEA oil such that the DDF of NEA oil after 1984 h aging has reached a very high value of 21%, which is almost 15 times greater than that of mineral oil with similar aging conditions.

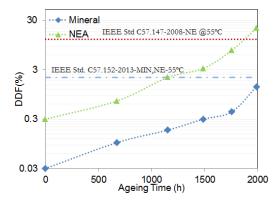


Figure 9. Change of DDF of oil at 55 °C over aging.

It is generally accepted that DDF of oil increases due to the presence of dissociable impurities such as soot, dust, and ageing by-products [18]. Thus, one could claim that aging of NE with cellulosic and metal substances in moisture-rich environments produces more conductive dissociable substances and consequently leads to higher DDF. On the other hand, conductive aging byproducts of paper insulation can largely dissolve in NEs because of their polar nature [31] and this could result in large increases in DDF of NE.

In this paper, the acceptable limiting values provided in [28,29] for DDF of mineral and NE insulating oil at 25 °C have been recalculated to 55 °C using activation energy of 0.41 eV. Figure 9 shows that DDF of any of the mineral oil samples has not reached limiting value indicating their suitability for further use. In case of NE, except the oil sample aged over 1984 h, all other samples are within the acceptable limits. However, reference [28] proposed the same limiting value for both mineral oil and NE oils. If one uses [28], except the sample aged over 674 h, all other NE oil samples would be categorized as being not suitable for further use.

5.4. Colour Change

Colour of oil is a visual parameter, which reflects the degree of degradation and possible contamination of oil during aging. Figure 10 shows that dramatic colour change has occurred in both types of oils over aging. This behaviour is more significant in NEA such that its colour has turned to black after 1488 h of aging whilst colour of mineral oil change to amber after 1752 h. Numeral value based on international colour standards (ASTM D1500) is generally used in expressing colour changes of oil. The colour number of oil at different aging conditions is estimated in this study and presented in Figure 11.

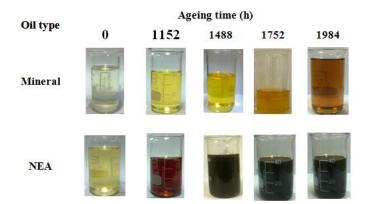


Figure 10. Change of oil colour over aging.

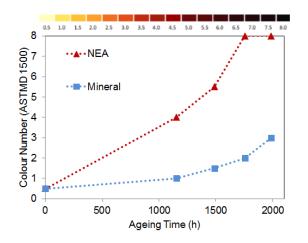


Figure 11. Estimated colour number of oil over aging.

Reference [28] provides guidelines for assessing the condition of mineral oil based on colour. According to that except 1984 h aged mineral oil, other mineral oil samples in this study are categorized as oil with good condition. However, if one applies the same interpretation scheme on NEA, oil samples at 1488 h, 1752 h, and 1984 h aging time can be rated as extremely bad oil whilst oil samples at 1152 h aging time can be characterized as severely aged oil. In the case of mineral oil, severely aged oil (brown in colour) and extremely bad oil (dark brown and/or black in colour) typically contains large amounts of sludge and they possess poor cooling characteristics due to an increase of viscosity [32]. Moreover, such oil contains high concentration of reactive acids. However, it has been observed that no sludge has been formed in the aged NEA oil and its viscosity has remained almost constant over the aging period. Moreover, acids produced in NEA oil are not reactive. Thereby, one can conclude that the overall condition of in-service aged NE oil cannot be determined only with the existing colour-based interpretation schemes.

5.5. Overall Analysis of Oil Condition

Table 2 summarizes the diagnostic results of mineral and NEA oil using their acidity value, DDF, and colour. It clearly shows that acidity and DDF diagnose all mineral oil samples as oil with good condition. However, the sample aged over 1984 h is required to be further investigated because of its higher colour number. In the case of NEA oil, all the oil samples tested in this study are categorized as bad oil by their acidity and colour despite their ability to reduce cellulose degradation. Moreover, viscosity of NEA oil which determines the cooling capability is similar to unaged oil even after 1984 h of aging. In addition, this study has measured the dielectric breakdown strength of 1984 h aged mineral and NEA oil samples using method prescribed in [33]. It has confirmed that the average dielectric breakdown strength of NEA oil is 68 kV and it is 13 kV higher than that of mineral oil. It means that, though aged NEA oil has a higher acidity and colour number, their insulation quality is better than mineral oil which has gone through the same aging process.

Aging Time (h) _	Mineral Oil			NE		
	Acidity	DDF	Colour	Acidity	DDF	Colour
672			-	х		-
1152				х		severe
1488				х		extreme
1752				х		extreme
1984			bad	х	x	extreme
$\sqrt{-}$	-acceptable fo	r further use,	, x—not in goo	d condition to f	further use	

Table 2. Summary of diagnostic results.

For an in-service transformer, moisture in its paper insulation can increase to about 2% after 10–15 years of operation. In such a situation, a rapid increase in acidity and colour of NE insulating oil will be expected. Moreover, retrofilling of an in-service transformer with NE oil could also create a similar environment. Thus, in this type of condition, acidity and colour change with an existing set of limits in the standards cannot be utilized to determine the suitability of in-service aged NE insulating oil for further use. As shown in Table 2, one could hypothesize that DDF with limiting values as defined in [29] could be a good indication of the quality of NE insulating oils when subjected to severe hydrolytic degradation. In addition to DDF, this study proposes to measure the viscosity and dielectric breakdown strength. Collectively, these three parameters could reflect the overall condition of NE insulating oils.

6. Conclusions

This study revealed that NE insulating oil possesses resistance to the aging of PB insulation. This behaviour is mainly caused by high moisture solubility and the hydrolysis reaction in NE insulating oil. Experimental results presented in this paper indicate that the furanic compounds may be less stable in NE insulating oils. Thus, it is necessary to further investigate whether 2-FAL can be used as a paper insulation aging indicator for NE-based insulation systems. This study pointed out that acidity and colour of NE ester oils could increase rapidly due to the pronounced hydrolytic degradation in moisture rich environment. This type of behaviour can be expected after retrofilling of an in-service transformer with NE oil. In such a condition, acidity and colour could not reflect the real condition of NE oil. On the other hand, DDF, viscosity, and dielectric breakdown voltage, collectively, can indicate the overall condition of NE insulation oils.

This study revealed that the acids produced by hydrolysis of NE are not detrimental to paper insulation. However, it is necessary to further investigate the effect of high acidity of NE oil on copper and steel materials, particularly its corrosion effects at high temperature.

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References

- 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]
- 2. Rouse, T.O. Mineral insulating oil in transformers. IEEE Mag. Electr. Insul. Mag. 1998, 14, 6–16. [CrossRef]
- Oommen, T.V.; Claiborne, C.C.; Mullen, J.T. Biodegradable electrical insulation fluids. In Proceedings of the Electrical Insulation and Electrical Manufacturing & Coil Winding Conference, Rosemont, IL, USA, 22–25 September 1997; pp. 465–468.
- McShane, C.P.; Corkran, J.; Rapp, K.; Luksich, J. Natural Ester Dielectric Fluid Development. In Proceedings of the IEEE PES Transmission and Distribution Conference and Exhibition, Dallas, TX, USA, 21–24 May 2006; pp. 18–22.
- 5. Tenbohlen, S.; Koch, M. Aging Performance and Moisture Solubility of Vegetable Oils for Power Transformers. *IEEE Trans. Power Deliv.* **2010**, *25*, 825–830. [CrossRef]
- 6. Dai, J.; Wang, Z.D. A Comparison of the Impregnation of Cellulose Insulation by Ester and Mineral Oil. *IEEE Trans. Dielectr. Electr. Insul.* **2008**, *15*, 374–381. [CrossRef]
- 7. Du, Y.; Zahn, M.; Lesieutre, B.C.; Mamishev, A.V.; Lindgren, S.R. Moisture equilibrium in transformer paper-oil systems. *IEEE Electr. Insul. Mag.* **1999**, *15*, 11–20. [CrossRef]
- 8. Emsley, A.M.; Stevens, G.C. Kinetics and mechanisms of the low-temperature degradation of cellulose. *J. Cellul.* **1994**, *1*, 26–56. [CrossRef]
- 9. Lundgaard, L.E.; Hansen, W.; Linhjell, D.; Painter, T.J. Aging of oil-impregnated paper in power transformers. *IEEE Trans. Power Deliv.* **2004**, *19*, 230–239. [CrossRef]
- 10. Lelekakis, N.; Wijaya, J.; Martin, D.; Saha, T.; Susa, D.; Krause, C. Aging rate of grade 3 presspaper insulation used in power transformers. *IEEE Trans. Dielectr. Electr. Insul.* **2014**, *21*, 2355–2362. [CrossRef]
- 11. Internaltional Electrotechnical Commision (IEC). *Measurement of the Average Viscometric Degree of Polymerization of New and Aged Cellulose Electrically Insualting Materials*; IEC Std. 60450:2004; IEC: Geneva, Switzerland, 2004.
- Hill, D.J.T.; Le, T.T.; Darveniza, M.; Saha, T. A study of the degradation of cellulosic insulation materials in a power transformer. Part III: Degradation products of cellulose insulation paper. *Polym. Degrad. Stab.* 1996, 51, 211–218. [CrossRef]
- Dissado, L.A.; Hill, R.M. Anomalous low-frequency dispersion. Near direct current conductivity in disordered low-dimensional materials. *J. Chem. Soc. Faraday Trans.* 2 *Mol. Chem. Phys.* 1984, 80, 291–319. [CrossRef]
- 14. Liao, R.; Liang, S.; Sun, C.; Yang, L.; Sun, H. A comparative study of thermal aging of transformer insulation paper impregnated in natural ester and in mineral oil. *Eur. Trans. Electr. Power* **2010**, *20*, 518–533. [CrossRef]

- McShane, C.P.; Rapp, K.J.; Corkran, J.L.; Gauger, G.A.; Luksich, J. Aging of Kraft paper in natural ester dielectric fluid. In Proceedings of the 2002 IEEE 14th International Conference on Dielectric Liquids, Graz, Austria, 7–12 July 2002; pp. 173–177.
- 16. Koch, M.; Tenbohlen, S.; Stirl, T. Diagnostic Application of Moisture Equilibrium for Power Transformers. *IEEE Trans. Power Deliv.* **2010**, *25*, 2574–2581. [CrossRef]
- 17. IEEE C57.91 Working Group. *IEEE Guide for Loading Mineral-Oil-Immersed Transformers and Step-Voltage Regulators—Redline;* IEEE Std C57.91-2011 (Revision of IEEE Std C57.91-1995)—Redline; IEEE: New York, NY, USA, 2012; pp. 1–172.
- Coulibaly, M.L.; Perrier, C.; Marugan, M.; Beroual, A. Aging behavior of cellulosic materials in presence of mineral oil and ester liquids under various conditions. *IEEE Trans. Dielectr. Electr. Insul.* 2013, 20, 1971–1976. [CrossRef]
- 19. Cigre Working Group TF D1.01.13. *Furanic Compounds for Diagnosis;* International Council on Large Electric Systems: Paris, France, 2012.
- 20. Scheirs, J.; Camino, G.; Avidano, M.; Tumiatti, W. Origin of furanic compounds in thermal degradation of cellulosic insulating paper. *J. Appl. Polym. Sci.* **1998**, *69*, 2541–2547. [CrossRef]
- 21. 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 ageing in oil. *IEE Proc. Sci. Meas. Technol.* **2000**, *147*, 115–119. [CrossRef]
- 22. Kachler, A.J.; Hohlein, I. Aging of cellulose at transformer service temperatures. Part 1: Influence of type of oil and air on the degree of polymerization of pressboard, dissolved gases, and furanic compounds in oil. *IEEE Electr. Insul. Mag.* **2005**, *21*, 15–21. [CrossRef]
- 23. Lijun, Y.; Ruijin, L.; Caixin, S.; Huigang, S. Study on the Influence of Natural Ester on Thermal Ageing Characteristics of Oil-paper in Power Transformer. In Proceedings of the International Conference on High Voltage Engineering and Application, Chongqing, China, 9–12 November 2008; pp. 437–440.
- 24. Emsley, A.M.; Stevens, G.C. Review of chemical indicators of degradation of cellulosic electrical paper insulation in oil-filled transformers. *IEE Proc. Sci. Meas. Technol.* **1994**, *141*, 324–334. [CrossRef]
- 25. De Pablo, A. Furfural and ageing: How are they related. In Proceedings of the IEE Colloquium on Insulating Liquids, Leatherhead, UK, 27 May 1999; pp. 5/1–5/4.
- 26. Levchik, S.; Scheirs, J.; Camino, G.; Tumiatti, W.; Avidano, M. Depolymerization processes in the thermal degradation of cellulosic paper insulation in electrical transformers. *Polym. Degrad. Stab.* **1998**, *61*, 507–511. [CrossRef]
- 27. Jung-Il, J.; Jung-Sik, A.; Chan-Su, H. Accelerated aging effects of mineral and vegetable transformer oils on medium voltage power transformers. *IEEE Trans. Dielectr. Electr. Insul.* **2012**, *19*, 156–161. [CrossRef]
- 28. IEEE Diagnostic Field Testing Power Transformers and Reactors Working Group. *IEEE Guide for Diagnostic Field Testing of Fluid-Filled Power Transformers, Regulators, and Reactors;* IEEE Std C57.152-2013; IEEE: New York, NY, USA, 2013.
- 29. IEEE Natural Easter Working Group. *IEEE Guide for Acceptance and Maintenance of Natural Ester Fluids in Transformers*; IEEE Std. C57.147-2008; IEEE: New York, NY, USA, 2008.
- Duy, C.T.; Denat, A.; Lesaint, O.; Bonifaci, N.; Bertrand, Y. Moisture and temperature effects on conduction and losses in modified rape-seed insulating oil. In Proceedings of the Conference on Electrical Insulation and Dielectric Phenomena, Vancouver, BC, Canada, 14–17 October 2007; pp. 647–650.
- 31. Fofana, I.; Bouaicha, A.; Farzaneh, M.; Sabau, J.; Bussieres, D.; Robertson, E.B. Decay products in the liquid insulation of power transformers. *IET Electr. Power Appl.* **2010**, *4*, 177–184. [CrossRef]
- 32. Fofana, I.; Bouaicha, A.; Hadjadj, Y.; N'Cho, J.S.; Aka-Ngnui, T.; Beroual, A. Early stage detection of insulating oil decaying. In Proceedings of the 2010 Annual Report Conference on Electrical Insulation and Dielectric Phenomena (CEIDP), West Lafayette, IN, USA, 17–20 October 2010; pp. 1–4.
- 33. Internaltional Electrotechnical Commision (IEC). *Insulating liquids -Determination of the Breakdown Voltage at Power Frequency—Test Method;* IEC Std. 60156; IEC: Geneva, Switzerland, 1995.



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