A COMPARATIVE AGING STUDY OF VARIOUS COMMERCIAL BIODEGRADABLE INSULATION FLUIDS

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Abstract

The aging behaviour of three insulation fluids from sustainable sources (natural ester, synthetic ester, and a bio-based hydrocarbon fluid) were compared with that of a conventional mineral oil. All samples contained kraft paper and its degree of polymerisation (DP) confirmed that the aged samples covered most of the transformer lifecycle. The reported mitigating effect of ester oils on paper aging was observed in both ester oils whilst the bio-based hydrocarbon fluid exhibited comparable behaviour to the mineral oil. Natural ester had the highest values of acidity, viscosity and dielectric loss after aging and the bio-based hydrocarbon oil the lowest. The bio-based hydrocarbon fluid would be an excellent replacement for mineral oil in plant, particularly due to its very low viscosity which would aid cooling but with the drawback that paper aging is not mitigated. A synthetic ester is preferable over a natural ester in plant since its chemical, physical and dielectric properties do not deteriorate dramatically after aging.

1 Introduction

High voltage transformers form an essential part of the electrical distribution system and ensuring ongoing operation of these assets is vital for a reliable power grid. Traditionally, these units use mineral oil, both as an impregnant for their paper lapped windings and as a cooling medium. Mineral oil, which is still used in most high voltage distribution transformers, has the disadvantage that it is from a non-sustainable source (crude oil), hence network operators have been gradually replacing these fluids with biodegradable alternatives such as synthetic and natural ester-based oils [1,2].

Ester oils, coming from renewable sources such as plant seeds, are sustainable and relatively benign to the environment. Ester oils have a high fire point (class K > 300 ˚C) which improves plant safety [1] whilst laboratory aging studies show that ester oils are better than mineral oil at preserving the condition of insulation paper [3][4][5]. Since the lifetime of a transformer is determined by the mechanical properties of its insulation paper rather than the condition of the oil [6], this is a significant advantage in terms of plant lifetime; furthermore, studies on live assets indicate excellent performance in ester filled units [5, 7]. The main challenges of ester oils are their susceptibility to oxidation [1, 7], higher cost and their high viscosity [8]. The latter reduces cooling efficiency, compared to mineral oil, and increases the hot spot temperature for any given loading level, but can be largely overcome by operating the plant at higher temperatures or, through design changes, such as larger oil ducts and pumped cooling [9].

We have identified nearly twenty commercial ester-based fluids specifically manufactured for high voltage transformers, but these can be split into only three major classes: synthetic esters, natural esters, and bio-based hydrocarbon fluids where an ester base oil is chemically processed to yield a long chain n-alkane. In these initial investigations, which form part of a larger project to compare the full range of commercially available fluids and assess their aging characteristics for use in high voltage electrical plant, we have compared the aging behaviour of a synthetic ester, a natural ester and a novel bio-based hydrocarbon fluid using a conventional mineral oil as a reference. Oils were aged under controlled conditions with kraft paper, and in some cases copper, to simulate aging in plant. Measurements of DP allowed the oils to be mapped onto the transformer lifecycle whilst chemical changes were assessed through measurements of water content and acidity. Physical changes were assessed using ultraviolet/visible (UV/Vis) spectroscopy and through measurements of viscosity, whilst the dielectric properties of the paper/oil insulation system were assessed using dielectric spectroscopy.

2. Methodology

2.1 Oils, sample preparation and aging

A total of four oils were used in this investigation as detailed in Table 1. A synthetic and a natural ester oil from Midel were employed along with a novel bio-based hydrocarbon fluid from Nynas. For reference purposes, a conventional mineral oil was also subjected to the same treatment and analysis. The density of each fluid (at 20 ˚C) was determined by weighing a 10 ml quantity and the results (Table 1) are in line with the values provided in the manufacturers' datasets within the uncertainties of ± 0.01 g/cm^3.

Small scale ageing of 25 ml samples was undertaken containing 1.25 g (dry weight) [10] of 0.1 mm thickness kraft paper in the form of twelve 42 mm diameter disks. Selected samples also included copper (0.1 mm thickness) as per our previous investigations on ester fluids [11]. Prior to aging the

copper sheets were polished with fine grade sandpaper to remove surface oxides and were then washed in acetone and stored under vacuum until needed. Kraft paper and the oils were degassed/dried separately at 60 ˚C for at least 24 h under vacuum. Complete drying of the paper was verified by weighing selected samples before and after the procedure and in all cases the mass loss was > 6 % [12]. After this, the oils were carefully poured into glass vials along with the prescribed amounts of copper and paper, and impregnation of the paper was then carried out under dynamic vacuum at 60 ˚C [13] until all signs of visible bubbling had stopped (~ 2 hours). After this, samples were covered with a glass dish to minimise oxygen ingress [14] and aging was performed at 130 ˚C for up to 21 days to provide oil samples spanning most of the transformer lifecycle [3][6][15].

Samples are referred to throughout using the nomenclature W-XY where W is the oil type (Table 1), X is the number of days aging and Y indicates whether copper is present; N = no copper, C = copper included, all samples include kraft paper.

Table 1 Oils used in these investigations; density is in g/cm^3.

Oil	Product	Type	Density
A	Midel 7131	Synthetic ester	0.94
B	Midel eN1204	Natural ester	0.93
C	Nynas Bio300X	Bio-based hydrocarbon	0.77
D	Nynas GeminiX	Mineral oil	0.84

2.2 Measurement of chemical changes

DP measurements were performed according to ASTM D4243 [12]. Here a single sheet of kraft paper was extracted from each vial and washed several times in a bath of acetone to remove all traces of oil. Then a 15 mg sample was dissolved for at least 4 h under constant stirring in 20 ml of 0.5 M Bis(ethylenediamine) copper(II) hydroxide solution. The solution was then drawn off into a viscometer tube (C = 0.01 mm^2/s^2) which was then placed into a viscometer bath held at 20 ± 1 ˚C. Five measurements of viscosity allowed the DP to be calculated. Typical uncertainty was ± 20 DP units.

Water content of 0.5 ml oil samples was measured by directly injecting samples into a GR Scientific Aquamax KF titrator which utilizes the potentiometric method, according to ASTM D6304-20, and all measurements were repeated. Typical uncertainty in the measurements was ± 5 mg/kg.

Total acid number of 1 ml oil samples was determined according to ASTM D974 by dissolving them into 50 ml of a solvent mixture composed of 1 part water, 99 parts isopropyl alcohol, 100 parts toluene and 2.5 mg of Naptholbenzein (as indicator). The amount of KOH solution (0.1 g KOH in 100 ml isopropyl alcohol) required for the now bright orange solution to become a stable green colour was then determined, and all measurements were repeated. Typical uncertainty in the measurements was ± 0.05 mgKOH/g.

2.3 Measurement of physical changes

UV/Vis spectroscopy was performed on 10 ml samples loaded into a quartz cuvette. A Perkin Elmer Lambda 35 spectrometer was used to record optical absorbance spectra over the range 200 to 1100 nm. The sample cuvette was cleaned with acetone, measurements were compared for consistency and repeats were performed as necessary.

Viscosity measurements were undertaken according to ASTM D445-21 on 20 ml oil samples. A calibrated glass viscometer tube (Paragon Scientific, C = 0.9328 mm^2/s^2; UKAS calibration) was used to perform measurements at 20 ± 1 ˚C, the temperature being maintained by immersing the tube into a thermostatically controlled water bath. The elution time was recorded using a stopwatch and all measurements were repeated three times. Typical uncertainty in the measurements was ± 3 mm^2/s.

2.4 Changes in dielectric properties

Measurements of dielectric loss and relative permittivity of oil-soaked paper disk samples was undertaken using a Schlumberger SI1260 dielectric analyser connected to a Solartron 1296 dielectric interface and controlled by a standard PC running SMART software. The test cell was composed of opposing 32 mm polished steel electrodes and all measurements were performed at room temperature using an applied voltage of 5 V_{rms} and a 10-cycle integration time. Measurements were compared for consistency and repeats were performed as necessary. Typical uncertainty in the dielectric loss (tan δ) measurements was ± 0.002 and relative permittivity measurements ± 0.1.

3 Results

3.1 Chemical changes

Measurements of DP, which correlate closely to the mechanical properties of the paper [6][12][15][16], are given in Figure 1 for all four oils. The initial DP of the as-new paper was 1100 but this was progressively reduced during aging a trend that was independent, within the uncertainties in the measurements, on whether copper was included. Both esters (oils A and B) exhibited a common behaviour as did the two hydrocarbon fluids (oils C and D). The values are consistent with expectations [3][15] and cover most of the transformer lifecycle. Since a higher DP is indicative of less aging, the findings confirm various reports on the mitigating effects of ester oils on paper aging [3][4][5][10].

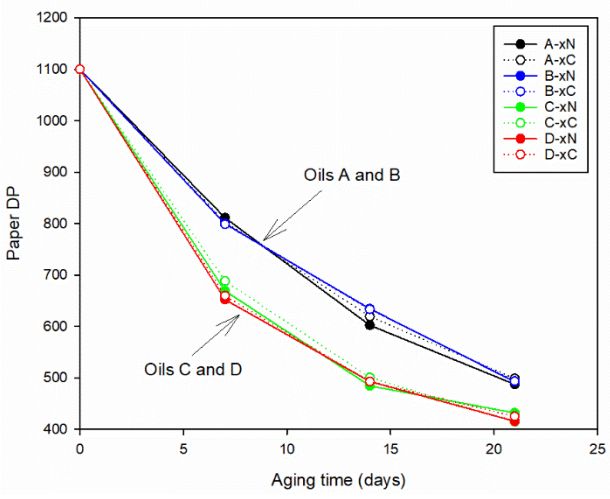

Figure 1. DP as a function of aging time

Results from water content measurements are shown in Figure 2. Initial values appear to follow differences in water saturation levels [14] and both ester oils have a consistent relative humidity of ~2 % prior to aging. Then during aging, dehydration of the oils takes place due to the high temperature [16], and then the water content subtly increases. The water content falls within the IEC acceptance limits of ≤ 300 mg/kg for used ester oils [17][18] and ≤ 20 mg/kg for used mineral oil [19] whilst oil C (Bio300X) closely follows the behaviour of oil D (mineral oil). Elsewhere [4][5][7][20], we find that 40 – 200 mg/kg is typical for aged ester oils and 5 – 30 mg/kg is typical for aged mineral oils, so our findings are as expected.

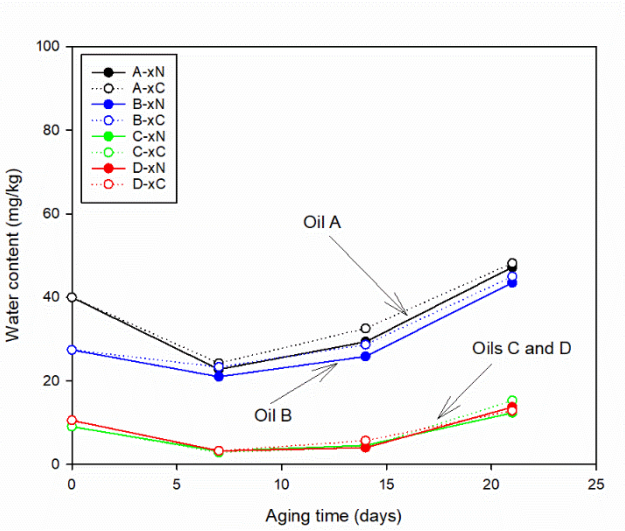

Figure 2. Water content as a function of aging time

Acid number (Figure 3) increases with aging time, especially in oil B (natural ester), and is slightly increased by copper. One study [20] confirms our findings with high values (> 1) being reported in aged natural ester oil whilst values < 0.3 are typical for aged synthetic ester and mineral oils [21][22]. The acid number of oil A (synthetic ester) and oil D (mineral oil) meet the relevant IEC acceptance limits for all aging times [17][19] whilst that of oil B (natural ester) only meets the requirements [18] for an aging time of < 10 days. The acid number of oil C (Bio300X) follows that of oil D (mineral oil).

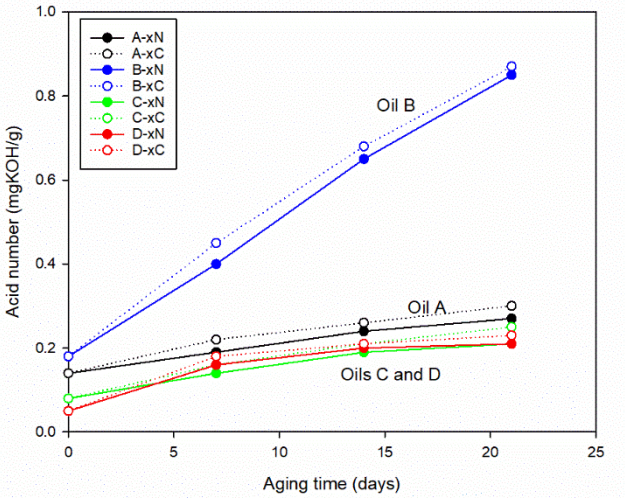

Figure 3. Acid number as a function of aging time

3.2 Physical changes

Figure 4 contains UV/Vis absorption spectra for oils A and B (ester oils). Oil A is initially colourless, so its absorption edge is located within UV wavelengths (~350 nm) whilst oil B is a bright yellow colour and hence, its absorption edge is located within visible wavelengths (~420 nm). On aging, the oils become darkened [10][11] and the absorption edge in the spectra is progressively shifted towards longer wavelengths. Copper clearly catalyses the creation of chromophores in the oil as noted elsewhere [11][21][22].

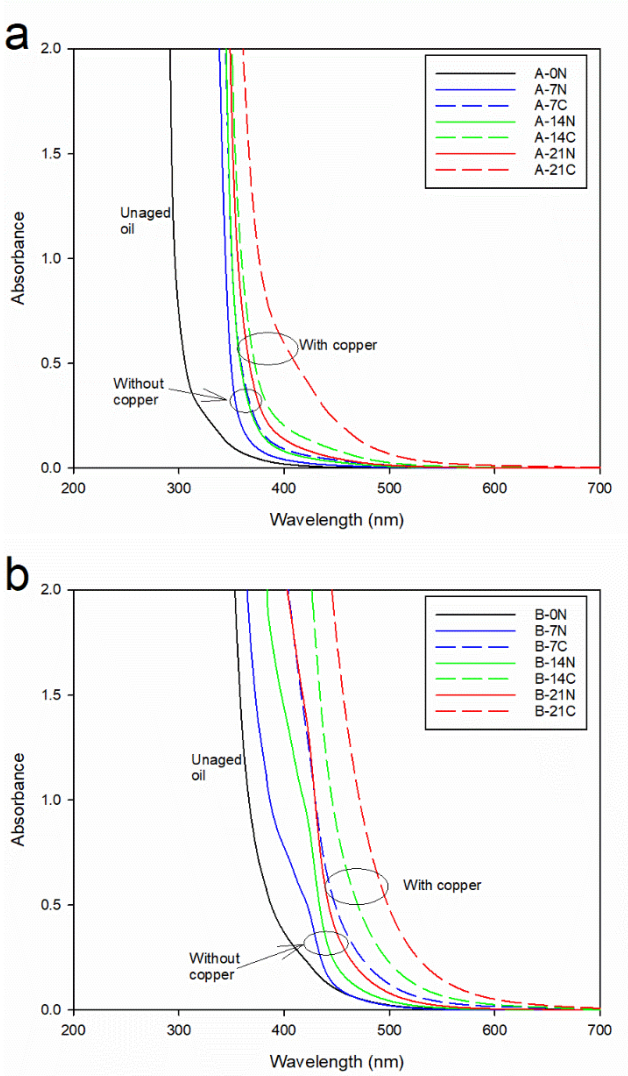

Figure 4. UV/Vis spectra from (a) oil A, (b) oil B. The circles indicate the extent of the changes between 7 and 21 d of aging.

Figure 5 contains UV/Vis absorption spectra for oils C and D (hydrocarbon oils). Both oils are initially colourless and hence the absorption edge of the unaged oils lies well within UV wavelengths (300 and 320 nm respectively). Whilst the oils are visibly darkened on aging in the same manner as the ester oils, this is manifested in a very different way in the spectra, through an increase in optical absorption over a wide range of wavelengths (350 – 500 nm) which is enhanced in the presence of copper. Visually oil D was always noticeably darker than oil C after any prescribed period of aging and in the spectra, this is manifested by increased absorbance over the above wavelength range for any given aging time. In studies on a

different mineral oil (Nynas Nytro 10 GBN) under oxidative conditions [21] a behaviour like that shown in Figure 4 was evident. This change probably reflects differences in oil chemistry between the two different types of mineral oil, nevertheless oils C and D behave remarkably similarly.

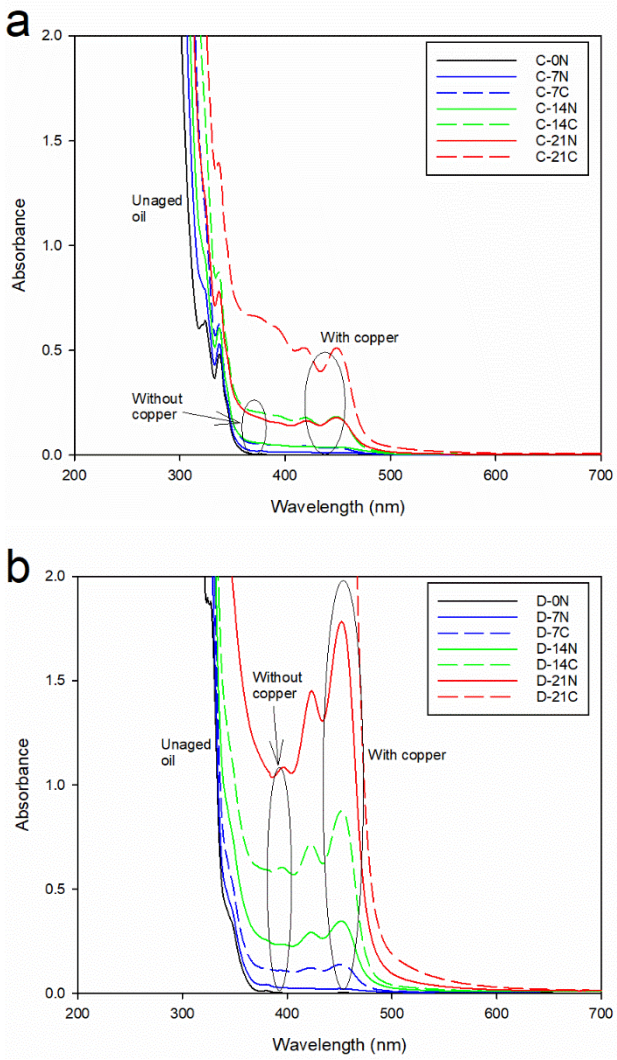

Figure 5. UV/Vis spectra from (a) oil C, (b) oil D. The circles indicate the extent of the changes between 7 and 21 d of aging

Figure 6 shows results of the viscosity measurements. Oil B (natural ester) shows a significant increase in viscosity after aging whilst that of oils A, C and D are largely unchanged. Within the uncertainties inherent to the measurements there is no significant effect of copper. The effects of aging agree with other comparative studies [20][22] and gelling in natural ester oils is a well-known problem [23]. Ester oils have a higher viscosity than mineral oils and the values here are consistent with those in the literature, typically 55 – 75 mm^2/s at 25 ˚C [1][2][8][11][13][20]. The IEC standard for used natural esters [18] allows for a 10 % increase in viscosity and oil B meets this requirement for < 10 days aging. Our measured value for oil D (mineral oil) is in good agreement with the literature [8] but that of oil C (Bio300X) is significantly lower (7 mm^2/s). The low viscosity of Bio300X could potentially provide improved cooling efficiency in a transformer through enhanced oil circulation [9].

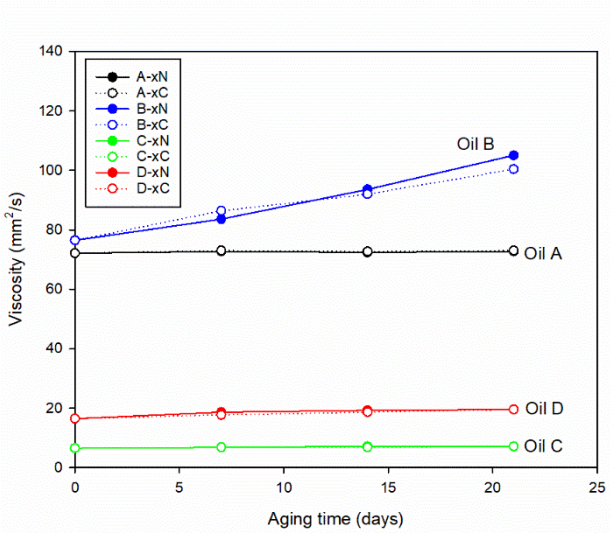

Figure 6. Viscosity as a function of aging time

3.3 Dielectric changes

Figures 7 and 8 shows results from dielectric spectroscopy measurements on the combined oil/paper systems. The relative permittivity was independent of frequency so Figure 7 shows a summary of average values as a function of aging time. The two ester oils behave similarly as do the two hydrocarbon oils, with only a slight effect of aging being evident in the former. In contrast, both hydrocarbon oils show values of around 2.8 which are not significantly affected by aging. The scatter in the datasets is consistent with the uncertainties in the measurements ± 0.1 (arising primarily from differences in paper thickness). The observed values are higher than those of both mineral oil (typically 2.2) [21] and vegetable oil (typically 3.0) [24] but comparable values are reported elsewhere for similar oil/paper systems [3][12][24].

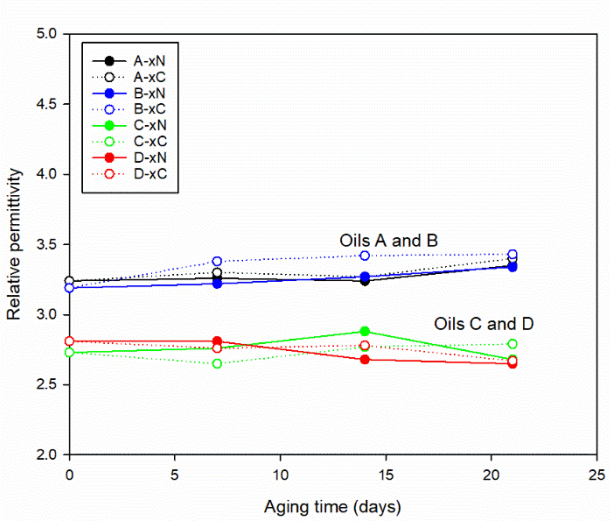

Figure 7. Relative permittivity as a function of aging time

As an example of the frequency dependence of dielectric loss, Figure 8a shows an example of curves obtained from all four oils aged for 21 d without copper. In the low frequency range, the dielectric loss varies inversely with frequency indicating ionic conductivity [25], and here the ester oils show a strong uplift which is much weaker in the hydrocarbon oils. Similar

behaviour was reported elsewhere in ester oil/paper [3] and mineral oil/paper [12] systems and it was shown that the low frequency uplift is due to water in the oil and mid-frequency relaxations are due to water in the paper. Therefore, the current data reflects the higher water content of the ester oils relative to the hydrocarbon oils (see Figure 2) whilst the absence of a mid-frequency relaxation confirms that the paper is dry.

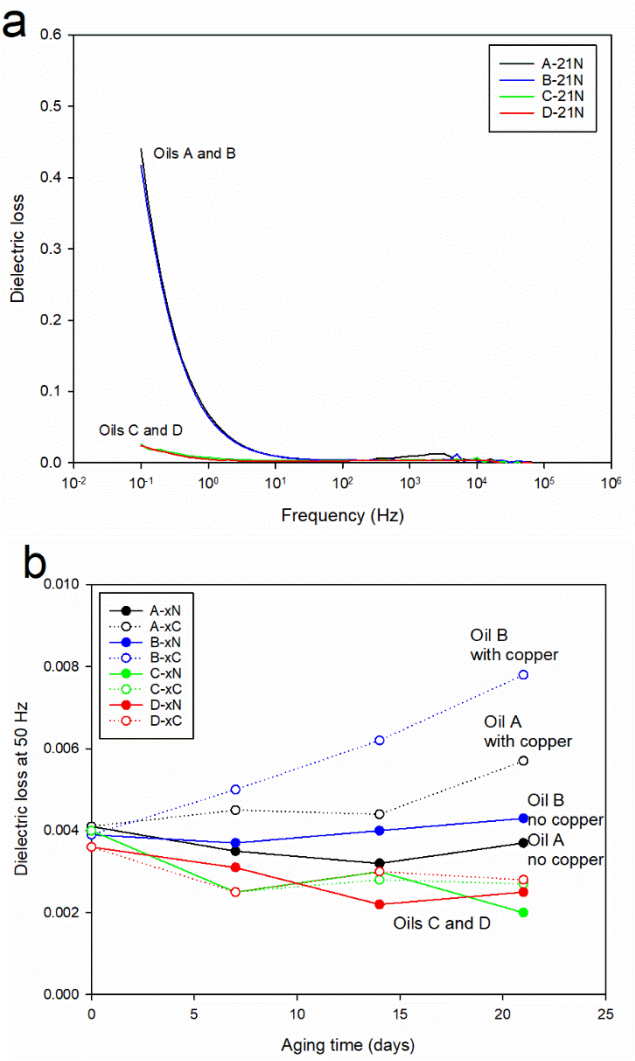

Figure 8: Dielectric loss measurements (a) example of frequency dependence, (b) summary of values at 50 Hz

A summary of the dielectric loss (tan δ) at power frequencies (50 Hz) is shown in Figure 8b. Whilst the dielectric loss of most of the paper/oil systems is unaffected by aging and follows to some degree variations in water content (see Figure 2), that of oil B, and to a lesser extent oil A, show an increased dielectric loss when aged with copper. Similar dielectric loss values for aged paper/oil systems at power frequencies are reported elsewhere [3][7][12][22][24] and show that our data are reasonable. Furthermore, comparable values (~ 0.003 for mineral oil and up to 0.009 for ester oils) are reported in the literature for oils aged in isolation [11][14] which verifies that dry paper only has a minor effect on the dielectric loss [12]. It is widely appreciated that ester oils have higher dielectric loss values than mineral oils [11][20][21][25] and that aging in the presence of copper leads to the highest values of dielectric loss - up to 0.01 in FR3 natural ester oil [11][22] and up to 0.005 in mineral oil [21], and the same trends are evident here. Whilst no specific standards exist for paper/oil systems, IEC recommendations for service aged natural ester oils stipulate a maximum tan δ of 0.005 [18] and clearly oil B exceeds this limit when aged for more than 8 days in the presence of copper.

4 Conclusions

A synthetic ester, a natural ester, a bio-based hydrocarbon fluid and a mineral oil were aged in the presence of kraft paper (some samples contained copper) at 130 ˚C for up to 21 d. A battery of analytical tests was then employed to characterise changes in their chemical, physical and dielectric properties.

- Samples spanned nearly the full transformer lifecycle and both ester oils reduce the aging rate of the paper, as evinced by a higher value of DP for any given aging period. DP was independent of whether copper was present during aging.
- The ester oils were always wetter than the hydrocarbon fluids. After an initial dehydration, the water content increased progressively with aging time. Water content was independent of whether copper was present during aging.
- Acidity increased dramatically with aging time in the natural ester oil, whilst the hydrocarbon oils and synthetic esters showed a more gradual increase. Copper had a weak effect and tended to increase the acid number.
- Both the ester and hydrocarbon oils darkened on aging but this was manifested in the UV/Vis spectra in different ways and copper had a clear catalytic effect on the creation of chromophores. Presumably the differences in the spectra reflect the different chemistries of the oils.
- The viscosity of the ester oils was higher than the hydrocarbon oils but only that of natural ester increased significantly after aging. The viscosity of the bio-based hydrocarbon fluid was significantly lower than that of mineral oil which may improve cooling efficiency in a high voltage transformer.
- The relative permittivity of paper soaked in ester oils was higher than that soaked in hydrocarbon oils and a low frequency uplift in the dielectric loss of the ester oils is consistent with the amount of water absorbed into the oil. The dielectric loss was hardly changed by aging, except when natural ester oil was aged in the presence of copper.

All the aged oils, including the natural ester aged for < 10 days, appear to meet the relevant IEC acceptance limits for service aged transformer oils. It is recommended that a synthetic rather than a natural ester be employed in plant to minimise increases in viscosity during aging. Nynas Bio300X could potentially improve cooling efficiency in a high voltage transformer whilst both ester oils can mitigate the aging of paper, potentially extending plant lifetime. It is planned to undertake infra-red spectroscopy and AC breakdown measurements on the current samples and then to undertake

identical aging tests using synthetic and natural ester oils obtained from a wide range of different manufacturers.

5 Acknowledgements

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