Effect of Aging on the Physical, Chemical and Dielectric Properties of Dodecylbenzene Cable Oil

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***Abstract*—In high voltage transformers a liquid dielectric, such as mineral oil, serves both as an electrical insulator (in conjunction with paper) and as a coolant. Similarly, in paper/oil cables mineral oil or dodecylbenzene in conjunction with paper serves as the electrical insulator. In such systems, the oil serves as a convenient medium for sampling to indicate plant health. In the current study dodecylbenzene was aged at elevated temperatures in the presence of air and copper. A battery of tests was then performed to assess the changes in physical, chemical and electrical properties. After aging the oils were yellowed and oils aged with copper showed oxidation, increased water content and the formation of a precipitate, whilst those aged in the absence of copper showed much less aging. Changes in electrical properties were noted such as increased dielectric loss, increased electrical conductivity and decreased dielectric breakdown strength. It was found that the presence of the precipitate did not affect the electrical properties of the oil.**

Keywords*— Dodecylbenzene; Aging; Oxidation; Electrical conductivity; Dielectric breakdown strength

I. Introduction

With much of the high voltage infrastructure in the UK approaching the end of its serviceable lifetime [1], routine condition monitoring is becoming more important to minimise equipment failure and costly outages. In this regard, oil provides a convenient medium for sampling to indicate plant health. High voltage transformers typically employ mineral oil in conjunction with paper as a dielectric medium; recent work has focussed on its replacement with vegetable oil to reduce environmental impact [2]. Similarly, current practice in existing paper/oil cable systems is to backfill with dodecylbenzene, a more environmentally friendly fluid. Many studies of the aging behaviour of mineral oil have been undertaken due to its widespread use in transformers [3-6] and indicators of aging such as yellowing [3], oxidation [4], increased water content [4, 5], increased dielectric loss [4] and reduced electrical breakdown strength [6, 7] were reported.

Similarly, the aging behaviour of dodecylbenzene [8, 9] vegetable oils [10] and silicone oils [11] has also been studied and all of this work has led to a number of "universal" indicators of aging, which can be used for routine condition monitoring. However, most of these studies did not consider the effects of aging on high field properties, such as electrical conductivity and electrical breakdown strength, which would be more applicable for plant. When this was done in silicone and vegetable oils [12, 13], anomolous results were obtained; i.e. the electrical breakdown strength *increased* with aging time. This was thought to be due to an increase in viscosity of these oils following aging, but this brings into question the reliability of such tests, particularly in the new generation of vegetable oil filled transformers.

In this study, dodecylbenzene was aged at high temperatures and the various aging indicators were examined with a focus on the high field behaviour. Dodecylbenzene was chosen as as a model oil system whose viscosity does not change after aging [10]. Furthermore, the effect of precipitate formation on the high field performance of such oils was studied in view of particulate "bridging", which can prove troublesome in paper/oil insulation systems [7, 14].

II. Experimental

Dodecylbenzene cable oil (BICC type C148 batch 5808) was used throughout. Separate samples (150 ml) were aged in fan ovens in tall glass jars at 135 ºC for periods of 72, 168 and 336 h, which were covered with a Petrie dish to minimize evaporation. To selected samples copper was added (in the form of 0.1 mm thickness sheet), total surface area 96 cm^2 to be consistent with earlier work [8-11]. Some oils were tested after centrifuging to remove visible particulate matter, whilst others were homogenized before testing.

Ultraviolet/visible (UV/Vis) spectroscopy was undertaken in 10 ml PMMA cuvettes (path length 10 mm) using a Perkin Elmer Lambda 35 spectrometer over a wavelength range of 300 – 1100 nm. Infrared (IR) spectroscopy was undertaken using a Perkin Elmer Spectrum GX instrument, the test cell was composed of two KBr windows separated by a polyethylene gasket to ensure a 0.1 mm thick oil film and spectra were recorded from 4000 to 400 cm^{-1}. The average water content of 3 separate 1 ml samples was determined using an Aquamax KF titrator (GR Scientific).

Dielectric spectroscopy was performed using a Solartron 1296 dielectric interface linked to a Schlumberger SI 1260 impedance-gain-phase analyzer. The test cell was composed of a 35 mm diameter cup and a 30 mm diameter plate. Oil was placed in the cup and a spacing of 0.2 mm was maintained using a PTFE slug. Measurements were made at room temperature using 1 V_{rms} and integrating over 10 cycles.

Electrical conductivity measurements were performed using a concentric cylindrical test cell (5 ml) with a separation of 2 mm into which the oil was placed. A voltage was applied using a computer controlled system employing a Spellman SL10 high voltage DC supply and a Keithley 6487 Picoammeter. Initially 100 V was applied, increasing in 100 V steps to 4 kV, recording the current 10s after application of each voltage to allow capacitive currents to decay.

AC breakdown measurements were performed using a system built in house. The test cell used was a Perspex cylinder containing opposing 25 mm diameter chrome steel ball bearings and an electrode separation of 1 mm was used throughout. The test cell had a volume of 8 ml and the applied (50 Hz AC) voltage was increased at a rate of 350 V/s and the voltage at breakdown was then noted. The oil was changed after each test and the ball bearings after every 5 tests. Tests were performed after allowing the oil to settle for ~2 min to eliminate air bubbles.

III. RESULTS AND DISCUSSION

A. UV/Vis spectroscopy

Fig. 1 shows spectra from oils which have been homogenized. On aging, the absorption edge shifts to longer wavelengths (arrowed) and the oil is visibly yellowed [3, 8, 9]. Aging with copper for 72 h is broadly equivalent to aging without copper for 168 h, thus copper is clearly accelerating the aging process. After 72 h aging in the presence of copper, a weak absorption at 680 nm (labelled "A") was detected which is indicative of the presence of copper carboxylates [8]. Further aging then results in the formation of a precipitate, which absorbs over all wavelengths, until finally the oil becomes black and opaque after 336 h aging.

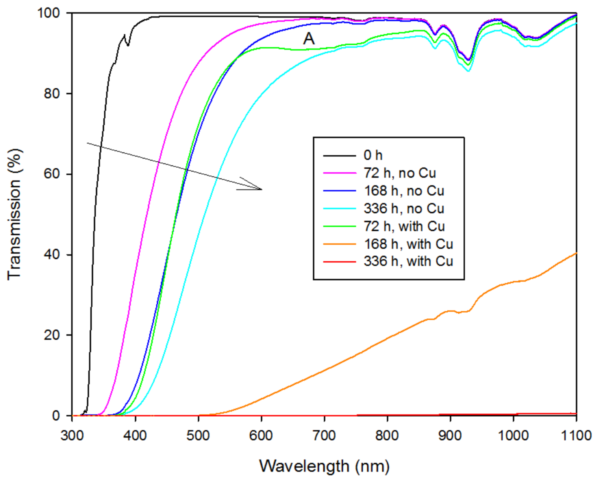

Fig. 1. UV/Vis spectra from homogenized oil samples

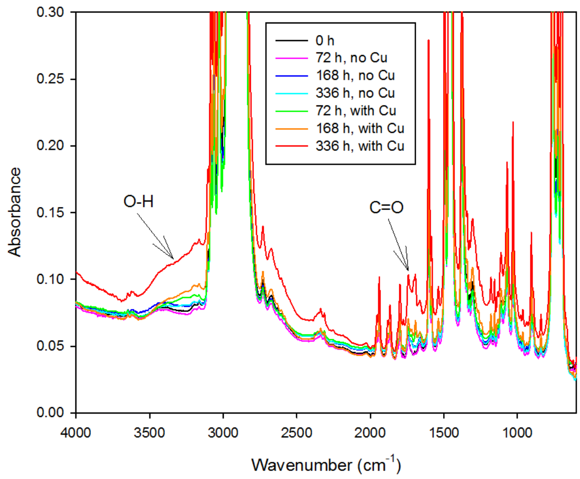

Fig. 2. Infrared spectra from centrifuged oil samples

B. Infrared spectroscopy

Fig. 2 shows infrared spectra from centrifuged samples. After aging without copper, no significant oxidation was observed. This should be contrasted to the previous small volume (5 ml) samples [8], which showed appreciable oxidation; here a reduced oxidation rate is a consequence of the larger volume and smaller surface area to volume ratio which clearly reduces oxygen diffusion. Aging with copper results in significant carbonyl (C=O) and hydroxyl (O-H) bands, whilst previous small volume samples indicated only carbonyl bands. It was suggested [8] that precipitate formation depletes the oil of hydroxyl rich compounds; however, here, the aging rate and the production of precipitate are reduced, presumably allowing a greater proportion of these compounds to remain in solution.

C. Water content

Fig. 3 shows the average water content as a function of aging time. The water content in the samples aged without copper hardly increases at all with aging time which correlates with the lack of oxidation observed in these oils. Centrifuged

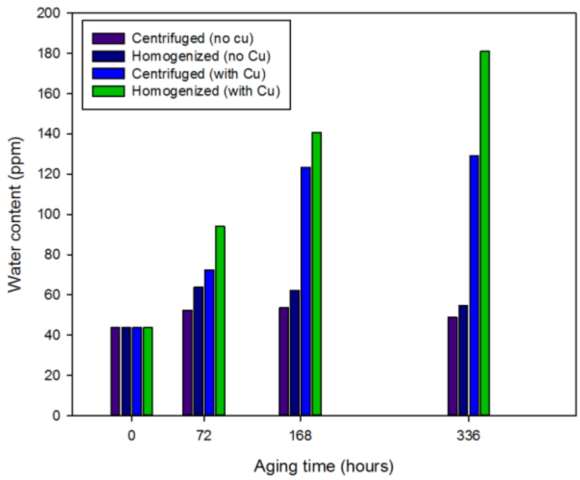

Fig. 3. Water content measurements, uncertainties ±10 PPM

samples aged in the presence of copper reach a stable value of ~120 ppm after 168 h aging time, this is where the production of aging products in the oil is balanced by their removal as precipitate. In contrast, the water content of homogenized samples continues to increase with aging time. In previous small volume samples [8] values as high as 300 ppm were reported, whilst more modest values were reported following aging under nitrogen [9]. As expected, the values recorded here lie somewhere between these two extremes.

D. Dielectric spectroscopy

Fig. 4a shows plots of relative permittivity of homogenized oils. On aging without copper, the permittivity is unchanged, whereas aging with copper results in an increase, particularly at low frequencies (indicating an increase in polarization). The values tend to saturate after 168 h aging time, which implies that the included precipitate is having only a minor effect on the dielectric properties. This is confirmed in the dielectric loss behavior shown in Fig. 4b. On aging without copper, the dielectric loss at 0.1 Hz increases from 0.1 to 0.7 whereas that at 50 Hz is largely unaffected (<10^{-3}) and lies within the noise. Comparable work on small volume samples [8] indicates a maximum dielectric loss of 0.03 at 50 Hz, which is much higher than here, reflecting the reduced aging in the current samples. On aging in the presence of copper, the dielectric loss at 50 Hz increases to 0.08 after 336 h aging time, again much lower than that of identically aged small volume samples (0.28), indicating reduced aging.

E. Electrical conductivity

Electrical conductivity data are shown in Fig. 5. On aging without copper there is no clear trend with aging time, little or no dependence on applied field and all of the results fall within the sample to sample variations which seem to be inherent to this technique; the observed behavior being consistent with similarly aged silicone and vegetable oils [12, 13]. In contrast, aging in the presence of copper, results in increased conductivity and clear saturation after 168 h aging time. The conductivity falls with increasing field, a behavior that was noted in aged silicone oil [12], which indicates that ionic species are being swept out of solution during the tests – such ions then contribute towards the increased polarization observed in Fig. 4a. In all of these tests there is no effect of sample processing (i.e. centrifuging or homogenization) confirming that the precipitate is having no significant influence on the measured electrical conductivity.

F. Electrical breakdown strength

An example Weibull plot from centrifuged oils is shown in Fig. 6 and numerical data are shown in Table I. On aging without copper, the breakdown strength is unchanged until 336 h aging, where it falls from 14 kV/mm to 9 kV/mm, and the data exhibit no significant change in β parameter. Samples aged with copper show a fall in breakdown strength, even after 72 h aging, reaching a minimum value of 7 kV/mm (Table I) with an increase in β value. Comparison with homogenized samples indicates no significant difference (Table I).

In aged silicone and vegetable oils [12, 13] an increase in oil viscosity led to increased breakdown strength whilst here, where the viscosity is unchanged after aging [10], the breakdown strength is reduced. The same pattern of behavior

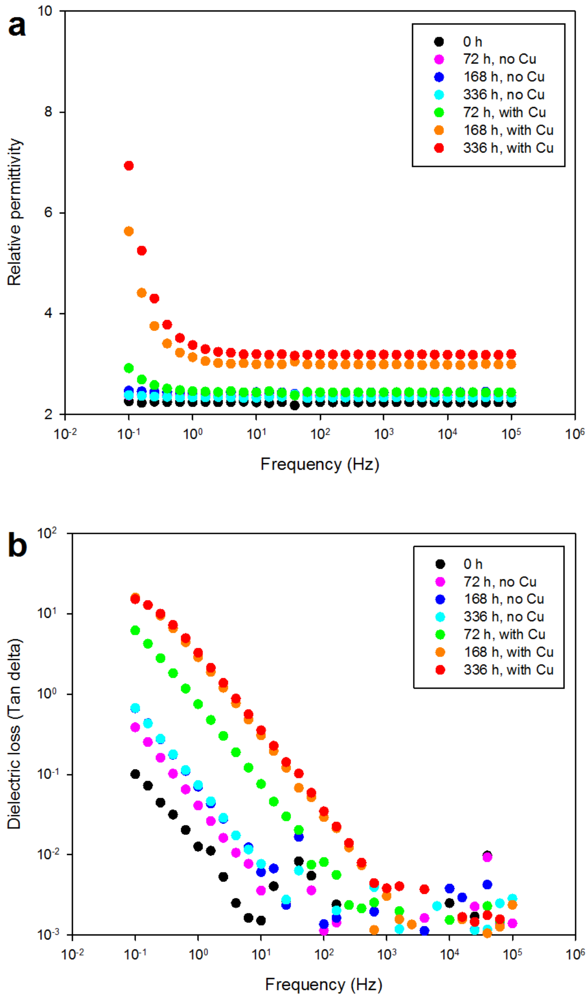

Fig. 4. Dielectric spectroscopy from homogenized oil samples; (a) relative permittivity, (b) dielectric loss

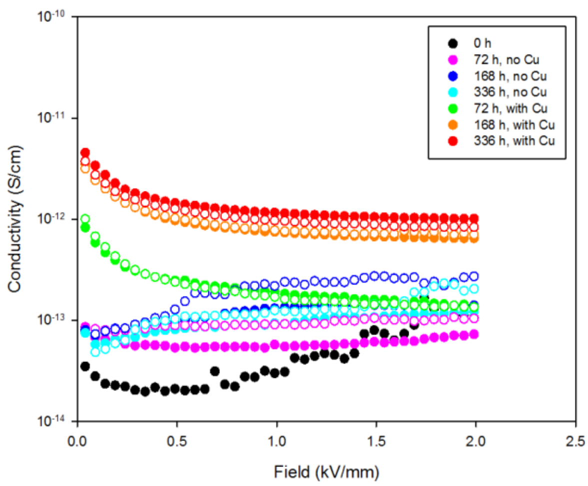

Fig. 5. Electrical conductivity of aged oil samples; centrifuged oils (closed symbols), homogenized oils (open symbols).

the aging rate of the current larger volume samples was reduced.

In this system where the oil viscosity is unchanged after aging, the breakdown strength falls with aging time; hence under these conditions, AC breakdown tests provide a reliable indicator of oil aging. The change in β parameter, which may indicate bridging phenomena, is interesting and should be investigated further in systems with known conducting and non-conducting particle contents.

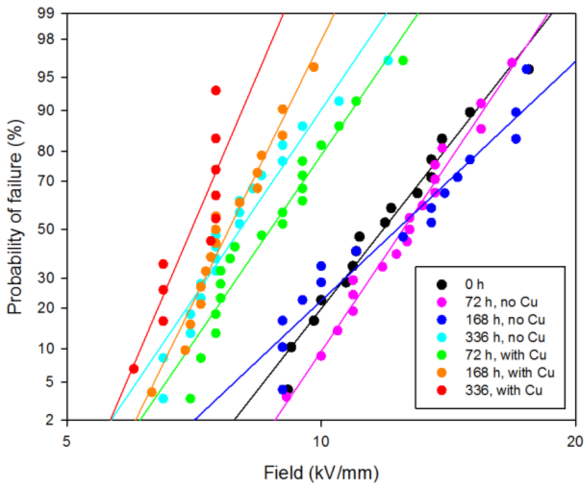

Fig. 6. Weibull plot of electrical breakdown data obtained from centrifuged oil samples

TABLE I. BREAKDOWN DATA

Aging conditions	Centrifuged		Homogenised	
	E (kV/mm)	***β***	***E (kV/mm)***	***β***
Unaged	13.0 ± 1.2	5.4		
72 h	13.5 ± 1.1	6.9		
168 h	13.7 ± 1.5	4.9		
336 h	8.7 ± 0.7	5.6		
72 h + Cu	9.4 ± 0.7	6.1	9.5 ± 0.7	6.9
168 h + Cu	8.2 ± 0.5	8.9	9.2 ± 0.5	9.7
336 h + Cu	7.3 ± 0.3	13.0	7.7 ± 0.4	12.7

was followed in other oils, where the viscosity was also unchanged after aging [6, 7, 12, 13], and in all these cases measurements of breakdown strength therefore provide a reliable indicator of oil aging. Finally, the increase in β value may indicate a subtle change of breakdown mechanism in oils that contain particulates, in such cases bridging was observed [12, 14] and the breakdown then presumably takes place via the bridge and not through the oil. The current results indicate that sufficient particulate matter remains suspended in the oil to form a bridge even after centrifuging.

IV. CONCLUSIONS

Large volume (150 ml) samples of dodecylbenzene were thermally aged at 135 °C in air and some samples included copper to investigate its catalytic effects. The same indicators of aging were found as observed in small volume samples (yellowing, oxidation, increased water content, increased dielectric loss and increased electrical conductivity) particularly after aging in the presence of copper. However,

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