Measurements of Mobility in Aged Mineral Oil in the Presence of Nanoparticles

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Abstract— **The addition of nanoparticles into insulating liquids has been a popular area of research for the last 20 years as improvements have been observed in the breakdown strength of aged insulating liquids. This paper reports on the changes in the conductivity and the mobility of charge carriers in oil as a result of ageing and how these are effected by the addition of nanoparticles to the aged insulation.**

Keywords—conductivity, mobility, ageing, nanofluids.

I. INTRODUCTION

Insulating liquids, particularly in power applications, are expected to maintain their insulating properties over periods of up to 40 years. During this time, they will undergo a wide range of ageing stresses. These stresses can lead to changes in the chemical, physical and dielectric properties of the insulating liquid, which may reduce its breakdown strength or increase the conductivity, leading to increased losses in the system. The addition of nanoparticles into insulating liquids has been a popular area of research for the last 20 years, since the addition of magnetite nanoparticles in an attempt to improve heat transfer through a mineral oil was also shown to improve the electrical breakdown strength [1]. Data has also been reported that indicates that the breakdown strength of thermally-aged mineral oil can be improved through the addition of nanoparticles after ageing, for example [2]. These changes in the properties of the oil have been attributed to electron scavenging and trapping by the nanoparticles, following the approach of Hwang et. al. [3].

Although there is strong evidence that the addition of either conducting or semiconducting nanoparticles to aged insulating liquids has resulted in improvements in the electrical properties of the aged, base liquids, little research has been conducted to determine the effects that the addition of such nanoparticles have on the ageing rate of the liquid or on changes in the properties of the liquid as a result of ageing.

II. EXPERIMENTAL METHODS

A. Ageing protocol

This paper reports the changes in the apparent mobility and the d.c. conductivity of samples of (Shell Diala S3 ZX-IG) insulating oil subjected to thermal ageing at a temperature of 120 °C. The oil was aged in borosilicate media bottles, the tops of which were loosely covered with aluminium foil to prevent contamination of the liquid during ageing, while still exposing the oil to the ambient atmosphere. The oil samples were aged for periods of up to 8 days under these conditions, and significant darkening of the oil was observed over this ageing period.

B. Nanoparticles added to system

The nanoparticles used came in the form of the commercially-available EFH1 Ferro-Fluid, manufactured by Ferrotec (USA), and supplied in the UK by FIRST 4 MAGNETS. The specific gravity of this ferrofluid was quoted as being in the range of 0.92 to 1.47. Paraffin was used as the carrier liquid. The mean particle diameter is 11.6 nm and Cyclodextrins ($C_{42}O_{35}H_{70}$) was used as a surfactant to prevent the aggregation of the nanoparticles [6]. The range of mass concentration of the nanoparticles for this ferrofluid was not precisely defined, but was in the range of 0.03 to 0.15 kg/L [7]. A volume of 0.02 ml EFH1 ferrofluid was added to 200ml of oil. The sample was then treated in an ultrasonic bath for 30 minutes, operating at a power density of 23.3 W/L, to disperse the nanoparticles [8]. The stability of these suspensions was good, with no precipitation phenomenon observed after the samples were left undisturbed for a period of four weeks. The concentration of the nanoparticles in the oil samples was in the range of 0.3% g/L to 1.5% g/L. However, as a common stock bottle of ferrofluid was used to prepare all samples, the concentration between samples should have been consistent.

C. Measurement Techniques

The test cell used for the mobility and conductivity measurements was constructed from stainless steel and followed the geometry of the IEC 60247:2004 standard [4]. The separation between the inner and outer electrodes was 1 mm. As the test cell had a broadly coaxial geometry, the electric field across the gap was not uniform: the fields at the inner and outer electrodes were calculated in terms of E_0, the field expected in a uniform gap, as 1.038 E_0 and 0.964 E_0, respectively.

1) Current Transient, Time of Flight and Mobility

The voltage applied to the test cell was produced by a Keithly 617 electrometer, which was also used to measure the currents in the system. The inner electrode of the test cell was

connected to the voltage source and the outer electrode was connected through the current-measurement circuitry of the electrometer to the ground termination of the source. Time-of-Flight (TOF) measurements were performed using a bipolar measurement technique. This is preferred to the monopolar approach as the distribution of charge carriers resulting from the initial polarization is more consistent and independent of the previous measurement history of the sample [5]. The sample was first polarized by applying a negative potential to the inner electrode, leading to a non-equilibrium distribution of charge carriers close to the electrodes. The voltage was then reversed, allowing the transit of these charge carriers across the system to be observed by monitoring the current. A typical current waveform associated with carrier transit, observed by the authors in unaged oil, is shown in Fig. 1.

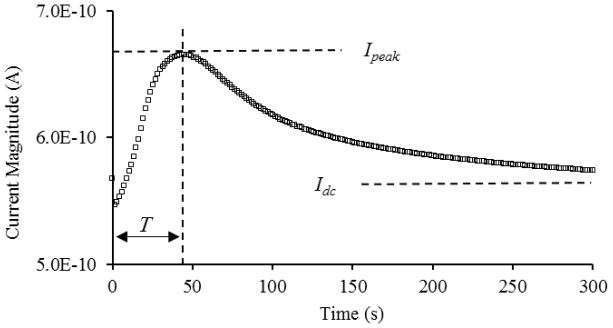

Fig. 1 Reverse polarity transient with parameters measured

The TOF T is defined as the interval between the reversal of the voltage applied to the test cell and the observed peak in the measured current, as shown in Fig. 1, and is assumed to represent the transit time of charge carriers crossing the inter-electrode gap. With knowledge of the geometry of the test cell and the applied voltage V, a value for the mobility of the charge carriers can be calculated.

D. Measurement protocol

After the test cell had been cleaned and filled with an oil sample, it was sealed with paraffin wax to prevent the ingress of water vapour. It was then placed in an oil-filled beaker in a Grant GP200 thermostatic water bath. The temperature of the inner electrode was monitored using a RS1319A digital thermometer during measurements. With the water bath temperature set to 30 °C, after 120 minutes, when the system had achieved a thermal equilibrium, the temperature of the inner electrode was maintained at 29.5 ± 0.5 °C. In the experimental procedure used in [5], the bipolar voltages applied were symmetrical. In the results reported in this paper, the current transient was measured 5 times in succession. For each measurement, the initial polarization used a voltage of −50 V, corresponding to a field of 0.5 kVcm^{-1}, for a period of 1800 s. The reverse polarizations followed a consistent sequence of voltages: 70 V; 30 V; 40 V 60 V and 50 V, corresponding to fields between 0.3 and 0.7 kVcm^{-1}. This approach was adopted so that all TOF measurements were obtained from a common initial charge distribution within the system. The current transient was also measured over a period of 1800 s. Over this time period, the current had decayed to close to its asymptotic value and the average over the last 30 s of measurement was assumed to represent the current under d.c conditions, I_{dc}. The peak current I_{peak} was also determined from the current transients.

E. Transient Behaviour in Repeated Measurements

The measurement sequence described above was repeated on the sample daily, over a 5-day period. Systematic changes were observed in the calculated values of the mobility and the measured values of I_{peak} and I_{dc}, as shown in Fig. 2.

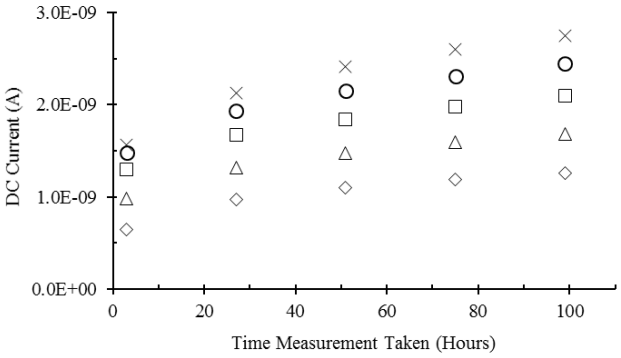

Fig. 2 Transient behaviour observed in sample of oil aged for 2 days under repeated measurement. Polarisation voltages.: ◇30V; △ 40V; □ 60V; ○ 60V; × 70V

This transient behaviour would be expected if the change in the observed properties was occurring due to a process following first-order reaction kinetics. Therefore, the time-dependent behavior was fitted to exponential relationships. This allowed expected values for experimental parameters to be derived at $t = 0$ (when the sample was first placed within the test cell) and at $t = \infty$ (the value expected when equilibrium had been achieved). A common fit, minimizing the residual sum of squares, was performed across the 5 sets of data for I_{dc} and I_{peak}. The quality of these fits indicated that the changes in I_{dc} and I_{peak} could be described by a common time constant. Exponential fits to the data for T were also performed and good fits were achieved to a common time constant, but one with a different value than that obtained for I_{dc} and I_{peak}. In this paper, the values derived for the parameters at equilibrium, $t = \infty$, are reported.

III. Experimental Results

Fig. 3 shows the changes observed in I_{dc} as a function of applied voltage and ageing time for oil without nanoparticles. Fig. 4 shows the corresponding data for I_{peak}. It can be seen that the thermal ageing of the oil has a significant impact on I_{dc}, increasing the currents from the range of tens of picoamps for the unaged sample, into the range of nanoamps for the aged samples. Similar behaviours were observed for I_{peak}. For each ageing condition, a linear relationship was observed for both I_{dc} and I_{peak}, suggesting that an Ohmic behaviour was occurring. However, the lines of best fit through the data do not pass through the origin. The gradients of the line corresponding to a dynamic conductance increase with ageing time.

Adding the EFH1 nanoparticles to unaged oil and to oil after ageing had an additional impact on the behaviour of both I_{dc}

and I_{peak}, with a significant increase in the current occurring due to the addition of the nanoparticles, Fig. 5 and Fig. 6. The current again shows a linear dependence on voltage, but the lines of best fit again do not pass through the origin. The gradients of the lines of best fit again increase with ageing time.

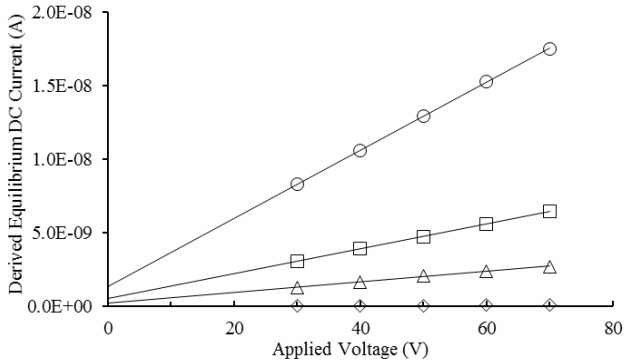

Fig. 3 Behaviour of I_{dc} observed in oil samples:◇unaged; △ aged 2 days;□ aged 4 days;○ aged 8 days.

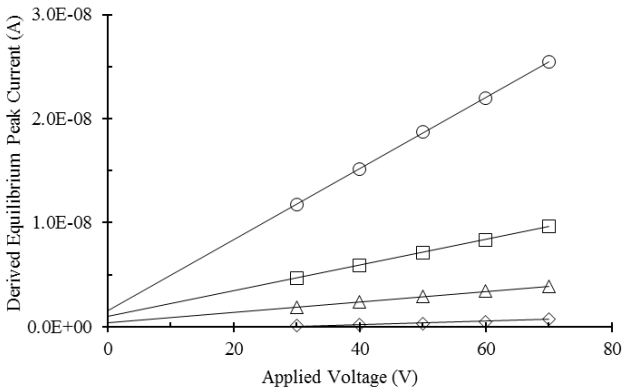

Fig. 4 Behaviour of I_{peak} observed in oil samples:◇unaged; △ aged 2 days;□ aged 4 days;○ aged 8 days.

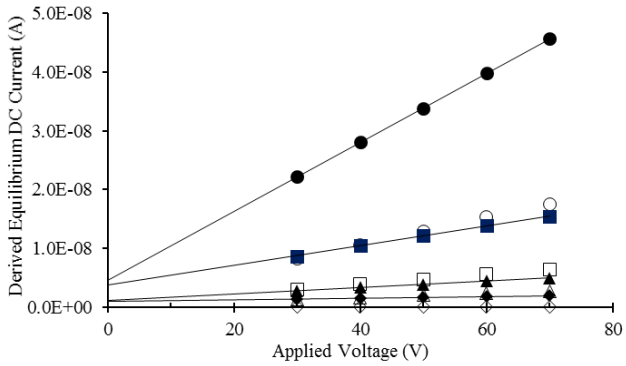

Fig. 5 Behaviour of I_{dc} observed in oil samples. Open symbols without nanoparticles, filled symbols with nanoparticles: ◇unaged; △ aged 2 days; □ aged 4 days; ○ aged 8 days.

The derived values of apparent mobility are shown in Fig 7 for both the aged samples and the samples which had nanoparticles added after thermal ageing. The behaviour of the mobility as a function of ageing is complicated. For the unaged oil, the mobility appears to have a strong field dependence.

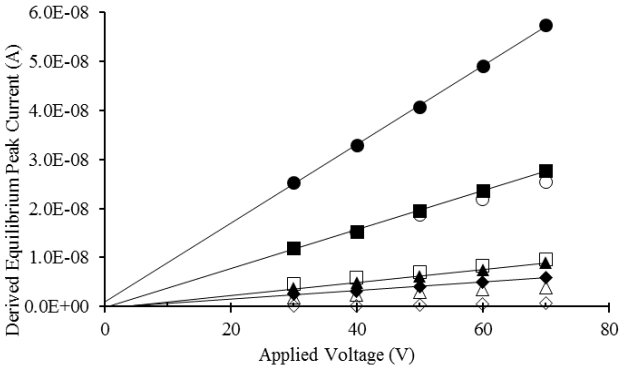

Fig. 6 Behaviour of I_{peak} observed in oil samples. Open symbols without nanoparticles, filled symbols with nanoparticles: ◇unaged; △ aged 2 days; □ aged 4 days; ○ aged 8 days.

The mobility for aged oil samples without nanoparticles is lower than that for the unaged oil, and any field dependence of the mobility is negligible. The mobility increases as the ageing time increases beyond two days, but does not recover to the values associated with the unaged oil. Adding nanoparticles to the unaged oil appears to reduce the mobility of charge carriers in the system significantly, and also reduces the field dependence of the mobility. The addition of nanoparticles to the aged samples significantly increases the mobility of the charge carriers to values higher than those observed in the unaged oil in the absence of nanoparticles.

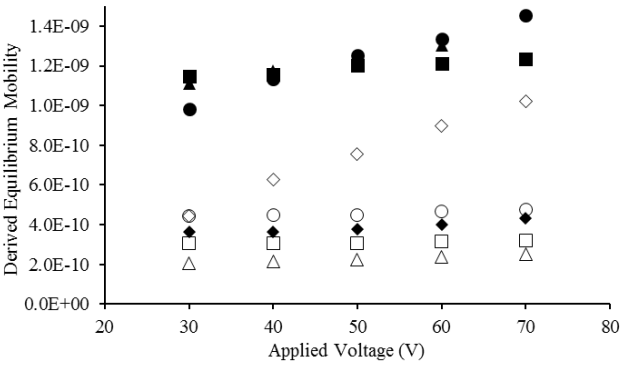

Fig. 7 Derived apparent mobility in oil samples. Open symbols without nanoparticles, filled symbols with nanoparticles: ◇unaged; △ aged 2 days;□ aged 4 days;○ aged 8 days.

IV. Discussion

From the results observed in the oil without the addition of nanoparticles, thermal ageing results in a significant increase in the measured values of d.c. current, while the measured mobility values have fallen. This would seem to suggest that the charge carrier density within the samples is increasing as a result of ageing. However, it is not certain that the mobility measured under transient conditions controls the conduction process at long times, where charge-injection processes occurring at the electrodes may dominate the measured conductivity. It has been suggested that a process analogous to Schottky electron emission may control charge injection [9]. This may explain why the fit lines in Fig. 3 to Fig. 6 do not

pass through the origin. In this process, charge carriers formed close to the electrode have to have sufficient energy to overcome the work function associated with the electrostatic image force. The presence of an applied field modifies the barrier height for the charge carriers and, therefore, leads to a field dependence on the injection current. The general form of the current expected for such a charge-injection process is:

$$I = \alpha \exp\left(-\frac{\phi - \gamma E^{0.5}}{kT}\right) = \alpha \exp\left(-\frac{\phi}{kT}\right)\exp\left(\beta E^{0.5}\right) \quad (1)$$

The term α corresponds to the number of charge carriers attempting to leave the electrode per second, ϕ is the work function for the charge carriers, and γ is a coefficient for the reduction in the effective barrier height as a result of the applied field, which will depend upon the charge carried by each carrier. If the current does follow the behaviour predicted in (1), a plot of $ln(I)$ vs. $V^{0.5}$ will result in a straight line with gradient corresponding to β, and with intercept corresponding to $\ln(\alpha) - \phi/kT$. Fig. 8 shows the plots obtained for the oil samples that had nanoparticles added to them.

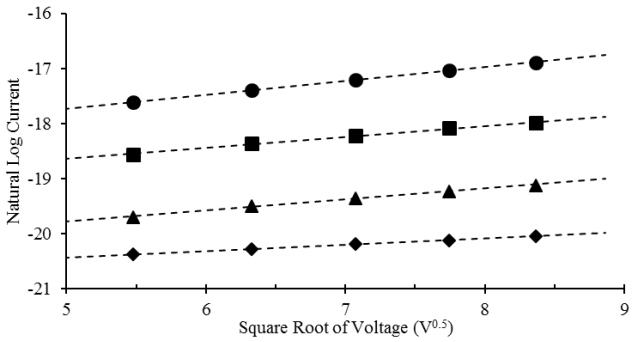

Fig. 8 $\ln(I)$ vs $V^{0.5}$ plots for oil samples with nanoparticles added: ◇unaged; △ aged 2 days;□ aged 4 days;○ aged 8 days.

The fits suggest that the Schottky-type emission described in (1) agrees with the observed behaviour of the d.c. current. Good fits to (1) can also be made to the data for the aged oil without nanoparticles. A summary of the parameters measured or derived from the experimental data is shown in Table I. For the aged oils without nanoparticles, the parameter β appears to be constant in value. As this parameter depends on the charge on each carrier and the temperature, it is reasonable that it remains constant. The values of $\alpha\exp(-\phi/kT)$ increase with ageing time. This suggests that there is a change in the value of the work function as a result of ageing, perhaps due to an increase in the relative permittivity of the liquid. Alternatively, the number of charge carriers attempting to leave the electrode per second may be increasing. For the aged oil with nanoparticles added, there seems to be much greater variation of the parameter β. As aforementioned, this parameter would be expected to be constant, unless, rather than having a constant quantity of charge on each carrier, there is a distribution in the quantity of charge, and this distribution changes with the degree of ageing of the samples. As with the aged oil without nanoparticles, the values of $\alpha\exp(-\phi/kT)$ generally increase with ageing time.

V. Conclusions

From the measurements of current transients in aged oils and aged oils with added nanoparticles, it is clear that the thermal ageing carried out by the authors has significant effects on both the conductivity of the liquid, and on the mobility of charge carriers within the liquid. The addition of the nanofluid used, which has been shown to increase the breakdown strength of oil in [10], leads to a significant increase in the conductivity of the insulating system.

TABLE I. SUMMARY OF MEASURED PARAMETERS

Ageing Time (Days)		0	2	4	8
$\frac{dI}{dV}$ ($S\times10^{-12}$)	*Pure*	0.869	40.5	84.7	231
	+ *EFH1*	13.7	5.4.4	167	588
Mobility at 50 V ($m^2V^{-1}s^{-1}\times10^{-9}$)	*Pure*	0.754	0.221	0.305	0.447
	+ *EFH1*	0.379	1.18	1.21	1.25
$I_0 = \alpha \exp\left(-\frac{\phi}{kT}\right)$ ($A\times10^{-12}$)	*Pure*	8.42	279	758	2060
	+ *EFH1*	758	926	2840	5830
β ($V^{-0.5}m^{0.5}$)	*Pure*	0.25	0.28	0.26	0.26
	+ *EFH1*	0.12	0.20	0.19	0.25

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