The Effect of Oxidative and Paper Degradation Impurities on Partial Discharge Characteristics of Hexadecane

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ABSTRACT
Partial discharge (PD) characteristics of hexadecane were studied in a needle-plane electrode geometry under AC field with a tungsten needle of 20 μm tip radius. PD experiments were conducted on samples containing known concentrations of oil/paper degradation compounds. Partial discharge inception voltage (PDIV), streamer repetition rates, and phase resolved PD (PRPD) patterns were acquired. Ionization potentials (IP) and electron affinities (EA) of hexadecane and a selection of additives were calculated with density functional theory (DFT) and correlated to PD characteristics. IP did not have a significant effect on the number of streamers initiated as most additives had higher IP relative to hexadecane. The presence of electronegative oxygen changes substantially the PD characteristics and, for most additives, increases the number of positive and negative streamers initiated. The greatest changes in PD characteristics, a reduced number of negative streamers, was observed for compounds with large electron capture cross section, even those with negative EA.

Index Terms — Streamer, partial discharge, phase resolved PD pattern, dielectric fluid, insulating liquid, additives, ionization potential, electron affinity, density functional theory.

1 INTRODUCTION
ORGANIC fluids are used widely as insulation and cooling media in fluid filled equipment such as transformers, capacitors, pipe-type cables, and circuit breakers. Liquid-paper dielectrics are used extensively as a result of their greater electrical breakdown strength and thermal conductivity relative to gaseous and bulk liquid insulations. The ability of liquid-paper dielectrics to conform to complex geometries often makes them more practical than solid insulators [1]. Over the lifetime of liquid-paper dielectrics, the insulation is often subject to gradual deterioration due to electrical, thermal, mechanical, and chemical stresses, and the interaction among these stresses can cause premature ageing of the insulation or even failure in extreme cases. As with all insulation systems, failure can cause a great deal of damage, whether physical, environmental, or financial, which encourages monitoring and maintenance of insulation integrity to ensure reliable operation. For this reason standards have been introduced to verify liquid insulation integrity through a wide range of test procedures.

Figure 1 displays a schematic of an oil-immersed transformer. The disc windings are wrapped with Kraft paper and separated with pressboard, while the rest of the transformer is filled with dielectric fluid. The main ageing effects seen in transformers are associated with oxidation of the fluid and overheating of the cellulose. Oxidation of the fluid reduces volume resistivity, increases dielectric loss, reduces interfacial tension, increases total acid number, increases moisture (from cellulose degradation), and increases dissolved gases within the fluid [2-9]. Thermal and oxidative degradation of the paper causes a decrease in the degree of polymerization and generation of furanic compounds and moisture [10-18]. As a result, methods have been devised to obtain electrical, chemical, and physical characteristics of liquid dielectrics, which include determining the breakdown voltage at power frequency, partial discharge inception voltage (PDIV), dissolved gas (DGA), total acid number, dielectric loss, interfacial tension, and volume resistivity, changes in which can be indicative of impurities within the fluid.
In all of the commonly used standards, the state of the insulating fluid is characterized by a single number for each measured parameter. The present research was carried out to develop an experimental approach to analyzing the effect of chemical impurities on PD characteristics as a basis for condition assessment. A needle-plane electrode geometry with a barrier on the plane electrode was employed, as these conditions are necessary for any practical diagnostic based on PD. This approach allows not only for PDIV to be measured but also the discharge rate and phase resolved PD (PRPD) pattern under defined conditions to be acquired.

The most important parameter governing the initiation and propagation of streamers in liquids at high electric field is ionization potential (IP) of the insulating fluid, along with the effects of any additives present [19-28]. Electron affinity (EA) is also an important molecular parameter used to describe qualitative changes in streamer initiation and propagation through formation of anion radicals [25-28]. Density functional theory (DFT) calculations on IP and EA were conducted for hexadecane and a selection of additives, and the results were compared to their respective PD characteristics.

1.1 TECHNICAL BACKGROUND

Heat, hot electrons, and/or UV radiation from electrical discharges, can cause bond cleavage of polymers resulting in formation of very reactive free radicals. Small fractions of broken molecules can react with one another to generate low molecular weight gases that dissolve in the oil and which can be detected with DGA based on gas chromatography (GC). Large free radicals can combine to form higher molecular weight compounds that form insoluble colloidal suspensions, known as “sludge” or “x-waxes”. The most common bond cleavage is from hydrogen abstraction and, if the small free radicals are surrounded by normal hydrocarbon chains, all pairs may recombine to no net effect, which is known as a “cage effect” [4]. Presence of molecular oxygen results in the formation of water, alcohols, and carbonyl groups (aldehydes, ketones, carboxylic acids, etc.) [29, 30]. This process is known as auto-oxidation and arises from the paramagnetic nature of molecular oxygen, as its ground state contains two unpaired electrons that are very reactive with the unpaired electron of a free radical. For the detailed explanation of the auto-oxidation reactions, the reader is referred to [31] which provides a thorough examination of the oxidative chemical reactions that occur during surface and interfacial tracking of crosslinked polyethylene, ethylene propylene rubber, and silicone rubber compounds.

Insulating paper used in transformers is usually made by the Kraft pulping process, which removes lignins and hemicelluloses from wood pulp. This process increases the cellulose fraction of the paper to about 90% [10]. A great deal of research has been devoted to understanding the mechanisms of cellulose degradation in electrical apparatus, with much of the work focused on thermal, oxidative, and hydrolytic degradation processes. In all processes, depolymerization of cellulose results in degraded forms of glucose and, as a result, many of the studies have focused on decomposition to monomeric glucose [10, 15]. The degradation of glucose yields furans and related compounds, the most common being 2-furaldehyde (also known as furfural), 5-methyl-2-furaldehyde, 5-hydroxymethyl-2-furaldehyde, 2-acetyl furan, and 2-furfural, where 2-furaldehyde is the most abundant form. The formation mechanisms are explained in detail in [10]. These products are of technical importance in power transformers, as they are partially soluble in oil and can be quantified by using high-performance liquid chromatography as a basis for routine condition monitoring [11-13, 15-17].

2 EXPERIMENTAL

The wide array of molecular species within transformer fluid causes studies with mineral-based fluids to be problematic. As a result, studies were conducted with the paraffinic hydrocarbon, hexadecane, purchased from Chevron Phillips. Hexadecane was selected to provide a relatively pure base fluid (>95 wt.%) with a molecular weight distribution very similar to that of common dielectric fluids used in transformers, as can be seen in the gas chromatography mass spectrometry (GCMS) chromatogram in Figure 2. Hexadecane

![Figure 1. Schematic view of the interior of an oil-immersed transformer [2].](image1)

![Figure 2. Overlay of GCMS chromatograms for Shell Diala transformer oil (green) and n-hexadecane (black). Retention time 0-9 min was omitted, as no compounds were detected for either fluid.](image2)
was degassed at 60°C prior to all ageing experiments to remove as much moisture as possible. The moisture within the fluid was measured with a Doble Moisture-in-Oil sensor. Following heating and degassing, the fluid had a moisture content of 1-3 ppm.

### 2.1 SIMULATED AGEING IMPURITIES

The long term objective of this work is to correlate changes in PD characteristics with loss in the insulating properties of oil/paper as a result of chemical “impurities” introduced by ageing. PD characteristics were therefore correlated with the concentration of naturally occurring degradation products from oil/paper and the electrochemical characteristics of those products. Various chemical additives were employed, the chemical structures of which are shown in Figure 3 and IP of additives with known experimental literature values is shown in Table 1. Solutions of 0.01 mol/l were made by mixing the chemicals into degassed hexadecane with a magnetic stirrer within the test cell without pre-treatment of the additives. This paper presents the variation in PD characteristics for degradation products typical of oxidation in the oil and paper degradation due to overheated cellulose.

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**Figure 3.** Chemical structures and names of the additives used in the simulated ageing experiments.
Table 1. List of additives that have known experimental IP. All values were obtained from [32], except for tert-butanol, which was obtained from [33].

<table>
<thead>
<tr>
<th>Additive</th>
<th>IP (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,3-dimethyl-2-butanone</td>
<td>9.12</td>
</tr>
<tr>
<td>Acetone</td>
<td>9.703</td>
</tr>
<tr>
<td>2-Butanone</td>
<td>9.52</td>
</tr>
<tr>
<td>tert-Butanol</td>
<td>9.90</td>
</tr>
<tr>
<td>Isobutyraldehyde</td>
<td>9.71</td>
</tr>
<tr>
<td>2-Furaldehyde</td>
<td>9.22</td>
</tr>
<tr>
<td>2-Acetylfuran</td>
<td>9.02</td>
</tr>
</tbody>
</table>

2.2 PD MEASUREMENTS

The PD characteristics were measured with the BAUR DTA 100C Breakdown Tester modified to incorporate a conventional PD coupling circuit in accordance to IEC 60270 [34]. The PD was detected and recorded using a digital PD measuring system (Doble Lemke LDS-6). Prior to the measurements, the system including a fluid sample was calibrated with a known pulse charge magnitude, as is necessary for accurate PD measurements. A tungsten needle of 3 cm length, 1 mm diameter, and tip radius of 20 μm was employed. The 5 cm diameter plane electrode consisted of an aluminum electrode with a barrier to preclude needle damaging breakdowns. The needle-plane geometry was installed in a 400 ml test cell with a gap separation of 1 cm from the needle tip to the plane electrode. Figure 4 shows a 2D axisymmetric electric potential contour plot of the test cell with a differential potential of +1 V on the needle and -1 V on the plane electrode, along with the Laplacian electric field distribution at the needle tip as calculated by finite element analysis (FEA).

The test method employed a 60 Hz AC voltage with a rise rate of 0.5 kV/s to 30 kV RMS which was held for 1 minute. Measurements were separated by 2-3 minutes to allow residual space charge to redistribute within the test cell. A total of 20 measurements was conducted for each sample, of which 10 measurements focused on positive and 10 on negative streamers as a result of the large difference in charge magnitudes between the two streamer types. All measured data were recorded, saved, and subsequently exported to ASCII files for analysis.

The Laplacian electric field at the needle tip can be estimated according to Equation (1) [35], where $E_{tip}$ is the electric field at the needle tip, $V$ is the applied voltage, $r$ is the tip radius, and $a$ is the electrode gap separation.

$$E_{tip} = \frac{2V}{r \ln \left( \frac{a}{r} \right)}$$

For our electrode configuration, a 20 μm needle produces a Laplacian electric field of 395 MV/m at 30 kV RMS. Based on FEA, the field at the tip with 30 kV applied is 423 MV/m, which is reasonably close to the estimate provided by Equation (1). The actual (Poisson) field is likely to be lower as a result of space charge effects. The field enhancement is greatest at the needle tip and decreases sharply along the z axis.

3 RESULTS

3.1 IONIZATION POTENTIALS AND ELECTRON AFFINITIES

IP is defined as the energy difference between a cation (N-1) and the neutral molecule (N), while EA is the energy difference between a neutral molecule and an anion (N+1)

$$IP = W(N-1) - W(N)$$

$$EA = W(N) - W(N+1)$$

where, $W$ and $N$ denote the total energy and the number of electrons in the molecule, respectively. The evaluation of IP and EA from the above equations using computational quantum mechanics (DFT) requires two calculations of total molecular energy, one with N and one with N-1 electrons for IP or N+1 electrons for EA, respectively. This method, generally referred to as Delta self-consistent-field (ΔSCF) method, provides a good estimate of IP and EA (typically within a few tenths of an eV) for atoms and molecules [24, 36].

The Density Functional Theory (DFT) calculations were carried out using the Fritz Haber Institute ab initio molecular simulations (FHI-aims) [37] code and the Perdew-Burke-Ernzerhof (PBE) [38] exchange-correlation functional was used. The FHI-aims employs a basis set of numerical atom-centered orbitals (NAO). The standard NAO basis set of tier2 was used consistently throughout the present study for all the atomic species. The atomic coordinates of the molecules (neutral, positively and negatively charged ions) studied here were relaxed until the total energy and the total force converged to better than $10^{-6}$ eV and $10^{-2}$ eV/Å, respectively. The calculations on the cations, anions, and the neutral O$_2$ molecule were carried out using unrestricted open-shell method.

Next, we focus on IP of the molecules in presence of
external electric field. The definition of IP given in Equation (2) cannot be used for a molecule in an external electric field owing to the absence of a proper reference. In other words, the energy of an ion placed in an external electric field depends on the choice of origin. However, both theoretical [24] and experimental [39, 40] evidence demonstrates that the field dependence of the IP can be captured, with sufficient accuracy by assuming the following classical behavior (for the external fields as high as 300 MV/m),

$$ IP = IP_0 - \frac{2e^2}{4\pi\varepsilon_0\alpha_0} \sqrt{\frac{4\pi\varepsilon_0\alpha_0^2 E}{e}} $$

Here, $IP$ and $IP_0$ denote the ionization potentials of a given molecule in presence and absence of the external field, $E$, $\alpha_0$, $\varepsilon_0$, and $e$ represent the Bohr radius, permittivity of vacuum and electronic charge, respectively. As intuition would suggest, a high external electric field reduces the effective IP.

Table 2 shows the results of the DFT computation for zero field IP and EA of a number of small molecules along with experimental values from the literature. Table 1 shows that only a few experimental IP values could be found for a few of the additives utilized in the experiments, and no literature values could be found for EA. As a result, DFT calculations were conducted to determine IP and EA of a few of the molecules (i.e., hexadecane, decanoic acid, and hexadecanol) for which literature experimental values do not exist. Figure 5 shows parity plots for IP and EA calculations to demonstrate that the DFT-based computational method is accurate.

### Table 2. DFT computation results of IP and EA for a number of small molecules compared to their experimental values [32].

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Ionization Potential (eV)</th>
<th>Electron Affinity (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated</td>
<td>Experimental</td>
</tr>
<tr>
<td>2-Butanone</td>
<td>9.20</td>
<td>9.52</td>
</tr>
<tr>
<td>2-Furaldehyde</td>
<td>9.09</td>
<td>9.22</td>
</tr>
<tr>
<td>3,3-Dimethyl-2-butane</td>
<td>8.68</td>
<td>9.12</td>
</tr>
<tr>
<td>Acetone</td>
<td>9.45</td>
<td>9.70</td>
</tr>
<tr>
<td>C3H6</td>
<td>11.23</td>
<td>11.56</td>
</tr>
<tr>
<td>C2H4N</td>
<td>7.64</td>
<td>7.82</td>
</tr>
<tr>
<td>CH2Cl</td>
<td>11.04</td>
<td>11.22</td>
</tr>
<tr>
<td>CH2F</td>
<td>12.20</td>
<td>12.47</td>
</tr>
<tr>
<td>CH2OH</td>
<td>10.42</td>
<td>10.85</td>
</tr>
<tr>
<td>CH4</td>
<td>12.51</td>
<td>12.61</td>
</tr>
<tr>
<td>CO2</td>
<td>13.71</td>
<td>13.77</td>
</tr>
<tr>
<td>HCOOH</td>
<td>11.02</td>
<td>11.33</td>
</tr>
<tr>
<td>iso-Butyraldehyde</td>
<td>9.36</td>
<td>9.71</td>
</tr>
<tr>
<td>NH3</td>
<td>10.20</td>
<td>10.35</td>
</tr>
<tr>
<td>tert-Butanol</td>
<td>9.36</td>
<td>9.90</td>
</tr>
<tr>
<td>O2</td>
<td>12.37</td>
<td>12.07</td>
</tr>
<tr>
<td>N2</td>
<td>15.40</td>
<td>15.58</td>
</tr>
<tr>
<td>F2</td>
<td>15.37</td>
<td>15.70</td>
</tr>
<tr>
<td>CCl4</td>
<td>10.60</td>
<td>11.47</td>
</tr>
<tr>
<td>O3</td>
<td>12.58</td>
<td>12.43</td>
</tr>
<tr>
<td>CF3Br</td>
<td>11.26</td>
<td>11.96</td>
</tr>
<tr>
<td>CF3I</td>
<td>10.28</td>
<td>10.23</td>
</tr>
<tr>
<td>CH3I</td>
<td>9.63</td>
<td>9.54</td>
</tr>
<tr>
<td>I2</td>
<td>9.22</td>
<td>9.31</td>
</tr>
<tr>
<td>IBr</td>
<td>9.68</td>
<td>9.79</td>
</tr>
<tr>
<td>Decanoic Acid</td>
<td>8.61</td>
<td></td>
</tr>
<tr>
<td>Hexadecane</td>
<td>8.30</td>
<td></td>
</tr>
<tr>
<td>Hexadecanol</td>
<td>8.01</td>
<td></td>
</tr>
</tbody>
</table>

3.2 PARTIAL DISCHARGE INCEPTION VOLTAGE

PDIV was determined according to IEC 61294 [41] as the lowest voltage at which PD occurs with an apparent charge magnitude equal to or greater than 100 pC. Figure 6 lists the average values from 20 measurements conducted per sample along with 90% confidence intervals based on a Normal distribution. Hexadecane was measured numerous times as the control fluid, and, as a result, its PDIV is listed as an average value from 110 measurements.

As can be seen in Figure 6, PDIV tends to decrease with the introduction of a known concentration of typical oxidation degradation products. Figure 6 also shows that samples with a known concentration of paper degradation products tend to increase PDIV relative to degassed hexadecane. Based on overlapping of 90% confidence intervals on the means, only
roughly two-thirds of the samples differ at a statistically significant level from the PDIV of hexadecane. The 0.01 mol/l 5-hydroxymethylfuraldehyde sample had a large confidence interval, as the molecule is extremely polar and difficult to dissolve in a non-polar hydrocarbon.

### 3.3 Discharge Repetition Rates

The number of streamers detected above a certain apparent charge magnitude was determined from the ASCII files. Figure 7 shows the average number of positive and negative streamers with 90% confidence intervals for the simulated oxidative degradation and paper degradation products. All samples correspond to an average of 10 measurements, except for hexadecane which is given as an average of 50 measurements.

### 3.4 Phase Resolved PD Patterns

All PRPD pattern plots use the same color scheme as shown in Figure 8. The color corresponds to the number of pulses per AC voltage cycle during the measurement above a set threshold. Figure 9 displays the typical PRPD pattern of hexadecane, which was measured as the control substance. The PD pattern is typical of a needle-plane immersed in a dielectric fluid [42, 43]. Mainly negative streamers are detected during the measurements, as these tend to have high repetition rates. The positive streamers are less frequent but have much larger charge magnitudes (6,000-10,000 pC). The positive streamers are of the same type detected under impulse voltages [43] and the PRPD patterns show a tendency for the pulses to bunch together at the peak of the positive AC waveform, similar to corona discharges in a gaseous medium. The negative streamer discharge characteristics are similar to that of a small void in solid insulation.

Table 3 displays the typical PRPD patterns for a selection of chemicals generated during ageing which cover the main functional groups related to oxidative degradation, i.e., alcohols, aldehydes, ketones, and carboxylic acids, as well as the most abundant paper degradation product (2-furaldehyde). In addition, a few samples with two compounds were included to see which PD characteristics would dominate in a mixture. All PD patterns correspond to the initial measurements, as the effect of space charge from previous measurements was negligible.
Figure 9. Typical PRPD pattern of hexadecane using a 20 µm tungsten needle with the positive streamers (top) and negative streamers (bottom).

From Table 3, we see that the PRPD patterns differ substantially with functional group. Alcohols tend to increase the number of positive and negative streamers in comparison to pure hexadecane. The positive streamers achieve the same maximum apparent charge amplitude (~10,000 pC), yet there are also many smaller positive streamers close to the apparent charge baseline, which is uncharacteristic of positive streamer propagation in dielectric fluids such as hexadecane. The negative streamers have the same bulb-shape PRPD pattern as with hexadecane, but with a substantial increase in pulse rate. Ketones result in similar PD patterns, with an increase in the number of both positive and negative streamers compared to hexadecane. The most fundamental differences in PD patterns occur with carboxylic acids and aldehydes. Acids tend to increase the positive streamer pulse rate, while decreasing the negative streamer pulse rate. Aldehydes also increase the positive streamer pulse rate; however, the major differences are seen in the negative streamer PD pattern, where the pulse rate decreases and the bulb-shape discharge pattern increases in PD magnitude. 5-hydroxymethylfuraldehyde produced interesting results, as the positive and negative streamers had similar apparent charge magnitudes, as is common in solid dielectrics and is uncommon in dielectric fluids. 5-hydroxymethylfuraldehyde is extremely polar and forms a colloidal suspension in hexadecane which acts as a barrier to streamer formation and propagation. Interesting results were also obtained when mixtures were analyzed, as seen in Table 3, which shows that acids tend to dominate the discharge pattern, regardless of their concentration relative to other chemicals present in solution.

4 DISCUSSION

Many theories describing the initiation and propagation of positive streamers in dielectric fluids have been devised in the past. A great deal of computational modeling conducted, which agrees well with experimental data, suggests that filamentary positive streamers initiate once a critical field at the needle electrode has been reached, where electric field dependent molecular ionization creates slow positive ions and fast electrons [20-22]. The highly mobile electrons will either be swept towards the anode or trapped by electronegative species within the fluid to create a region of net positive space charge at the streamer tip. The effect of homocharge, as the electrons are swept away towards the anode, causes an increase in the positive electric field at the tip of the streamer, allowing it to propagate until the voltage drop across the streamer channel is too large to sustain the necessary field at its tip. The fast migration of electrons toward the anode under the influence of the local electric field facilitates impact ionization within the low density streamer channel, causing an electron avalanche to occur. Using the LDS-6 instrument, these Townsend discharges [44] can only be observed when the focus of the PD pattern is drawn to the negative discharges, as their maximum charge magnitude is 40-50 pC so that they cannot be seen at the PD magnitude scale requires for much larger positive streamers. Many of the discharges are buried in the background noise which was 12 pC. The PD pattern from these Townsend discharges within the positive streamer channels is similar to that from a small void in solid insulation, as the gaseous channel volume is fairly stable. The critical field at which positive streamers initiate is usually at or near the peak of the positive AC halfwave and hence, the subsequent Townsend discharges will also occur at that position.

Negative streamers arise from the ability of the cathode to provide seed electrons into the oil. Electrons can penetrate into the liquid, causing vaporization and streamer growth through heating and creation of a microbubble [21, 45-48]. Gas discharges can take place causing local vaporization through inelastic collisions of electrons and the liquid/streamer interface which provides energy input for the bubble to expand. Once the voltage reverses, the bubble eventually detaches from the electrode and moves into the bulk of the liquid [48, 49]. PD in dielectric fluid appear in the form of a train of pulses which have duration of a few µs and are integrated to a single PD event by a narrowband PD detector [50].

The presence of oxidative degradation products in the form of aldehydes, ketones, and especially carboxylic acids, as well as paper degradation products in the form of furans and furanones, can influence streamer activity through increased electronegative oxygen present in the oil. Intuitively, the presence of an electron scavenger should initially suppress the overall pulse rate for negative discharges, as electronegative species will trap electrons to form slow anions and thereby hinder discharge development. This has been shown for a number of electron scavenging additives under impulse voltages [23, 26-28] and also under AC excitation, where 1,1,1-trichloroethane was used as a highly electronegative
Table 3. PRPD patterns generated during the 1 minute recordings at 30 kV<sub>rms</sub> for the positive and negative streamers from several degradation compounds in hexadecane. N/A is given for the negative PRPD pattern of 5-hydroxymethylfuraldehyde because the positive and negative discharges have similar charge magnitude and can, therefore, be displayed in one pattern.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Positive streamer PRPD Pattern at 30 kV</th>
<th>Negative streamer PRPD Pattern at 30 kV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01 mol/l Hexadecanol</td>
<td><img src="image1.png" alt="Graph" /></td>
<td><img src="image2.png" alt="Graph" /></td>
</tr>
<tr>
<td>0.01 mol/l iso-Butyraldehyde</td>
<td><img src="image3.png" alt="Graph" /></td>
<td><img src="image4.png" alt="Graph" /></td>
</tr>
<tr>
<td>0.01 mol/l 2-Butanone</td>
<td><img src="image5.png" alt="Graph" /></td>
<td><img src="image6.png" alt="Graph" /></td>
</tr>
<tr>
<td>0.01 mol/l Lauric Acid</td>
<td><img src="image7.png" alt="Graph" /></td>
<td><img src="image8.png" alt="Graph" /></td>
</tr>
<tr>
<td>0.01 mol/l 2-Furaldehyde</td>
<td><img src="image9.png" alt="Graph" /></td>
<td><img src="image10.png" alt="Graph" /></td>
</tr>
</tbody>
</table>
additive [51]. As the electrons are attached and less are able to diffuse, negative space charge decreases the local electric field, puts the fluid under “tension”, and increases the negative charge density. With increasing negative voltage, a field is reached at which electrons can detach from the negative ions by impact ionization, which results in a large, fast negative streamer as a result of the stored negative charge [26, 27].

### 4.1 IONIZATION POTENTIAL AND ELECTRON AFFINITY

Combining the IP and EA data of Table 2, the discharge repetition rate data of Figure 7, and the PRPD patterns of Table 3 reveals some surprising results. Based on the increase in repetition rate of positive streamers following the introduction of additives in Figure 7, one would assume that the effect of the additives on the PD characteristics was due to lower IP. The DFT calculations reveal that hexadecane has a lower IP than all of the additives measured except for hexadecanol. This suggests that the liquid IP of the additives, which is known to be lower than their gas phase IP [52], is lower than for hexadecane. However liquids with a dielectric constant $\varepsilon_r \approx 2$ decrease the liquid IP by 1.6 eV or ~15% [53], and this does not help to explain the increase in positive streamers caused by the additives, which would have higher dielectric constants due to permanent dipole groups.

The decrease in discharge repetition rate of negative streamers relative to hexadecane from acidic, furanic impurities, and aldehyde impurities suggests that these impurities have positive EA, i.e., the additive readily attaches an electron to form a radical anion and thereby reduces the

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Positive streamer PRPD Pattern at 30 kV</th>
<th>Negative streamer PRPD Pattern at 30 kV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01 mol/l 5-Hydroxymethylfuraldehyde</td>
<td>[Image]</td>
<td>N/A</td>
</tr>
<tr>
<td>0.01 mol/l 2-Butanone + 0.01 mol/l Decanoic Acid</td>
<td>[Image]</td>
<td>[Image]</td>
</tr>
<tr>
<td>0.01 mol/l iso-Butyraldehyde + 0.005 mol/l Docosanoic Acid</td>
<td>[Image]</td>
<td>[Image]</td>
</tr>
<tr>
<td>0.01 mol/l 2-Butanone + 0.01 mol/l iso-Butyraldehyde</td>
<td>[Image]</td>
<td>[Image]</td>
</tr>
</tbody>
</table>
number of negative streamers initiated. The DFT calculations revealed that most additives have negative EA values and, therefore, should not readily attach an electron. The most negative EA value was associated with hexadecane and, along with its low IP, suggests that the base fluid should produce the greatest positive and negative streamer repetition rate due to a decrease in the mean-free path required for impact ionization. However, this does not explain the increase of negative streamers for alcohols and ketones relative to hexadecane. According to the basic molecular parameter of EA, only 2-furaldehyde shows the general trend in conventional wisdom of a positive EA with respect to a decrease in negative streamers when compared to hexadecane. The discharge characteristics of hexadecanol can also be explained well using IP and EA as molecular parameters, owing to the low IP and negative EA value, which results in increased numbers of positive and negative streamers relative to hexadecane.

Although IP and EA are extremely important parameters to consider for the initiation and propagation of streamers, evidently other chemical effects within the fluid take precedence. The DFT computations are for an ideal situation in which a single molecule is in the gas phase with no interactions to neighboring molecules. Although the discharges take place in a low density region within the dielectric fluid, the DFT computations do not include many phenomena which take place in this high temperature, low density region. These may include, but are not limited to, attractive intermolecular forces, such as dipole-dipole interactions, solvent effects, decomposition of the additives within the streamer channels, and the effect of a highly divergent electric field, which was shown in Equation (4) to reduce the effective IP.

4.2 CARBOXYLIC ACIDS AND FURANIC COMPOUNDS

The changes in PD characteristics for carboxylic acids and furanic compounds can be attributed to a high density of electron-negative oxygen and resulting large electron capture cross section. Conjugation within the furanic compounds augments their ability to trap electrons, as shown in Figure 10 and indicated by the positive EA of 2-furaldehyde (0.238 eV). DFT computations indicate that carbonyl and conjugated double bonds create deeper traps for electrons than hydroxyl or non-conjugated double and triple bonds [54]. Since most oxidative and paper degradation products have permanent dipole groups, attractive intermolecular forces will cause formation of clusters. The clusters will remain soluble as the long chain non-polar alkane tails interact well with non-polar hexadecane. Likewise, carboxylic acids hydrogen bond which creates clusters with many electron-negative oxygen atoms in close proximity, further increasing the electron capture cross section as shown in Figure 10. As a result, negative streamer propagation is hindered by the electron capture cross section [27], even though EA of the impurity molecule is negative and intuitively less likely to capture an electron. This can be seen in the substantial decrease in negative streamers initiated in the presence of carboxylic acids which have negative EA, compared to the furanic compounds which have positive EA. A similar effect was seen in [51], where 1,1,1-trichloroethane was used as an additive within hexadecane and displayed similar negative discharge characteristics to carboxylic acids due to a large electron capture cross section of the chlorine atoms and despite an experimental EA value of -0.42 eV. At increasing acid concentrations, the negative streamers tend to become faster and more filamentary; hence, their charge magnitudes become comparable with those of positive streamers [51]. This is shown in Figure 11 for a solution of 0.07 mol/l decanoic acid, a 7-fold increase in concentration compared to the solutions in Table 3, which correlates to a 7-fold increase in charge magnitude of the negative streamers. At high electric fields, traps lead to conduction by trap assisted tunneling or hopping conduction [55, 56]. Filled traps or areas of higher electron affinity can provide seed electrons necessary for electron avalanches to initiate, as an anion has a low ionization potential.

An increase in negatively charged species within the oil creates a field enhancement upon polarity reversal to the positive halfwave, especially if slow positive ions, which have a typical mobility value of 10⁻⁹ m²/Vs [57], are close to the needle tip. The resulting enhanced field at the needle tip promotes greater numbers of positive streamers to initiate. Although positive streamers are fast and filamentary in contrast to the slow and bushy negative streamers, branching...
occurs as determined by optical methods such as Schlieren photography, which indicate that positive streamers tend to propagate over the range of 45-60° from the axis of symmetry (2D axisymmetric geometry) [26-28, 58]. Data analysis of the ASCII files from the PD detection system indicate that many positive streamers can occur in the same voltage half cycle at phase intervals in the range of 0.1°-0.5°, which corresponds to a time difference of 4.63-23.1 μs, and probably results from branching. Additional small branches are likely to spread out from the main filament; however, they become integrated to a single PD event by the integration time of the PD detector (~10 μs) [59]. In general, two main branches emanating from the anode during the positive AC halfwave seems more common than one filamentary streamer. Increased electronegative oxygen within the fluid caused positive streamers to become more filamentary, with a greater fraction of single streamers per half cycle as determined by the positive streamer distribution in the ASCII files.

4.3 ALDEHYDES

The change in PD characteristics after the addition of iso-butyraldehyde cannot be described by conjugation effects. However, the absence of a large side chain in aldehydes does allow attractive intermolecular forces to cluster the permanent dipoles more efficiently due to less restricting steric effects of neighboring molecules. Therefore, a greater number of electronegative oxygen atoms are in close proximity, which has the effect of creating a large electron capture cross section. This could explain the significant reduction in the number of negative discharges detected relative to hexadecane, as more electrons are captured to form slow anions, even though iso-butyraldehyde also has a negative EA value based on DFT computations.

Another possibility is that during the PD experiments, a Norrish type I fragmentation occurs, which is a photochemical reaction that cleaves the iso-butyraldehyde to form an acyl radical. The hydrogen can be abstracted very easily by a streamer, and absorption of a photon will convert the aldehyde into a photoactivated species in its singlet or triplet excited state through intersystem crossing [60]. DGA was conducted to determine that 4900 ppm of oxygen was present within the oil following heating and degassing. This oxygen entered the fluid during the transfer of the fluid from the vacuum flask to a syringe for DGA analysis and, therefore, a similar oxygen concentration was probably present during the PD measurements. As the polar oxygen tends to be in the same vicinity as the aldehyde and is an extremely reactive diradical, it could readily react with the acyl radical to form carboxylic acids or esters as shown in the reaction mechanism in Figure 12. Hence, the PD characteristics suggest a tendency to form carboxylic acids or esters during the PD experiments, based on the significant decrease in negative streamer repetition rate relative to hexadecane and the characteristic negative streamer PD pattern. This hypothesis was reinforced by GCMS analysis of the fluid following the measurements, which detected trace amounts of high electron capture cross section species. This tends to confirm the importance of electronegative species, even at trace concentrations. The chromatogram is shown in Figure 13, and the structure of the compounds detected are shown in Figure 14. These compounds have the ability to hydrogen bond and should, therefore, show a similar behavior to carboxylic acids.

4.4 ALCOHOLS AND KETONES

Alcohols and ketones cannot undergo conjugation effects as were seen with the furanic compounds, and lacking a large electron capture cross section as for carboxylic acids, they should not affect the negative streamer repetition rate. The effect of the attractive intermolecular forces will be less in ketones due to steric hindrance of the side chains with neighboring molecules within the fluid. However, the presence of electronegative oxygen in close proximity, especially
through hydrogen bonding with alcohols in conjunction with the IP data of Table 2 suggest that the number of negative streamers should decrease. In addition, the number of positive streamers should increase due to the field enhancement upon reversal of the voltage polarity to the positive halfwave created by increased presence of electronegative oxygen. According to our measured data, only the latter statement is confirmed. This further emphasizes the important effect of a large electron capture cross section. At a fixed concentration of 0.01 mol/l for the additives, dramatic reduction in the negative streamer repetition rate was observed only for the carboxylic acids, furanic compounds, and aldehydes, even though ketones also tend to form deep traps for electron capture [52]. The increased number of positive streamers has an indirect effect on the number of negative streamers initiated. As was mentioned above, a positive streamer will collapse into microbubbles once the voltage drop across the streamer channel is too large to sustain the necessary electric field at the streamer tip. Upon polarity reversal, a region of low density fluid is present in which negative discharges can take place, and this promotes negative pulse bursts. Therefore, even if the IP of alcohols or ketones is higher than the base fluid, an increase in positive streamers will create the conditions for negative pulse bursts upon polarity reversal. Figure 15 shows an oscilloscope screen shot that demonstrates the phenomenon. Following a positive pulse, there was a short burst of a greater number of negative pulses in the subsequent negative halfwave relative to the preceding one.

5 CONCLUSION

Conventional PD detector has been used to measure the variation in PD characteristics among samples with known concentrations of naturally occurring oxidative and paper degradation products. IP and EA are extremely important parameters for the initiation and propagation of streamers, especially as related to the mean-free path for impact ionization and the tendency for molecules to trap electrons to form anion radicals. However, comparison of IP and EA computed using DFT with the PD characteristics of hexadecane with additives indicates that these two molecular parameters do not govern the discharge processes. A negative EA value does not assure increased initiation of negative streamers, as intuition would suggest. The presence of electronegative oxygen within the base fluid appears to govern the discharge characteristics. The critical field necessary for positive streamer initiation is decreased due to field enhancements caused by anions based on electronegative oxygen within the system, which promotes negative streamer pulse bursts and an increase in negative streamer initiation even following addition of a higher IP additive relative to the base fluid. Furanic compounds can undergo conjugation effects to trap and delocalize free electrons and, hence exhibit positive EA values. Hydrogen bonding within carboxylic acids decreases the number of negative streamers initiated by increasing the electron capture cross section, as acids tend to have negative EA values. A strongly oxidized sample contains a large concentration of permanent dipole impurity compounds, which form soluble agglomerations within a non-polar hydrocarbon. A greater concentration of anions decreases the overall number of streamers; however, when subjected to a high electric field, the anions enhance high field trap-assisted tunneling or hopping conduction to form filamentary negative streamers. In addition, positive streamers become more filamentary in the presence of anions.

Further research needs be conducted on the effects of aromatic and corrosive sulfur compounds in hexadecane to understand the effect of the chemical composition on the discharge characteristics within insulating fluids.

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7 REFERENCES


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