"BEHAVIOUR OF INSULATING LIQUIDS SUBJECTED TO HIGH ELECTRICAL FIELDS"

by

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Thesis presented for a degree of Doctor of Philosophy
in the Faculty of Engineering of the University of London.

December 1967.
Abstract of Thesis

The effect of applying high electrical stresses to liquid paraffin and transformer oil with fluorescent compounds in solution was investigated under various experimental conditions to allow the conduction and associated electroluminescence phenomena to be observed.

The samples were highly degassed to minimise the possibility of oxygen quenching processes, electroluminescence in the stressed region of the gap being observed particularly in the anode region.

The conduction current and electroluminescence signals were recorded during each experiment to allow stress conditioning and breakdown effects to be studied. The cross-correlation between, and the magnitude of, the two signals was observed to increase in the period of electrical stressing following a breakdown, the cross-correlation effect becoming more marked as the number of breakdowns increased.

Breakdown of the sample was found to result in the formation of thin wax layers on the electrodes, the latter being accompanied by an increase in the breakdown strength of the gap. The thickness of the anode coating was always greater than that on the cathode, and was found to be in keeping with the total breakdown energy in the sample calculated by reference to the test recording.

The electroluminescence signal was strongly current dependent, logarithmic plots extending over five decades yielded approximately linear characteristics. Little or no gap dependence being observed.
Ultra-violet absorption and emission spectra were obtained from each of the samples before and after testing. No effects attributable to spectral electrical testing were detected. The data was then used to modify the electroluminescence characteristics in an attempt to compensate for the optical characteristics of the sample. The modified characteristics, thought to represent the electrical excitation processes producing electroluminescence were then used with the electrode coating data to discuss the conduction current characteristics.
## Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract of Thesis</td>
<td>11</td>
</tr>
<tr>
<td>1. Introduction and summary</td>
<td>1</td>
</tr>
<tr>
<td>2. Review of previous work</td>
<td>6</td>
</tr>
<tr>
<td>2.1. Summary</td>
<td>6</td>
</tr>
<tr>
<td>2.1.1. General</td>
<td>9</td>
</tr>
<tr>
<td>2.2. Electrical breakdown phenomena</td>
<td>9</td>
</tr>
<tr>
<td>2.2.1. Electrode materials and coatings</td>
<td>12</td>
</tr>
<tr>
<td>2.3. Conduction current phenomena</td>
<td>15</td>
</tr>
<tr>
<td>2.3.1. Effect of electrode coatings</td>
<td>16</td>
</tr>
<tr>
<td>2.3.2. Gap dependence</td>
<td>17</td>
</tr>
<tr>
<td>2.3.3. Additive effects</td>
<td>19</td>
</tr>
<tr>
<td>2.3.4. Pressure dependence</td>
<td>19</td>
</tr>
<tr>
<td>2.3.5. Liquid motion</td>
<td>20</td>
</tr>
<tr>
<td>2.3.6. Effect of temperature</td>
<td>21</td>
</tr>
<tr>
<td>2.4. Conduction current fluctuations</td>
<td>22</td>
</tr>
<tr>
<td>2.4.1. Analysis of conduction current fluctuations</td>
<td>24</td>
</tr>
<tr>
<td>2.4.2. Effects of additives and temperature on pulse activity</td>
<td>26</td>
</tr>
<tr>
<td>2.5. Gas evolution in liquids under stress</td>
<td>27</td>
</tr>
<tr>
<td>2.6. Miscellaneous</td>
<td>29</td>
</tr>
<tr>
<td>2.7. Electroluminescence</td>
<td>30</td>
</tr>
<tr>
<td>2.7.1. Electroluminescence in organic liquids</td>
<td>31</td>
</tr>
<tr>
<td>2.7.2. Light pulses</td>
<td>33</td>
</tr>
<tr>
<td>2.7.3. Pre-breakdown light emission</td>
<td>35</td>
</tr>
<tr>
<td>2.7.4. Electroluminescence with steady d.c. fields</td>
<td>36</td>
</tr>
<tr>
<td>2.7.5. Effect of fluorescent additives</td>
<td>38</td>
</tr>
</tbody>
</table>
2.7.6. Electroluminescence spectra 39
2.7.7. Correlation between the conduction current and electroluminescence signals 42
2.7.8. Effect of dissolved gas on electroluminescence 45
2.8. Fluorescence phenomena 47
2.8.1. Basic processes 47
2.8.2. Fluorescent materials 50
2.8.3. Quenching effects 51
2.8.4. Effect of change of state and molecular size 53
3. Experimental apparatus and test procedure 55
3.1. Introduction 55
3.1.1. The high voltage supply 55
3.1.2. Diverter unit 57
3.1.3. Measurement and recording of the conduction current and electroluminescence signals 59
3.1.4. Detection of electroluminescence 60
3.1.4.1. Photomultiplier details 60
3.1.4.2. Photomultiplier high voltage supply and potential divider 62
3.1.4.3. Anode current characteristics 64
3.1.5. Visible observation of electroluminescence 66
3.1.6. Spurious light output 67
3.1.7. Determination of spectra 69
3.2. The oil purification system 70
3.3. Vacuum system 74
3.4. The test cell 77
3.5. Measurement and observation of the electrode spacing 79
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.6</td>
<td>The gas system</td>
<td>81</td>
</tr>
<tr>
<td>3.7</td>
<td>Preparation of electrodes</td>
<td>82</td>
</tr>
<tr>
<td>3.8</td>
<td>Cleaning the liquid system and the test cell</td>
<td>83</td>
</tr>
<tr>
<td>3.9</td>
<td>Preparation of the test liquids</td>
<td>87</td>
</tr>
<tr>
<td>3.10</td>
<td>Degassing the sample</td>
<td>88</td>
</tr>
<tr>
<td>3.11</td>
<td>Test procedure</td>
<td>91</td>
</tr>
<tr>
<td>3.12</td>
<td>Gap settings and electrical stress range</td>
<td>91</td>
</tr>
<tr>
<td>4.</td>
<td>Experimental results</td>
<td>93</td>
</tr>
<tr>
<td>4.1</td>
<td>Introduction</td>
<td>93</td>
</tr>
<tr>
<td>4.1.1</td>
<td>Phenomena noted during the preliminary tests</td>
<td>93</td>
</tr>
<tr>
<td>4.1.1.1</td>
<td>Particle activity</td>
<td>93</td>
</tr>
<tr>
<td>4.1.1.2</td>
<td>Wax formation on electrodes</td>
<td>94</td>
</tr>
<tr>
<td>4.1.1.3</td>
<td>Effect of prolonged stressing of sample on the electroluminescence</td>
<td>94</td>
</tr>
<tr>
<td>4.1.1.4</td>
<td>Use of soda glass filter</td>
<td>96</td>
</tr>
<tr>
<td>4.1.1.5</td>
<td>Conduction current characteristics under repeated stress cycling conditions</td>
<td>96</td>
</tr>
<tr>
<td>4.1.1.6</td>
<td>Photomultiplier anode current pulses</td>
<td>96</td>
</tr>
<tr>
<td>4.1.2</td>
<td>Stress conditioning</td>
<td>100</td>
</tr>
<tr>
<td>4.1.3</td>
<td>Stress cycling</td>
<td>100</td>
</tr>
<tr>
<td>4.2</td>
<td>Tests using neat liquid paraffin</td>
<td>101</td>
</tr>
<tr>
<td>4.2.1</td>
<td>General</td>
<td>101</td>
</tr>
<tr>
<td>4.2.2</td>
<td>Conduction current - stress characteristics</td>
<td>102</td>
</tr>
<tr>
<td>4.2.3</td>
<td>Electroluminescence - conduction current characteristics</td>
<td>108</td>
</tr>
<tr>
<td>4.2.4</td>
<td>Electroluminescence - stress characteristics</td>
<td>115</td>
</tr>
<tr>
<td>4.2.5</td>
<td>Visible observation of electroluminescence</td>
<td>115</td>
</tr>
</tbody>
</table>
4.2.6. Recorded fluctuations of electroluminescence and conduction current
4.2.7. Liquid paraffin spectra
4.2.8. Summary of liquid paraffin results
4.3. Tests on 1-methyl-naphthalene and liquid paraffin mixtures
4.3.1. General
4.3.2. Test on 0.01% by volume methyl-naphthalene in liquid paraffin
4.3.2.1. Stress conditioning
4.3.2.2. Conduction current - stress characteristics
4.3.2.3. Inspection of electrodes
4.3.2.4. Visual observation of electroluminescence
4.3.2.5. Electroluminescence - conduction current characteristics
4.3.3. Tests on 1% by volume 1-methyl-naphthalene in liquid paraffin
4.3.3.1. Sample 'a'
4.3.3.2. Sample 'b'
4.3.4. Test on neat methyl-naphthalene
4.3.4.1. Stress conditioning
4.3.4.2. Conduction current - stress characteristics
4.3.4.3. Electroluminescence - conduction current characteristics
4.3.4.4. Visual observation of electroluminescence
4.3.5. Inspection of electrodes
4.3.5.1. General
4.3.5.2. 0.01% by vol.methyl-naphthalene in liquid paraffin

Page no.
117
119
127
130
130
131
131
136
136
136
139
139
141
144
144
146
146
149
151
152
152
4.3.5.3. Spectra for 1% by vol. methyl-naphthalene in liquid paraffin

4.3.5.4. Neat methyl-naphthalene spectra

4.3.6. Summary of methyl-naphthalene results

4.4. Tests using anthracene in liquid paraffin

4.4.1. General

4.4.2. Test on 5 x10^{-6} M/100g anthracene in liquid paraffin

4.4.2.1. Stress conditioning

4.4.2.2. Conduction current - stress characteristics

4.4.2.3. Electroluminescence - conduction current characteristics

4.4.2.4. Visual observation of electroluminescence

4.4.2.5. Inspection of electrodes

4.4.3. Test on 1 x10^{-4} M/100g anthracene in liquid paraffin

4.4.3.1. Stress conditioning

4.4.3.2. Conduction current - stress characteristics

4.4.3.3. Electroluminescence - conduction current characteristics

4.4.3.4. Visible observation of electroluminescence and illuminated gap

4.4.3.5. Inspection of electrodes and irradiation with ultra-violet light

4.4.4. Spectra

4.4.4.1. 5 x10^{-6} M/100g anthracene in liquid paraffin

4.4.4.2. 1 x10^{-4} M/100g anthracene in liquid paraffin

4.4.5. Summary of test results

4.5. Tests with Popop in liquid paraffin

4.5.1. General

4.5.2. Test using 2 x10^{-7} M/100g Popop in liquid paraffin
<table>
<thead>
<tr>
<th>Section</th>
<th>Description</th>
<th>Page no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5.2.1</td>
<td>Stress conditioning</td>
<td>185</td>
</tr>
<tr>
<td>4.5.2.2</td>
<td>Conduction current characteristics</td>
<td>185</td>
</tr>
<tr>
<td>4.5.2.3</td>
<td>Electroluminescence - conduction current characteristics</td>
<td>187</td>
</tr>
<tr>
<td>4.5.2.4</td>
<td>Visual observation of electroluminescence</td>
<td>187</td>
</tr>
<tr>
<td>4.5.2.5</td>
<td>Inspection of electrodes</td>
<td>190</td>
</tr>
<tr>
<td>4.5.3</td>
<td>Test using $2 \times 10^{-6}$M/100g Popop in liquid paraffin</td>
<td>190</td>
</tr>
<tr>
<td>4.5.3.1</td>
<td>Stress conditioning</td>
<td>190</td>
</tr>
<tr>
<td>4.5.3.2</td>
<td>Conduction current - stress characteristics</td>
<td>191</td>
</tr>
<tr>
<td>4.5.3.3</td>
<td>Electroluminescence - conduction current characteristics</td>
<td>194</td>
</tr>
<tr>
<td>4.5.3.4</td>
<td>Visual observation of the electroluminescence</td>
<td>194</td>
</tr>
<tr>
<td>4.5.3.5</td>
<td>Inspection of electrodes</td>
<td>197</td>
</tr>
<tr>
<td>4.5.4</td>
<td>Test using $2 \times 10^{-5}$M/100g Popop in liquid paraffin</td>
<td>197</td>
</tr>
<tr>
<td>4.5.4.1</td>
<td>Stress conditioning</td>
<td>197</td>
</tr>
<tr>
<td>4.5.4.2</td>
<td>Conduction current characteristics</td>
<td>198</td>
</tr>
<tr>
<td>4.5.4.3</td>
<td>Electroluminescence - current characteristics</td>
<td>198</td>
</tr>
<tr>
<td>4.5.4.4</td>
<td>Visual observation of electroluminescence</td>
<td>200</td>
</tr>
<tr>
<td>4.5.4.5</td>
<td>Inspection of electrodes</td>
<td>200</td>
</tr>
<tr>
<td>4.5.5</td>
<td>Spectra</td>
<td>202</td>
</tr>
<tr>
<td>4.5.5.1</td>
<td>$2 \times 10^{-7}$M/100g Popop in liquid paraffin</td>
<td>202</td>
</tr>
<tr>
<td>4.5.5.2</td>
<td>$2 \times 10^{-6}$M/100g Popop in liquid paraffin</td>
<td>204</td>
</tr>
<tr>
<td>4.5.5.3</td>
<td>$2 \times 10^{-5}$M/100g Popop in liquid paraffin</td>
<td>208</td>
</tr>
<tr>
<td>4.5.6</td>
<td>Summary of test results for Popop solutions</td>
<td>209</td>
</tr>
<tr>
<td>4.6</td>
<td>Test on transformer oil</td>
<td>211</td>
</tr>
<tr>
<td>4.6.1</td>
<td>General</td>
<td>211</td>
</tr>
<tr>
<td>4.6.2</td>
<td>Test on degassed transformer oil</td>
<td>213</td>
</tr>
<tr>
<td>Section</td>
<td>Title</td>
<td>Page no.</td>
</tr>
<tr>
<td>---------</td>
<td>----------------------------------------------------------------------</td>
<td>----------</td>
</tr>
<tr>
<td>4.6.2.1</td>
<td>Stress conditioning</td>
<td>213</td>
</tr>
<tr>
<td>4.6.2.2</td>
<td>Conduction current - stress characteristics</td>
<td>213</td>
</tr>
<tr>
<td>4.6.2.3</td>
<td>Electroluminescence - conduction current characteristics</td>
<td>215</td>
</tr>
<tr>
<td>4.6.2.4</td>
<td>Visual observations of electroluminescence and the illuminated gap</td>
<td>215</td>
</tr>
<tr>
<td>4.6.2.5</td>
<td>Inspection of electrodes</td>
<td>218</td>
</tr>
<tr>
<td>4.6.3</td>
<td>Spectra</td>
<td>218</td>
</tr>
<tr>
<td>4.6.2</td>
<td>Summary of results</td>
<td>221</td>
</tr>
<tr>
<td>4.7</td>
<td>Use of transformer oil as a solvent</td>
<td>223</td>
</tr>
<tr>
<td>5.</td>
<td>Discussion of results</td>
<td>224</td>
</tr>
<tr>
<td>5.1</td>
<td>Stress conditioning</td>
<td>224</td>
</tr>
<tr>
<td>5.2</td>
<td>Breakdown deposits</td>
<td>225</td>
</tr>
<tr>
<td>5.3</td>
<td>Effect of aromatics on wax deposits</td>
<td>227</td>
</tr>
<tr>
<td>5.4</td>
<td>Cathode effects</td>
<td>228</td>
</tr>
<tr>
<td>5.5</td>
<td>Phenomena in the cathode region</td>
<td>229</td>
</tr>
<tr>
<td>5.6</td>
<td>Anode effects</td>
<td>231</td>
</tr>
<tr>
<td>5.7</td>
<td>Inter dependence of anode and cathode processes</td>
<td>232</td>
</tr>
<tr>
<td>5.8</td>
<td>Bulk effects and gap dependence</td>
<td>233</td>
</tr>
<tr>
<td>5.9</td>
<td>Stress effects</td>
<td>233</td>
</tr>
<tr>
<td>5.10</td>
<td>Electroluminescence phenomena</td>
<td>235</td>
</tr>
<tr>
<td>5.11</td>
<td>Electrode coatings</td>
<td>242</td>
</tr>
<tr>
<td>5.12</td>
<td>The effect of electrode coatings</td>
<td>244</td>
</tr>
<tr>
<td>5.13</td>
<td>Electroluminescence processes</td>
<td>250</td>
</tr>
<tr>
<td>5.14</td>
<td>Effect of additives</td>
<td>252</td>
</tr>
<tr>
<td>5.15</td>
<td>Miscellaneous</td>
<td>254</td>
</tr>
<tr>
<td>5.16</td>
<td>Conclusions</td>
<td>256</td>
</tr>
</tbody>
</table>
5.17. Suggestions for future work 257
Appendix A - Preparation of new glassware used in tests 260
Appendix B - Physical properties of test liquids 261
Appendix C - Relative values of irradiation intensities 262
Appendix D - Reprint of Nature, 201, 1219, 1966 263
Acknowledgments 264
References 265
1. INTRODUCTION AND SUMMARY

This thesis forms part of a research programme undertaken in the liquid dielectrics laboratory of the Electrical Engineering department of the University of Surrey (formerly Battersea College of Technology).

The main object of the work was to investigate the relationship between conduction current and electroluminescence in stressed liquid dielectrics. The phenomenon was first observed by Darveniza (19) and later by Gosling (18) whose measurements suggested the possibility of a correlation between conduction current and electroluminescence intensity.

Although Darveniza obtained a graph relating current and electroluminescence over a range of about one decade, he did not measure the two quantities simultaneously. He derived the relationship from separate measurements of current against stress and electroluminescence against stress.

The manner in which the properties of liquid insulants are affected by dissolved gas, moisture, impurities etc. was not sufficiently appreciated by early workers in this field. In this work considerable attention has been paid to the techniques of preparing and testing of samples.

Electroluminescence may be a function of the solvent or of the solute, or of both. To investigate this various fluorescent solutes were used, dissolved either in transformer oil or in liquid paraffin. Both liquids have a low vapour pressure which allows a high degree of degassing to be achieved, and both are used in practice as insulators.
The experimental technique used in the tests was based on that originally due to Gosling (18) and developed by Angerer (22), Nossier and Megahed (26,27).

The sample was first pre-filtered and roughly degassed before degassing in the test apparatus.

The degassing treatment was continued for eight to ten days until the pressure that could be maintained over the liquid with the flask sealed approached the liquid vapour pressure. During this time the test cell and filtering system were thoroughly degassed to outgas the electrodes and prevent oxidisation.

After degassing the liquid was passed through a 1µm pore size filter and kept overnight in the test cell prior to electrical testing.

Each electrical test commenced with a stress conditioning period lasting about two hours. This was followed by the stress cycling procedure during which the conduction current and electroluminescence characteristics were generated. The nominal stress in the gap was varied in 100 kV/cm steps to produce several complete cycles in the characteristics for each gap setting. The range of stress available was limited by the onset of particle activity at stresses below 300 kV/cm and the breakdown strength of the liquid at high stresses. In most tests it was found necessary to spend an appreciable proportion of the time spent during the stress cycling period at the higher stresses to enable the electroluminescence phenomena to be observed.

The electroluminescence was measured by a photomultiplier followed by an amplifier whose output was fed to a pen recorder. The
potential drop across a small resistance in series with the specimen was amplified and applied to a second pen on the same recorder. The correlation between electroluminescence and current could then be measured directly.

In general the correlation between the electroluminescence and conduction current was found to increase steadily in the period of electrical stressing following a breakdown and as a number of breakdowns in the liquid increased. It was found that thin layers of wax formed on electrodes after the occurrence of a breakdown. The breakdown strength of the gap was often found to be increased by the presence of a wax deposit. The anode layer was always found to be thicker than that on the cathode.

The conduction current and electroluminescence for a given nominal stress also increased in value as the number of breakdowns and the thickness of the wax layers increased.

Conduction current/stress gap dependence effects were often complicated by the incidence of high stress breakdowns at the end of the test at the previous gap setting. However in general it was found that when thick coatings were present on the electrodes the conduction current increased with reduced gap setting suggesting that recombination processes exist in the liquid bulk.

The electroluminescence was found to be strongly current dependent, the logarithm of the electroluminescence plotted against the logarithm of the conduction current giving an approximately straight
line characteristic over four or five decades. The relative positions of these characteristics were affected by breakdown and occasionally a permanent shift in the characteristics would result for no obvious reason. The visual observation of electrode electroluminescence and the presence of wax layers on the electrodes strongly suggests that the above characteristics are affected by the existence of electrode interface phenomena.

The electroluminescence signal was observed to consist of a series of discrete pulses. However due to amplitude distributions introduced by the emission processes in the photomultiplier it was not possible to say that the pulses were entirely due to molecular events nor to eliminate the possibility of micro-discharges at the electrode coatings.

The absorption and emission spectra of the liquids was measured and it was confirmed that the colour and intensity of the electroluminescence were consistent with these properties of the liquid. Liquid paraffin was used in preference to transformer oil for most of the tests due to its superior optical properties.

There are several theories as to the mechanism of breakdown and conduction in liquids. It is possible that particle motion, ionisation, and bubble formation all play a part. In the review of previous work the author has not attempted to favour any particular point of view; the present work in fact suggests that electrode layers are a possible explanation of some phenomena.
In a field in which conflicting views exist it is as important not to suppress information as to give information. For this reason the results given include data which was recorded but has not been further used in this thesis. Such data may be of value to later workers in the field.
2. REVIEW OF PREVIOUS WORK

2.1. Summary

The work reviewed in this Section has been collated under the respective headings of breakdown, conduction and electroluminescence phenomena under high stress conditions.

The above phenomena can occur in a liquid insulant for a variety of reasons most of which have little connection with the intrinsic properties of the insulant. Water or its vapour, dissolved gas, vapour bubbles and solid impurities and particles are always present to some degree and are difficult to remove. Therefore it is not surprising that many of the proposed mechanisms involve non-intrinsic factors in addition to properties intrinsic to the insulant.

The following paragraphs summarise aspects of the work covered in the review and are accompanied by the pertinent references.

Breakdown phenomena

Bridge formation of particles at medium stresses has been reported (24) and the initiation of breakdown at higher stresses due to particle activity (18,25-27,31,34). Breakdown initiation in gassy liquids due to the presence of vapour or gas bubbles has been proposed (18-20,30,61) whilst electron trapping mechanisms are suggested to account for the increase in breakdown strength with low gas contents (29 – 31). Pressure dependence effects have been found to support the foregoing (15,16,30,32-35).

Attempts to relate the breakdown strength with molecular size have been made but no simple picture has emerged (10,11,14).
Gas evolution due to high energy electrons (30) and vapourisation of the liquid (34,35) have been proposed as basic initiating processes leading to breakdown. Hydrogenation of aromatic constituents account for the increased strength of transformer oil (18,22,26,27,30).

Electrode surface conditions including oxidisation, electrode material and gas absorption have been studied (8,13-15,18,20,36-39,44) and space charge effects suggested (45). Reduced work function effects (40,44) and the existence of wax coatings (28, 43, 45) have been noted. It is generally agreed that space charge layers exist and that electron emission occurs.

**Conduction current phenomena**

The production of charge carriers in the liquid by various mechanisms has been proposed as follows: Schottky emission (46,52,61, 63,64), field emission (53), combination of both (54); dissociation of liquid molecules (55), of impurities (59,60); by ionic impurities (61).

Many workers have reported a reduction in the effective work function (5,44,56-59,62-64,84). The formation of ion sheaths at each electrode over insulating layers has been suggested (62,65). Gap dependent charge multiplication processes have been investigated by various workers (52,57,58,63,65,67) without positive evidence, though it is suggested that it might occur at stresses about 1,500 kV/cm (52).

The increased conduction current when gas is present in small quantities has generally been associated with electron trapping mechanisms resulting in the formation of negative ions (5,18,22,25-27).

Many investigators have studied temperature effects and the
variation in conduction current attributed to changes in; gas solubility (25-27,88), electrode work function (54), and viscosity (27,54,59,61,79,90).

Most workers report conditioning effects (18-23,25-31,52,61,68,79-82) and the existence of conduction current fluctuations (18-27,31,34,46,52,54,61,68,79-83,85,88), gas evolution, hydrogenation and wax formation under high stress conditions have also been reported (43,92,93,96,97,122).

Electroluminescence

This subject has not been studied as extensively as those of breakdown and conduction, most observations being incidental to the investigation in hand.

Electroluminescent spots have been noted by most workers (107-113,115,119) these usually occur on the cathode and are generally attributed to the existence of electron energies exceeding 3 eV.

Discrete pulses of light have been noted (113,115,116,119) and some correlation with the conduction current observed (115,116,119). Ionisation and recombination processes have also been proposed (113,115). Pre-breakdown pulses have also been detected (115,117) the speed of propagation into the gap and the wavelength of the emitted light suggesting a purely electronic mechanism.

Electroluminescence—current—stress characteristics extending over approximately one decade have been obtained (114,120) using steady d.c. fields and dissimilar spectra of the emitted light published (113,114).

Dissolved O₂ was found to quench the electroluminescence (18,124) and effect the intensity distribution in the gap. This distribution appears to comprise both electrode and bulk liquid effects (18,19,51,114,116,118,124).
2.1.1. **General**

The phenomena occurring in insulating dielectric liquids have been studied for a considerable period of time during which a number of reviews of the previous work have been published summarising the results obtained by the many workers in the field. Whitehead (1) and Gemant (2) reviewed the work up to 1933 and Lewis (3), Watson and Shaughnaugh (4) have given summaries of work up to 1961. Shorter reviews (5-9) by other workers have become available more recently.

The following paragraphs of this Section are concerned with introducing previous work felt to be relevant to the experimental observations of Section 4.

2.2. **Electrical breakdown phenomena**

The electrical strength of pure hydrocarbon liquids has been the subject of many experimental investigations. Attempts have been made to correlate the electrical strength of the liquid with its molecular structure (10,11 and 14). For pure hydrocarbon liquids Lewis and Shaughnaugh have suggested that the breakdown strength increases with the chain length.

Almost all dielectric liquids such as hexane, benzene, commercial oils and liquified gases, under both direct and impulse voltage conditions show an increase in breakdown strength as the gap is reduced (14-18,37 and 38). This effect is more pronounced at electrode spacings less than 50μ.

Using direct voltages Darveniza (19) and Khambanonda (20), and Hancox (21) with impulses found no gap dependence for transformer oil. Gosling (18) found that with degassed liquids the breakdown voltage against gap setting
characteristics passed through the origin, whilst for liquids with gas in solution an apparent intercept was obtained for zero gap setting. This intercept increased with gas content and he concluded that a surface layer was formed on the electrode when gas was present in the liquid.

A similar effect was observed by Angerer (22,23) using transformer oil and liquid paraffin with oxidised organic additives in solution.

Tropper (30) has recently given a resume of the experimental observations made under his supervision over a number of years, regarding the effect of dissolved gasses and hydrostatic pressure on the electrical conduction and breakdown of transformer oil. His results for the effect of low and high gas contents are shown in Figs. 1 and 2 respectively. The increase in breakdown voltage for small amounts of dissolved air is attributed to electron trapping by $O_2$ molecules and the subsequent decrease for larger gas contents is explained by the greater ease of micro bubble formation with the suspended impurities forming nucleation sites.

The effect of hydrostatic pressure on breakdown strength has been investigated by many workers and is important since it serves to indicate the presence of a vapour or gaseous phase in the breakdown mechanism.

Watson and Higham (16 & 32) found a pressure dependence immediately above atmospheric pressure which led them to suggest a breakdown mechanism involving cavitation and bubble formation. A strong pressure dependence under impulse conditions was also reported by Kao and Higham (33) and Eldine and Tropper (15). Gosling found little or no pressure dependence for degassed oil and a dependence with gas in solution.

It has been suggested by Tropper (30) that the electroluminescence observed by Darveniza indicates that electrons having energies of several
Variation of the electric strength of transformer oil with the amount of dissolved air

(After Tropper)
ADDENDUM

The permittivity of most solids exceeds that of dielectric liquids such as transformer oil or liquid paraffin. Such particles present in the liquid will experience an electrostatic force component towards regions of higher electric stress. Charged particles moving along the curved stress lines will also experience a centrifugal force in opposition to the dielectric force. Thus particles of low permittivity (e.g., about 4 say), will be more readily ejected from the gap than high permittivity or metallic particles.

Any particle with a permittivity less than that of the liquid will be ejected by electrostatic forces, however such particles are unlikely to be found in transformer oil or liquid paraffin.

Gosling found that as stress conditioning proceeded at high values of stress (about 600 kV/cm) particles activity and the associated current fluctuations steadily decreased as particles were ejected from the gap or became attached to the electrodes.

When the stress was reduced to about 300 kV/cm, a particular type of particle activity sometimes occurred. A particle would be seen to enter an otherwise clear gap and a large current fluctuation would take place. Raising the stress for a time would then result in the particle leaving the gap.
electron volts are present on the highly stressed region of the liquid. It is known that electrons of this energy may cause dissociation reactions giving rise to gaseous products in the liquid. When the rate of gas evolution exceeds that at which it can be dissolved gas bubbles will form leading to a breakdown.

The presence of minute solid particles in the liquid has been found by many investigators to reduce the electrical strength of the liquid to a marked degree. Kok (24) associates breakdown in liquids with the presence of impurity particles which will exist even in a carefully filtered sample.

Gosling (18) using well filtered and degassed oil, observed particle activity in the stressed region of the gap. Particles were seen to oscillate between the electrodes following definite trajectories and occasionally forming a bridge. This bridge formation was mainly responsible for breakdowns at low voltages. He found that particle activity commenced at stresses at about 300 kV/cm, the violence of the activity becoming greater as the stress was increased until, at higher stresses particles appeared to be ejected from the gap. \( \text{See adjacent addendum}. \)

Other workers have since confirmed Gosling's observations (25-27). Kao and Calderwood (61) suggest that small vapour bubbles would also be ejected from the highly stressed regions of the gap by electromechanical forces (61).

2.2.1. **Electrode materials and coatings**

The effect of electrode materials on breakdown strength has been investigated by many workers (13, 14, 15, 18, 20, 36, 37 & 44). But no definite correlation between the electrode material work function and the breakdown strength has been established.
A small electrode dependence under uniform field conditions was found by Lewis (14) who found that with a steel point and plane of different materials an electrode dependence occurred only when the plane was the cathode (36). Maksiejewski and Tropper (37) found the electrode dependence in hexane was reduced when the liquid was degassed. Oxidisation of the electrode was found by Hancox (21) to increase the impulse strength.

The influence of electrode coatings on the breakdown strength of the gap has been investigated by Zaky et alia (8,39). Using uncoated electrodes they found that thin films of breakdown by-products formed over the electrodes and that conditioning effects consistent with the formation of space charges at each electrode occurred whenever the gap setting was abruptly altered.

The existence of space charges at the electrodes has also been suggested by Ward and Lewis (45) when explaining the effect of static stress conditioning on the impulse strength of hexane. Swan and Lewis (40) and Gallagher and Lewis (44) investigating the electric strength of liquified gases found that the strength depended on the nature of the electrode material and suggested that the reduced electrode material dependence found with liquid hydrocarbons was due to the formation of surface deposits due to breakdown. They concluded that positive space charges at the cathode would increase emission and that the existence of a negative space charge at the anode may give rise to an ionisation process at the anode, both effects tending to lower the breakdown strength. The production of wax deposits on the electrodes has also been noted by other workers (28,43,45).
Zaky, Eldine and Hawley (38, 39) using electrodes coated with a thin film of thermoplastic 'Penton' obtained a large increase in gap breakdown strength for the first breakdown, the strength for subsequent breakdowns with a punctured layer being much lower. Carbonised regions were always found on the coating around the breakdown site suggesting a localised surface discharge of the film. Space charge measurements (41) using bare and coated electrodes show that the coating is highly stressed due to the presence of space charges.

Little and Smith (42) using a specially modified electron microscope and carefully polished nickel electrodes found that at stresses in vacuum of about 400 kV/cm and above, sharply pointed projections or asperities appeared on electrode surface, some having height to base ratios approaching 10 to 1. Current streamers from and to asperities slowly burnt them away at high current densities, other asperities rising as either the stress was increased or the stressing period prolonged.

The production of asperities would be encouraged by the presence of a highly stressed thin wax film. The growth of an asperity in the wax layer would lead to a large increase in the local stress so promoting a breakdown. Other forms of breakdown initiation have been suggested in earlier work, such as localised bursts of emission from the cathode (47 & 48 these may be associated with incident positive ions (49), dust particles (31) or micro bubbles (22 & 50).

The model proposed by Sletten (31) involved the initiation of a streamer by a charged particle arriving at the cathode, whereas Nossier, Hawley and Clothier (51) studying electroluminescence in transformer oil
containing sulphur hexafluoride found that breakdown was preceded by initiating events at anode sites, breakdown sparks starting from the anode and proceeding to the cathode.

2.3. Conduction current phenomena

Various theories have been advanced from time to time relating to the problem of high field conduction in liquid insulants and dielectrics. Unfortunately these theories are as often of a contradictory nature as of a complementary one, and it is clear that the problem is not completely understood.

The commonly accepted sources of charge carriers in liquid dielectrics are:

Field assisted thermionic emission from the cathode (Schottky emission).

Field emission of electrons from the cathode (cold emission).

Field assisted ionisation of molecular impurities present in the liquid and/or ionic dissociation of the dielectric liquid molecules.

Schottky emission processes have been proposed by House (52) and Baker and Boltz (46). However Dornte (53) found no temperature dependence in n-heptane and suggested that field assisted emission was the more probable process. A combination of the two processes was proposed by Le Page and Du Bridge (54). Plumley (55) found no change in current on reversal of polarity when using electrodes of different materials and concluded that dissociation rather than emission was the main source of charge carriers. The dissociation process proposed by Plumley was also
proposed by Coelho and Bono (59, 60); Plumley proposing molecular dissociation of the dielectric liquid and Coelho and Bono dissociation of impurities in the liquid.

Kao and Calderwood (61) using n-hexane, carbon tetrachloride and transformer oil, obtained a linear conduction current/stress plot up to about 300 kV/cm and a non-linear plot at higher stresses. They attributed the linear portion to ionic impurity conduction processes and the non-linear contribution to field assisted thermal emission from the cathode.

Cullingford et alia (62) using transformer oil obtained similarly shaped characteristics with coated electrodes and suggested that the existence of space charges enhanced the field emission processes taking place at the cathode. Green, in earlier work on n-hexane (63 & 64) which also produced similar characteristics to those described above, expressed the opinion that positive ions collected over a surface layer on the cathode producing an intense local field.

Swan (5) reviewing recent work (56, 57 & 58) suggests that the effect of electrode layers and space charge formation reduces the effective work function. Morant (84) supports this view by showing that the potential barrier of electron emission should be independent of the metal work function when equilibrium space charges exist at the metal-dielectric interface. Gallagher and Lewis (44) also conclude that electrode surface layers due to discharge products mask electrode effects which would otherwise be present.

2.3.1. Effect of electrode coatings

Eldine et alia (62, 65) have investigated the effect of coating the electrodes with a pore-free thermoplastic film using air saturated transforme
oil as the liquid dielectric. Conduction current characteristics were obtained with bare electrodes, either anode or cathode coated and both electrodes coated. Fig. 3 shows the respective characteristics. They conclude that a positive ion sheath is set up at the cathode and a negative ion sheath at the anode. The latter causes ionisation at the anode, feeding back positive ions to the cathode so enhancing the cathode field. Coating the cathode produces two competing effects, the coating reducing the emission on the one hand, but on the other increasing the local field and hence the emission by preventing the positive ion sheath from discharging to the electrode.

2.3.2. Gap dependence

Gap dependence effects are generally taken to indicate bulk liquid effects as distinct from the electrode surface phenomena reviewed above. Two general effects of competing nature may be present in the liquid bulk, charge multiplication and recombination. The latter will only be present to any significant degree if both positive and negative charge carriers are present. Charge multiplication processes however will generally result in the production of ions of each polarity so that recombination will also be present to an unknown extent.

Little definite evidence exists for direct charge multiplication, Goodwin and Macfadyean (67) using n-hexane came to the conclusion that a multiplication process similar to the Townsend alpha process occurred in the gap. Watson and Sharbaugh using a pulse conduction current technique (66) measured conduction currents in hexane (57, 58) but found no evidence of charge multiplication with fields up to 1.2 MV/cm. At 1.3 MV/cm it was
Anode

Cathode

1.5mm oil gap

0.5mm thick thermoplastic coatings

bare electrodes both electrodes anode coated cathode coated

Conduction current-stress characteristics for coated and uncoated electrodes.

(After El-Dine et al).

Fig. (3).
thought that a marginal onset of the process occurred. They also suggested that the current originates either by Schottky or field emission from asperities on the cathode.

House (52) considered that positive evidence existed for charge multiplication for fields of 1.5 MV/cm. Green (63) concluded that if an ionisation factor existed for fields in excess of 800 kV/cm up to 1.03 MV/cm it must be very small.

2.3.3 Additive effects

Gosling (18) found that a high conduction current does not necessarily mean a low breakdown strength observing that O₂ in solution increased both the conduction current and breakdown strength. Angerer (22) found that when oxidising additives are added to transformer oil and liquid paraffin the optimum concentration for lowest conduction current and highest breakdown strength did not coincide. The addition of 7% of ethyl alcohol to n-hexane was found by Kao and Calderwood (61) to increase both current and strength.

Zaky, House and Tropper (68) obtained different current values using the same electrodes but different liquid samples of n-hexane. They found that electrode material effects were only dominant at very high stresses when cathode emission could be expected. They concluded that the shape of the conduction characteristics was more significant than the relative current values.

2.3.4 Pressure dependence

Little current dependence on pressure has been found in experimental work so far. Darveniza (19) and Gosling (18) found no significant dependence
in the pressure range ± 1 atmosphere of atmosphere. But Angerer (22) suggested that due to surface tension effects, the internal pressure in micro-bubbles could be of the order of several atmospheres even in a degassed liquid under equilibrium conditions. Kao and Calderwood (61) using an applied pressure range of up to 11 atmospheres did not detect any pressure dependence, however Elder and Zeier (69) observed a decrease in conduction current at pressures approaching 200 atmospheres, however at pressures of this order the liquid tends to compress, both the viscosity and density increasing with pressure (70). It would therefore appear from the foregoing that the conduction process is not sensitive to the existence of micro-bubbles in the liquid, however as will be discussed later, Kao and Calderwood found that conduction current fluctuations were reduced as the pressure increased.

2.3.5. Liquid motion:

A hydro-dynamic theory of electrical conduction has recently been proposed by Ostroumov (71,72,73) which proposes motion of the liquid when under electrical stress. Ostroumov applied his theory to the results of Goodwin and Macfadyean (67) plotting Log I against V, $\sqrt{V}$ and $\sqrt[3]{V}$ respectively, in each case obtaining a linear region over successively increasing ranges of voltage. The first linear region represents the voltage range over which the liquid was stationary with low current density where ohms law holds. The second, where the liquid was in motion with a turbulent flow and the third region where the liquid motion was of laminar nature.

Angerer and Tropper (74) have very recently applied the Ostroumov theory to their experimental results, those of Gosling (18) for transformer
oil and those of House (75) and found an appreciable degree of agreement.

Secker and Lewis (76) have conducted a series of very interesting experiments using a 'field emitter' device to obtain charge injection into hexane or acetone. The field emitter consists of an array of razor blades whose edges face a gauze electrode on the far side of which is the anode, the whole cell forming a three electrode device. By maintaining approximately 8 kV between the grid and the razor blades a current of about two microamperes per razor blade is obtained, presumably by electron injection forming negative carriers between the blades and the gauze grid. Applying a positive potential to the anode, of some 70 kV with a grid-anode spacing of about 1 cm draws currents approaching one microampere through the grid to the anode. The high value of current for such a low stress strongly suggests that electrodes have a very pronounced effect on the apparent properties of insulating liquids. The device was found to have crude 'triode' characteristics and experimental work is in progress (77) to separate ionic effects from those of motion and to determine the intrinsic mobility of ions within the liquid as distinct from the mobilities relative to the electrodes measured in previous work.

2.3.6. Effect of temperature

Temperature effects have been studied by many workers investigating the effect on electrode work function and on viscosity.

Coelho and Bono (59) using a wire, cylinder configuration obtained larger currents when the wire was positive, this difference disappearing as the temperature was increased. They suggested that this might be explained by the existence of a negative ion space charge
adjacent to the anode enhancing the field more significantly when the wire was positive due to the field configuration. Conversely, when the wire was negative, field emission space charge would lower the field against the wire.

Kao and Calderwood (61) have also investigated the effect of temperature on the conductivity of hexane and carbon tetrachloride finding an increase in conduction current with temperature. They attributed this increase to an increase in ionic mobility and an increase in ions formed by a temperature enhanced dissociation of impurities. Relative fluidity \( \frac{1}{\text{viscosity}} \) and conduction current were plotted by log scales against \( \frac{1}{\text{Temp}} \) and gave straight lines for each, the greater slope for the conduction current being ascribed to dissociation of impurities.

### 2.4. Conduction current fluctuations

Most workers investigating conduction current phenomena in liquids report fluctuations in the conduction current.

Race (80) using 'Dowtherm' liquid and Khambanonda (20) and Darvenza (19) using transformer oil found very erratic currents during the initial stressing of the liquid but after a few breakdowns more stable currents were obtained.

Some years before, Baker and Boltz (46) had experienced difficulty in making measurements due to erratic fluctuations when using electrodes with absorbed oxygen. Le Page and Dubridge (54) found that the conduction current became more erratic when the temperature was raised and House (52) found two types of current pulse, one type occurring at lower stresses about 250-400 kV/cm and the other at stresses about 1000 kV/cm. The latter
were 'sharp and needle like' in form and were attributed to ionisation events, whereas the lower stress pulses were thought to be due to the detachment of high work function material from the electrodes. Zaky (82) observed similar phenomena except that the needle like pulses occurred at 700-800 kV/cm.

Zaky and House (79) using 'Pyrocolor' found that adequate conditioning of both electrodes and sample was essential if high stresses were to be achieved without breakdown. They also found that the existence of large pulses that failed to reduce in value as conditioning proceeded, rapidly increased with stress and invariably resulted in an early breakdown. Similar effects were obtained by Kao and Calderwood (61) who found that the fluctuations were greatly reduced under high hydrostatic pressure. The latter led them to suggest that the current fluctuations might be due to the presence of minute transient bubbles occasionally forming in the gap. Zaky, Tropper and House (68) also observed similar phenomena to that of Zaky and House (79), in hexane and thought that the low stress pulses occurring during the conditioning process were due to the removal of the more loosely absorbed gases from the electrode surfaces, whilst the high stress pulses were attributed to field induced desorption from discrete areas on the electrode surface. Gosling (18) and others have found that increasing the stress results in ejection of particles from the gap after a deliberate increase of stress so that the associated reduction in conduction current pulses is more probably due to the removal of particles or possibly vapour bubbles (61,81) as described on page 12.

Sletton (31) obtained very erratic conduction current fluctuations in hexane; bursts of current occasionally occurred causing the value to
change by several orders. Microscopic observation of the gap showed occasional coincidence of the current burst with the arrival of a particle at the cathode. This visual observation did not always hold, but this is not necessarily meaningful since both Lewis and Sletten (34) and Gosling (18) have stated that unsuitable dark field illumination of the gap might have suggested a particle free gap whilst in fact it was not.

Sletten and Lewis (34) observed that with $O_2$ in solution the pulse activity was similar to gas free hexane but that the current bursts were less frequent and higher fields could be reached. Gosling (18) also found steadier conduction currents in transformer oil when $O_2$ was in solution. Sletten and Lewis believed the current bursts to be due to the incidence of a positively charged particle at the cathode arriving at suitable spots on the electrode and producing a burst of electron emission.

2.4.1. Analysis of conduction current fluctuations

Analysis of the conduction current fluctuations on a statistical basis was first carried out by Yamanakia and Suita (85) by measuring the pulse distribution for mineral oil, toluene and carbon tetrachloride. Fig. 4 shows typical distributions obtained during their work. In the figure the number of pulses per second greater than a certain magnitude is plotted against that magnitude. The characteristics were considered as being due to two processes, the upper linear region suggesting impact ionisation due to its correspondence with a Furry (86,87) distribution and the lower linear region was considered to be due to the sweeping of space charge ions produced by the initial avalanche. Similar tests were carried out using point-plane electrodes, the negative point configuration giving more pulses than the positive point.
Frequency of avalanche.

Magnitude of avalanche.

Typical avalanche distributions at various stresses in liquid dielectrics.

(After Yamanaka and Suita).

Fig. (4).
2.4.2. Effects of additives and temperature on pulse activity.

One of the first systematic studies of conduction current fluctuations in insulating oils was carried out by Huq (25) who used a square law detector to measure the mean square value of the fluctuations. He reported a decrease in mean square value when O₂ was added to transformer oil and an increase when O₂ was added to liquid paraffin.

Nossier (26) and Megahed (27) continued Huq's work, but by a different technique, using a high speed tape recorder so that subsequent analyses of the recording could be made after the test. Pulse height distributions, auto correlation functions and power frequency spectra were obtained under various experimental conditions.

The pulses were also found to be gap as well as stress dependent and in all cases an exponential pulse height distribution was obtained indicative of a multiplication process in the gap.

The observed reduction in large amplitude pulses during conditioning was attributed to the removal of particles from the gap (18, 81) and the increase in small amplitude pulses to the formation of space charge layers. The observed acceleration of the growth of these processes at higher temperatures would be expected as a consequence of the reduced viscosity.

Megahed concluded in agreement with Huq and Nossier that small oxygen concentrations probably resulted in the trapping of electrons in a similar manner to that known to occur in gases (78). Such trapping would tend to quench incipient avalanche phenomena, reducing the pulse activity in the current. When a larger gas content is present in the
liquid, micro-bubble formation is more likely with internal ionisation at higher stresses producing increased pulse activity. The increase in pulse activity with temperature is attributed to the reduction in gas solubility as the temperature is raised.

The reduction in hydrogen evolution when aromatic constituents are present in the insulant has been studied fairly extensively by various workers and is discussed in the next section.

This reduction is attributed to hydrogenation of the aromatic constituent removing nascent hydrogen produced by dissociation processes in the stressed region. Although the rate of hydrogen evolution is very low even in a highly stressed liquid it seems reasonable to suppose that hydrogen micro bubbles will form more rapidly in the case of liquid paraffin than in transformer oil or liquid paraffin with 10% of aromatic constituent. This would explain the reduced pulse activity observed by Megahed when an aromatic is present in the liquid.

2.5. Gas evolution in liquids under stress

The gassing tendencies of insulating liquids under electrical stress have been studied by various workers. Basseches and McLean (92) using a highly paraffinic oil (Primol D), found a pronounced reduction in gassing when aromatics were added. Plain degassed Primol D was found to produce a brown waxy solid deposit on the electrodes and on glass spacers between the electrodes, the deposit was highly insoluble and found to be approximately 80% carbon, 10% hydrogen, a 2% residue believed to be silica and an 8% deficiency which the analysing technique could not identify, thought to be oxygen. Since the analysis of the wax took place some months after the
test the high percentage of oxygen was probably mainly due to absorption
during the waiting period between testing and analysis. The wax was thought
to be similar to cable or 'X' wax, which is found in high voltage cables and
similar to that reported by Shoepfke and Fellows (43). It was also found
that the amount of wax produced decreased if the gas evolved was decreased
by the presence of an additive. By adding free radicals to the oil under
test the gassing rate was reduced suggesting that free radicals are
produced as an intermediate stage in the decomposition process.

They conclude that the only way by which free radicals can be
formed in the stressed oil is by rupture of a covalent bond and that the
methyl radicals so produced are more likely to combine with each other
than recombine with the nascent hydrogen produced in the dissociation
process, the nascent hydrogen combining to form molecular hydrogen.

They also conclude that the waxy material formed by a breakdown
is probably unsaturated, and suggest that cross linking and polymerisation
of unsaturated molecules could occur to the extent that high molecular
weight products are produced, such products being highly insoluble.

Later work by Basseches and Barnes (93) indicated that a discrete
gas phase is essential to start the gassing process. They suggest that
bubbles of smaller size than could be detected by the apparatus of Garton
and Church (94) (who did not detect bubbles) could exist in a liquid such
that internal ionisation is possible. The proposal of an ionisation
process was supported by the presence of a faint blue discharge between
the electrodes whilst gassing was taking place. Increasing the hydrostatic
pressure would decrease the bubble size so that ionisation and hence
gassing would be stopped. Gas evolution was much reduced when the bubble population was reduced by degassing the liquid. They suggested that high speed photography of the electrode region would give information concerning the formation of bubbles.

A short review of gas evolution in insulating oils has been made by Zaky and Hawley (96) in which they remark that when aromatics are present in a degassed, highly paraffinic liquid the rate of gas evolution is reduced with a corresponding decrease in the solid material produced. This was taken as evidence that hydrogenation of the unsaturated bonds in the aromatic additive was taking place, so reducing the evolution of gas (97). Hawley (122) also noted that electrical discharges in oil impregnated insulation set in more or less simultaneously with the evolution of gas bubbles.

2.6. Miscellaneous

Krasucki (98) using high speed photography and a very viscous liquid (hexachlorodiphenyl) found that breakdown was proceeded by the formation and growth of a well defined shadow. The shadow was considered to fade too rapidly for it to consist of bubbles of gas and it probably represents a region of vapourised liquid. When the shadow bridged the gap total breakdown ensued.

Using a Schlieren optical technique Hakin and Higham (99) and Faragmand (100) obtained photographs disclosing a region of reduced refractive index at a needle cathode.

The development of the region was often followed by breakdown, but in the other cases where no breakdown resulted, the region dispersed.

By placing the sensitised side of a photographic plate against a
needle electrode with a plane electrode in contact with the other side of the photographic plate and immersing it in transformer oil, Toryania et al (101) obtained Lichtenberg figures with a tree like structure, the fact that treeing also resulted when the point was positive led them to suggest that breakdown phenomena could not be solely explained in terms of cathode electron emission leading to ionisation. They concluded however that some form of electronic ionisation process formed the tree growth, followed at the 'root' by a discharge in the gas phase and suggested that rupture of molecular bonding resulted from electron bombardment. In other experiments using a high speed camera (102) bubbles were found to grow from a cathode point towards the positive electrode. They considered these bubbles to be initiated by electron emission from the cathode point where they calculated the field to be approximately 1.6 MV/cm.

2.7. Electroluminescence

The effect of using a dielectric liquid (castor oil) on the electroluminophore, ZnS-Cu-Mn in a d.c. field was studied by Kazabin et alia (103). They found that a large current could be obtained due to the presence of excess Cu (which did not enter the Zn lattice). The excess copper increasing the conductivity and local stress.

The large current and the presence of Mn as an activator was found to produce intense and prolonged luminescence in a constant d.c. field. Orientation of the electroluminophore crystals along the field lines was observed, resulting in the formation of bridges across the gap, followed by an intensification of the light output by about 250%. Babotkin (104) reporting on the effects of the cell dielectric on the
Electroluminescence, considered cells that had either capacitive or ohmic conduction properties. The former type of cell emitted light when current flow resulted from a change in applied voltage whereas in the latter type continuous electroluminescence was observed. Here also alignment of chains of crystals was observed with the conductive type of cell. Sodomka (105) found a reduction in electroluminescence of ZnS-Mn phosphors in castor oil under d.c. stress when one of the two parallel electrodes was rotated about the common axis, at one to two revolutions per minute. A reduction in the conduction current also occurred. He was of the opinion that mechanical stirring of the dielectric resulted in displacement of the crystals changing their orientation relative to the field, so reducing the polarisation of the dielectric.

The brightness of d.c. electroluminescence of dissolved phosphors was found by Favorin and Kozina (106) to depend on the conduction current. They also found that for a given current the electroluminescence also depended on the stress and suggested that electrons entered the electroluminophore crystal, light emission resulting when excited centres returned to their initial state, the voltage dependence being explained in terms of electric potential and electron energy.

2.7.1. Electroluminescence in organic liquids

Random luminous spots on the electrodes were first observed by Dakin and Berg (107) in degassed, unfiltered transformer oil, both with a.c. and d.c. fields. Later, similar effects were observed by the same authors (108) in well filtered and degassed transformer oil using d.c. fields. The occurrence of the luminous spots was not affected by varying
the hydrostatic pressure from 10 mmHg to 2 atm. or by adding gassing inhibitors such as benzil (92). The spots were detected through a transparent conducting glass electrode at stresses as low as 50 kV/cm by placing a photographic plate against the glass and exposing for periods of up to ten minutes. Since spots were only detected on the negative electrode the electroluminescence was attributed to field emitted electrons from points of high localised stress on the electrode. The lack of pressure dependence and the negative results obtained with the gas inhibitor led them to suggest that emission did not depend on the existence of vapour bubbles, though they suggested that light emission signified the existence of electrons of energy greater than 3 eV, capable of producing decomposition.

Similar phenomena to that of Dakin and Berg were also reported by Eidel'berg using a.c. fields (109) using air saturated but filtered castor oil. Transient spots were noticed at low stresses being replaced as the stress or frequency was increased by weak stable luminescent spots whose brightness increased with voltage or frequency. At higher voltages still, yellow discharge sparks occurred on the electrode apparently unrelated to the luminous spots. For d.c. fields below 250 kV/cm no luminescence was observed. The author assumed that the luminescence of the molecules of castor oil or of some impurity was excited by electrons emitted from the cathode. Since the average field was not high enough to cause such emission an explanation similar to that of Dakin and Berg was presented with the additional supposition of local variation of the liquid-electrode interface work function.
Electroluminescence of liquid dielectric materials such as acridin-orange or carbozyl has been reported by Bernanose et al (110,111), Armstrong and Hancock (112) have reported electroluminescence in such materials as vaselin, paraffinic wax, toluene and polyvinylidene chloride. The authors conclude from their work that it is possible for the liquid dielectric as well as the phosphor to electroluminesce. All the dielectrics tested showed some emission under ultra-violet light.

Tumerman and Czaanow (113) who repeated and extended the experiments of Bernanose, found electroluminescence in paraffin wax, transformer oil and silicone oil when applying a.c. voltages or trapezoidal d.c. pulses of controlled wave shape, the applied stress extending up to values of 500 kV/cm.

When a.c. fields were applied the electroluminescence was similar to that observed in solutions containing phosphors. Above a threshold stress luminous spots were seen whose position on the electrode surface changed continuously, and in a similar manner to that already reported by Eidel’berg; stable spots appearing at higher stresses.

2.7.2. Light pulses

Tumerman and Czaanov (113) found that when trapezoidal d.c. pulses were applied to paraffin wax a single light pulse was emitted at the front and at the tail of the wave. However when the trapezoidal pulse was applied to the liquid dielectrics a series of discrete pulses was observed at an approximately regular rate for the period of the wave front or tail.

A very recent publication due to Gzowski et al (119) also reports the existence of light pulses in a statistical investigation of light pulses.
obtained from distilled, filtered and dried n-hexane with anthracene, subjected to a step function voltage pulse having a rise time of 2\(\mu\)s and duration of 200\(\mu\)s. The evidence obtained by the authors demonstrated that the light consisted of a series of pulses which occurred randomly. A statistical analysis of the time intervals between stress application and the first and second pulses allowed the mean rate of occurrence to be determined. This function was found to depend on the stress and on the electrode condition. A typical light pulse record is shown in Fig. (5). The magnitude and frequency of the pulses increased markedly with stress and appeared to depend on the electrode condition. It is suggested that dust or impurity particles not removed in the filtering process are responsible for initiating the events indicated by the occurrence of a light pulse. Such a particle approaching charge layers on insulating films on the electrode might enhance the local stress in the film sufficiently to produce a breakdown in the film. A micro-discharge of this sort could occur at anode or cathode, but the relative ease of emission at the cathode could produce a larger discharge there.

A spectroscopic investigation of light emission of stressed air saturated n-hexane was carried out by Smith, Kao and Calderwood very recently (115), using a point-plane electrode system. They found, as also found and reported previously, by the writer (116), that when the liquid was stressed under d.c. conditions the light emission consisted of a series of discrete pulses whose duration was less than the rise time of the photomultiplier and that large light pulses could be associated with a current fluctuation, suggesting charge multiplication and recombination processes.
The erratic nature of the electroluminescence and current was found to decrease with the length of the period of stress conditioning and this was attributed to impurity effects modifying the electrode conditions.

2.7.3. Pre-breakdown light emission

The experimental work carried out by Smith, Kao and Calderwood (115) was mainly concerned with pre-breakdown light emission phenomena. They observed that the light pulse preceding breakdown was much more intense (though faint) with a negative point than with a positive point. The pre-breakdown current pulse being accompanied by a pulse of light in the ultra-violet region. The main breakdown current and light pulse occurred a few microseconds later in the visible and ultra-violet spectral ranges. They concluded that due to the greater pre-breakdown light in the negative point case, electron emission from the cathode takes place and that high field conduction is not due to dissociated ions; for if the latter were the case, no polarity effect would have been apparent. The fact that the pre-breakdown light was in the ultra-violet led them to suggest that both it and the breakdown light were due to electron\textsuperscript{C} transitions.

Earlier, Sletten and Dakin (117), studying breakdown with uniform fields in air-saturated but filtered transformer oil using a 50 hertz 450 kV a.c. voltage, observed streamers preceding breakdown (also noted by Gosling (18)). Photomultipliers were used, focussed via lenses on the anode and cathode regions, but the streamer development time was found to be much faster than the rise time of the photomultiplier (which was about 10 ns) so that the propagation direction could not be determined. When the photomultiplier sensitivity was increased however, a pre-breakdown light
pulse was detected on the high voltage sphere (the other being earthed) regardless of its polarity. The intensity of the light pulse appeared to be greatest at the electrode but penetrated with decreasing intensity up to half the gap width. The oscillograms for the light pulse are shown in Fig. 6 for regions: (a) near the high voltage electrode, (b) at one quarter of the gap distance from the electrode and (c) at mid gap. They conclude that since the streamer development is complete in less than 10 ns, the propagation rate is in excess of \( 10^8 \) cm/s for the half inch gap used. Breakdown was always found to follow the pre-breakdown light pulse and before the light pulse propagates more than half way across the gap. They suggest that since the phenomenon is not polarity sensitive and is very rapid, an electronic process such as an avalanche mechanism in the liquid rather than ionisation in a bubble growth is responsible, the lack of cathode dependence precluding the usual electron emission hypothesis.

2.7.4. Electroluminescence with steady d.c. Fields

The work of Darveniza and Tropper (120) published in 1961 on the electrical properties of organic insulating liquids reported the observation of electroluminescence under steady d.c. conditions in transformer oil. The transformer oil was purified in a molecular still under reduced pressure in a dry air or nitrogen atmosphere between \( 10^{-2} \) and 5 mm Hg. A 1µ pore size filter similar to that used by other workers removed solid particles from the distillate. In order to reduce electrode dependence effects the authors found it necessary to spark condition the electrode prior to taking measurements, by 300 or so breakdowns in the liquid. The sample

*This effect was attributed to the more intense field at the high voltage sphere, estimated to be about 12% greater than that at the earthed sphere, due to the electrical asymmetry produced by the earthed enclosure around the test cell.*
Typical light pulse record at 430kV/cm
lcm = 25μs.

Fig. (5). (After Gzowski and Lewis).

Light signal development at various positions in the stressed region of the gap.

Fig. (6). (After Sletten and Dakin).
used for conditioning was then usually replaced by a fresh sample for measurement purposes.

A linear relationship was obtained between conduction current and electroluminescence and is shown in Fig. 7. 'Values were taken from the best curve drawn through the experimental results, within the limits of the observed fluctuations.'

It was found that whenever a fresh sample was used with spark conditioned electrodes, the electroluminescence decreased in value after the first few breakdowns the conduction current remaining unaltered. They concluded that some conditioning effect of the liquid rather than the electrodes must have taken place. Variation of the still temperature allowed the coloured fractions of the oil to be removed, resulting in a reduced current and light output showing that the light output was due to fluorescent molecules present in the sample.

The absence of any pressure dependence over the range - 350 mm Hg (tension) to + 760 mm Hg (absolute) leads the authors to suggest that the existence of micro-discharges in the vapour phase is unlikely.

2.7.5. Effect of fluorescent additives

The electroluminescence of various dielectric liquids with admixed fluorescent materials when subjected to d.c. fields approaching 1 MV/cm was studied by Kalinowski and Dera (114). The results presented in the paper were obtained using a benzenic solution of POPOP (1,4-bis(2-(5-phenyl-oxazolyl-benzene))) (see Section 4.5.1 for the structural configuration of the molecule) and a solution of anthracene in benzene.
The samples were prepared by distillation and filtering but were not degassed. For anthracene in benzene they obtained a linear relationship between electroluminescence and conduction current spanning one decade and an electroluminescence characteristic similar to that of Darveniza (120). Considerable dispersion of the plots was noted. A similar plot of electroluminescence against current for the POPOP solution produced a curve as shown in Fig. 8. The conduction current and electroluminescence against stress characteristics are shown in Fig. 9 & 10. The variation of electroluminescence at constant stress is evident from the plots, similar fluctuations being noted by Darveniza. Similar characteristics were obtained after a breakdown had occurred, both the current and electroluminescence being much increased in value for a given stress. Kalinowski observed bright electroluminescence against both electrodes, that against the cathode being more intense than that at the anode.

2.7.6. *Electroluminescence spectra*

During their experimental work on transformer oil Darveniza and Tropper observed that the colour of the electroluminescence was blue and similar to that obtained under U.V. irradiation. Although the light intensity was too low for accurate spectral determination or photography it was thought that the peak emission wavelength shortened as the stress was increased.

A similar technique to that described in the previous section using spark conditioned electrodes was also employed to test n-hexane and benzene with anthracene added. No light emission was detected from n-hexane at stresses up to 1.1 MV/cm before doping with anthracene at a concentration of 1 gram per litre. Light emission typical of anthracene
Relation between light output and conduction current.
(After Darveniza and Tropper).

Electroluminescence—conduction current—stress characteristics, Popop in benzene.
(After Kalinowski and Dera).
was then observed. Further breakdown conditioning increased the strength from 610 kV/cm to 955 kV/cm, the light output steadily decreasing as the breakdown strength increased. Benzene was also tested without a fluorescent additive and a heavy conduction current and electroluminescence typical of the emission spectrum of benzene obtained.

The authors concluded that acceleration of free electrons took place in the liquid. The majority of these electrons would be retarded by the vibrational barriers of the liquid molecules (Lewis (11) and Adamezewski (121)). A statistically small proportion of the electrons might however achieve energies in excess of the vibrational values and accelerate in the electric field until electronic excitation of the fluorescent molecules resulted. From this reasoning the lower absorption energies would be excited first, followed by higher energy excitations as the stress is increased further, causing the electroluminescent spectral peak to move toward the ultra violet end of the emission spectrum with increase in stress.

Tumerman and Czaanow (113) also studied the light emission spectrum from paraffin wax, transformer oil and silicone oil and showed that it was characteristic of the material although it was found to cover the whole range of the visible spectrum. Comparison of the spectrum obtained for paraffinic wax containing acridin-orange with that for paraffinic wax did not show any significant difference. The authors concluded that insufficient data had been obtained on which to base a theory. They expressed the opinion that visible luminescence indicates an ionisation process which would ultimately lead to breakdown.

Using a spectrometer (which was possible with benzene and Popop, one
of the most fluorescent solutions known at the present time) Kalinowski and Dera found that the emission spectra were similar to that obtained when irradiating the solution with ultra-violet light save for a slight shift of the electroluminescence spectrum to the shorter wavelengths as shown in Fig. 11. This result should be contrasted with that of Tumerman and Czaanow (113) who found spectra covering the whole visible range, the spectra obtained by the latter authors for silicone oil and transformer oil are shown in Fig. 12. Kalinowski and Dera found no shift in the spectra with increasing stress and concluded that the electroluminescence occurred in the liquid and was engendered by accelerated charge carriers due to the field, whereas that at the cathode was more likely to be related to electron emission. No explanation was offered for the anode effect.

It would appear that electrons may gain energy, excite molecules and form negative ions. Light emission would be due to energy release from the recombination of electrons and ions, positive and negative ions or excited molecules, the existence of all these processes accounting for the wide range of the light spectrum (51, 113, 114, 115, 117, 118, 120).

2.7.7. Correlation between the conduction current and electroluminescence signals

Kalinowski (118) has just published the results of a study on conduction current and electroluminescence obtained using d.c. fields and a benzenic solution of POPOP which was prepared by distillation and filtering but not degassed. It was found that the light and current fluctuations initially erratic and uncorrelated showed increasing correlation and less fluctuation as stress conditioning proceeded in agreement with observations reported earlier by the writer (116). Kalinowski
electroluminescent spectrum at 790 kV/cm.

Spectra obtained from POP in benzene.
(after Kalinowski and Dera)

Fig: (11)

Electroluminescent spectrum from silicone oil

Electroluminescent spectrum from transformer oil.
(after Turnerman and Craakow)

Fig: (12)
(in common with other workers) was unable to separate electrode and bulk liquid effects. His conclusions were therefore limited to the following: due to the correlation between electroluminescence and conduction current it is probable that charge carriers are produced by the electric field in the electroluminescent volume in the liquid, however electroluminescence at the cathode (see review of previous paper, 114) could also be due to emitted electrons. He concludes that the most probable explanation is the existence of both processes coupled with the existence of heterocharge at each electrode. He further suggests that the electrode luminescence is due to mobile electrons emitted at the cathode and abstracted by the heterocharge field from liquid molecules to the anode. He then derives an expression assuming high field (cold) emission of electrons. This yields an expression for the electroluminescence in terms of the energy distribution of the electron population under equilibrium conditions, (assuming a general probability factor which remains constant, covering the processes of molecular excitation by electrons, energy transfer from solvent to the electroluminophore solute and its emission as light). The final expression relates the electroluminescence to the stress in the following manner:

$$\text{Electroluminescence} \, B = P \cdot E \exp \left( - \frac{G}{E} \right)$$

where $P$ and $G$ are constants and $E$ is the stress in the region of interest.

The results of Darvenzia and Tropper (120) and Kalinowski and Dera (114) were taken and plotted on a log-linear basis and are shown in Figs. 13 and 14. The deviations are ascribed by Kalinowski to errors resulting from the fluctuating nature of the electroluminescence at constant stress and neglect of bulk and anode electroluminescence. The deviation
in Fig. 13 at high stresses is ascribed to anode effects and ionisation avalanches heralding breakdown.

2.7.8. Effect of dissolved gas on electroluminescence

Darvenzi and Tropper (120) also tested samples containing nitrogen or air with partial pressures ranging from $10^{-2}$ to 1 mm.Hg. No significant effect on current or light output was observed. The absence of the expected quenching effect of oxygen was surprising but was probably due to the condensation of the oxygen from the air, which was dried by passing it through a liquid nitrogen trap.

Visual observation of the gap showed that the glow appeared to take a filamentary form of nearly constant intensity along the length of the filaments. These spanned the inter-electrode space, occupying a diameter of about three or four times the electrode spacing. At higher stresses the diameter occupied condensed to one or two times the spacing and became more intense and diffuse.

It has been suggested by Evans (123) that $O_2$ in the presence of aromatics can form molecular complexes which cause fluorescent quenching (125), this coupled with the electron trapping properties of $O_2$ may explain the continuous quenching effect found by Gosling (18) as oxygen is added to degassed transformer oil. A similar effect had already been noted by Race (124) using 'Dowtherm'. Fig. 15 shows sketches of visual observations of the electroluminescence as made by Gosling, showing the effect of increasing the gas content of the liquid under test.

The addition of oxygen would appear to rapidly confine the electroluminescence to the cathode region and completely extinguish it as
Characteristic plotted from results of Kalinowski and Derer.  
Fig. (13).  
(After Kalinowski)

Effect of increasing nitrogen content —

Effect of increasing oxygen content —

Fig. (15) Electroluminescence observations in transformer oil  
(after Gosling)
the gas content increases.

Nossier, Hawley and Clothier (51) experimented with initially degassed transformer oil with dissolved sulphur hexafluoride (SF₆), (an electronegative gas), at a partial pressure of 1 mm Hg. They found that when the liquid was subjected to d.c. stresses, the conduction current increased by up to two orders of magnitude, over some two hours, during the prestressing period. This current increase was accompanied by the appearance of electroluminescence in the liquid in the vicinity of the cathode which increased in intensity with the current. Photographs of pre-breakdown phenomena disclosed the existence of initiating events and breakdown sparks which appeared at the anode and proceeded towards the cathode.

2.8. Fluorescence phenomena

The similarity between the electroluminescence phenomena discussed in the previous paragraphs and the phenomena of fluorescence has been noted by various workers (18,19,113-116,118-120), and it is generally accepted that common basic principles are involved in both types of phenomena.

2.8.1. Basic processes

Fluorescence may be described as the process of energy absorption of a certain equivalent wavelength and the subsequently emission of some part of this energy at a longer wavelength, typically in the visible region of the electromagnetic spectrum.

The absorption process involves the passage of an electron from one orbital to another of higher energy. The reversal of the process corresponding to the emission of light.
The absorption transition energy and the resultant emission transition energy are not simply related, particularly in the more complex molecules. This is due to the fact that the probability of the transition occurring depends on the wavelength of the absorbed energy and on the vibrational and rotational energy state of the molecule.

Fig. 16 shows a simple potential energy diagram for a diatomic molecule. The molecule being in its unexcited or ground state when represented by the curve NCFXM. The potential energy of the molecule being plotted vertically against the interatomic distance A-B plotted horizontally. The horizontal lines such as C-F represent the range over which the interatomic spacing will oscillate due to the vibrational energy of the molecule. The vibrational energy at room temperature being represented by a horizontal ordinate such as 0 in the figure. The upper curve RDXS represents one of the possible upper electronically excited states.

Excitation of the molecule say by the absorption of light, will result in a transition from 0 to D (taking about $10^{-15}$ seconds) the molecule being compressed and vibrating with an amplitude given by the horizontal at D within the curve. Vibrational energy is thus coupled to electronic energy for a short period of time of about $10^{-8}$ sec. (128). During this time the reverse transition D-0 could occur resulting in emission at the same wavelength as absorption, but this is rarely observed due to the high probability of molecular collisions occurring (in a liquid about $10^{10}$ per second), transferring some of the excess vibrational energy by collision to adjacent molecules. It is also possible during this period for collisional (or external) quenching to occur, when de-excitation of the molecule results,
the electronic energy being transferred to an adjacent molecule where a radiationless energy transfer could take place. Most substances such as paints and inks exhibit radiationless characteristics, the excitation energy being dissipated as heat, the molecule returning to the ground state via the intersection at X (as will be discussed later). Some substances however exhibit fluorescent properties, and though polyatomic may be represented qualitatively by Fig.16. On absorbing energy (say light of frequency proportional to $v$) the molecule vibrates along the horizontal $D$ at about $10^{13}$ cycles per second. After several collisions with adjacent molecules the excess vibration energy $D-E$ is lost, and the interatomic spacing of the initially compressed molecule increases. The molecule finally returns to the ground state after about $10^{-8}$ seconds, emitting a photon of light whose frequency is proportional to the distance $E-F$. Collisional vibrations will then return the molecule to its ground vibrational state $0$, as the interatomic spacing returns to the original value.

The model can be used to demonstrate the commonly observed absorption and emission phenomena:

a) emission takes place at longer wavelengths than those of absorption. This difference in energy is primarily due to vibrational losses in the molecule.

b) absorption is from the ground state $0$ so that the absorption spectra will show the vibrational energy levels around $D$, the particular absorption wavelength and vibrational level of the excited state depending on the instantaneous inter-atomic spacing
during the vibration in the ground state (along the ordinate 0) of the molecule when receiving the photon. For a simple diatomic model the absorption spectrum would comprise various groups of closely spaced lines each group representing the vibrational states about a particular electronic transition 0-D. Due to the numerous possible interactions between the atomic centres of polycyclic molecules diffuse spectral absorption bands result. The spectrum becoming continuous particularly in the liquid and solid states, where the force fields of adjacent molecules interfere with the internal vibrational states of the molecule. A corresponding argument will apply to the emission spectra whose vibrational states are those about F.

2.8.2. **Fluorescent materials**

Only molecules possessing particularly stable upper electronic levels are capable of resisting deactivation by collision or internal effects during the excitation lifetime of about $10^{-8}$ seconds and these form the so-called fluorescent substances. Bowen (128) lists two main types.

1) Ions of transitional metals or rare earths and inorganic complexes where the electron is excited from a d or f orbital deep in the atomic shell and not from a valency orbital. An example is salts of bivalent manganese.
2) Organic compounds with conjugated systems of $\pi$ electrons, where due to delocalisation, excitation of the $\pi$ electron to a higher orbital has only a small influence on the structure and stability of the molecule. Benzene and its homologues are examples.

2.8.3. Quenching effects

The 'cross-over' of the ground and excited states of $X$ illustrates one form of fluorescence quenching that can take place. Collisional or external quenching has already been mentioned, another form of quenching termed internal quenching is possible. If $X$ is not too high above $E$ the excited molecule may absorb sufficient extra thermal energy by collision to raise its energy to $X$ so that electronic and vibrational excitation merge; the vibrational energy $L-X$ in the ground state appearing in place of the previous excited state, this vibrational energy being rapidly dissipated by collisional processes. Many non-fluorescent substances have only a small energy gap between $E$ and $X$ so that external quenching prevents fluorescence.

Most organic materials that show fluorescence have conjugated double bonds and a ring structure such that some electrons have non-localised orbitals. Additions to the molecule, such as oxygen, which reduced the degree of conjugation so localising the $\pi$ electrons, produce an internal quenching effect, reducing the fluorescence efficiency (125). Quenching of electroluminescence could also take place in the presence of free electrons due to the electron trapping effect of oxygen, so preventing excitation of a fluorescent centre (19).

A further form of quenching known as 'concentration quenching' can occur due to the formation of non-fluorescent molecular complexes or
'dimers' due to strong Van der Waals' forces(129). Birks and Christophorou(130) describe four observed forms of concentration quenching between identical molecules and also report the formation of dimers between dissimilar molecules.

Literature on absorption and emission phenomena now covers several thousand references and no generally accepted model of the phenomena involved has emerged.

Kallman and Furst (131) suggest that provided absorption takes place in the solvent at shorter wavelengths than in the solute, energy transfer from solvent to solute takes place, so accounting for the relatively high emission intensities of dilute concentrations of fluorescent solute in non-fluorescent solvent. They propose an exciton mechanism similar to that proposed by Northrop and Simpson for solid solutions (132). This involves the migration of quantised energy from molecule to molecule during the lifetime of the excited state (about $10^{-8}$ sec) the exciton passing via up to $10^5$ molecules during its lifetime. Emission occurs when the exciton rests on a fluorescent molecule and results in the annihilation of the exciton.

Birks (133) suggests that 'exciton migration' (a mechanism more applicable to the crystalline structure of the solid phosphors) cannot account for the experimental evidence obtained using solutions and proposes that a simple intermolecular energy transfer occurs by a process of photon emission and absorption, the molecular emission overlapping the absorption band and only appearing externally when the absorption becomes relatively insignificant.
2.8.4. **Effect of change of state and molecular size**

The molecular fluorescence of organic compounds is similar in the vapour, solution and solid states. Fig.17 illustrates the absorption and emission spectra for anthracene (134).

The absorption spectra for a given homologue series moves to the longer wavelengths as the size of the molecule increases. Those of the aromatics, benzene, naphthalene, anthracene and naphthacene being placed progressively from the ultra-violet into the visible wavelength regions. The paraffin molecules of corresponding molecular weight all yield absorption spectra lying in the ultra-violet region. This overlapping of absorption bands makes the spectroscopic analysis of complex organic solutions such as transformer oil extremely difficult.
Potential energy curves for a diatomic molecule

Fig: (16)

Absorption and emission spectra of Anthracene

Fig (17)
3. EXPERIMENTAL APPARATUS AND TEST PROCEDURE

3.1. Introduction

The test apparatus built for the preliminary tests was based on that used by Gosling and Angerer (18, 22).

Modifications were subsequently made to allow independent degassing of the sample and the cell and vacuum system.

The test cell was similar in construction to that of Gosling and Angerer suitably modified for the requirements of the present work.

The test apparatus consisted of an oil purification system in which the test cell formed an integral part, a vacuum system and a gas system.

The general arrangement of the test equipment is shown in Fig. 18.

3.1.1. The high voltage supply

A stabilised Brandenberg E.H.T. Generator type S0530 was used as the d.c. high voltage source for the test cell. The output voltage could be adjusted between 1 kV and 30 kV, the regulation at full load and with ±5% to -10% mains voltage fluctuation being better than 1%.

A filtering arrangement consisting of a 0.05 μF, 20 kV capacitor together with a 1 MΩ resistor was connected between the cell and power supply as shown in Fig. 19. The standing current through the 300 MΩ potential divider across the test cell ensured that negligible voltage regulation existed at the high voltage terminal of the cell due to conduction current fluctuations. The 1 MΩ resistor in the E.H.T. output lead served to
Fig. (18). General arrangement of apparatus.
limit the charging current to the capacitor and the 1 k\Omega resistor served to depress the thyatron anode voltage and limit grid current when the diverter operated. This resistor was of wire wound construction and oil immersed to dissipate the capacitor energy without damage.

All high voltage leads were of screened coaxial cable and joints and connections were carefully soldered and coated with Apezion Q compound to inhibit corona discharges. These precautions were necessary to avoid spurious signals appearing in the photomultiplier anode current.

The test cell voltage was measured using a 300 M\Omega oil immersed, high stability resistor chain in series with a 50 \mu A moving-coil meter (Taylor Instruments). Pye scalamp 0-15 and 0-40 kV electrostatic meters were used to calibrate the resistor chain which was found to be linear within \( \pm 1\% \) of \( V(kV) = 0.3 \times I(\mu A) \). The calibration was checked periodically and always found to be within \( \pm 2\% \) of the nominal value.

In order to minimise the effects of sudden supply voltage changes on the high voltage supply the apparatus was supplied from a Claude-Lyons automatic voltage stabiliser type BTR-13F.

3.1.2. Diverter unit

To minimise the effect of breakdown damage on the electrodes and decomposition in the test liquid it is very desirable to reduce the energy dissipated in the breakdown spark.

The energy stored in the gap cannot be diverted, but that in the external circuit can, by short-circuiting the high voltage terminal of the test cell to earth. Fig. 19 shows a circuit similar to one...
devised by Saxe and Lewis (137) and used by previous workers (18,19,22,26). The 2D21 thyratron is fired by the breakdown current pulse across the 100 kΩ cathode resistance. The thyratron discharges the 0.03 μF capacitor through the 500 Ω cathode resistance triggering the XH16-200 hydrogen filled thyratron and shorting the cell.

3.1.3. Measurement and recording of the conduction current and electroluminescence signals

The conduction current was measured using a T.I.A. electrometer type VC99 having ranges covering $10^{-5}$ to $10^{-12}$ Amperes, the maximum voltage drop occurring in the instrument was less than 1 Volt.

The electroluminescence from the sample was detected by means of a photomultiplier, the photocathode of which was placed as close as possible to the test cell.

The mean value of the photomultiplier anode current was measured using a General Radio Type 1230-A d.c. amplifier and electrometer. This had an input decade resistance adjustable over the range $10^4 - 10^{11}$ ohms and could measure voltage signals developed across the input resistance between the limits of 30 mV to 10V. The voltage was not permitted to exceed 3V so that photomultiplier linearity was preserved.

Both electrometers has facilities for recorder output and fed a Southern Instruments double channel amplifier and pen recorder. The time constant of each channel being approximately 30 m.s.

A complete record was made of each test so that the effects of stress conditioning and breakdown on the signal fluctuations and magnitudes could be studied. At the end of each test the recorder trace was
calibrated via each electrometer input.

3.1.4. Detection of Electroluminescence

The low intensity of the electroluminescence observed by Darveniza and Gosling made it evident that a high sensitivity photomultiplier was required with a small photo cathode area to minimise the dark current and with good U.V. sensitivity (since the observed luminescence was mainly blue in colour). An E.M.I. 9526B photomultiplier was chosen, this tube also has a reasonably fast rise time and good transit time spread characteristics. The tube data are given in the table below:

3.1.4.1. Photomultiplier details

The following data was supplied with the tube.

Fused Quartz window; 11 stage Cs.Cb. dynode, box and grid structure; Cs.Cb.O Photo-cathode 23 mm diameter with Sl3 spectral response, see Fig.(20).

<table>
<thead>
<tr>
<th>EMI 9526B Photomultiplier Tube</th>
<th>Typical Value</th>
<th>Actual Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode sensitivity µA/Lm</td>
<td>70</td>
<td>50</td>
</tr>
<tr>
<td>First dynode gain</td>
<td>6.5 at 150V</td>
<td>5.5 at 100V</td>
</tr>
<tr>
<td>Overall gain A/Lm</td>
<td>200 at 1100V</td>
<td>200 at 1260V</td>
</tr>
<tr>
<td>Dark current µA at anode</td>
<td>2 at 1100V</td>
<td>0.4 at 1260V</td>
</tr>
<tr>
<td>Rise time</td>
<td>10 ns</td>
<td></td>
</tr>
<tr>
<td>Transit time spread</td>
<td>20 ns</td>
<td></td>
</tr>
</tbody>
</table>

Mean Quantum efficiency 15% (see spectral response)

Mean current gain, \( G = \frac{200}{50} \times 10^6 = 4 \times 10^6 \) electrons per photo-electron
Spectral Response S13 Photo Cathode

Fig: (20)
3.1.4.2. Photomultiplier high voltage supply and potential divider

An Isotope Developments Ltd. E.H.T. unit, type 532D was used to supply the photomultiplier dynode resistor chain. This unit was designed specifically for photomultiplier supplies and was capable of supplying a dynode chain current of 5 mA when set on the 700-1500 V range. The photomultiplier was supplied at 1260 V throughout all the experimental work so that the calibration data supplied with the tube could be used. The supply unit specification included the following:

- Less than 0.02% output voltage regulation for ± 10% change in mains voltage or frequency, less than 50 mV peak to peak output voltage ripple.
- Short term drift better than 0.02% in 24 hours.

Dynode potential divider resistor chain

The total resistance of the chain shown in Fig. 21 was calculated to give the maximum permissible load on the power supply of 5 mA. The figure also shows the circuitry used for displaying the anode current pulses described in Section 4.1.1.6.

Effect of dynode currents on interstage voltages obtained from the potential divider

If

\[ n = \text{number of dynode stages} \]
\[ \delta = \text{mean secondary emission factor} \]
\[ I_k = \text{is the cathode current and} \]
\[ I_b = \text{the dynode resistor chain current} \]

It can be shown (136)

\[ \frac{\text{Variation in gain}}{\text{gain}} = \Delta G \bigg( \frac{\delta^n}{I_b} \bigg) \]

\[ \text{thus for a gain } G = 4 \times 10^6, \delta = 4.5, I_a < 100 \mu A \]

and \( I_b = 5 \text{ mA} \)

\[ \frac{\Delta G}{G} = 0.4\% \]

a figure regarded as satisfactorily small.
Photomultiplier dynode chain

Test point for $V_{C-D_1} = 100\text{V}$

8 off 17$k\Omega$ each.
3 off 34$k\Omega$

To photomultiplier base pins

-1260V IDL PHT Supply

100$k\Omega$

30$k\Omega$

Coaxial lead to C.R.O. matched termination

Grounded emitter impedance matching circuit

Electrometer measuring mean value of electroluminescence.
Incorporates photomultiplier anode resistance $\approx 10^6\Omega$.

**Fig. (21).** Photomultiplier circuitry.
3.1.4.3. **Anode current characteristics**

During the course of the preliminary experimental work the photomultiplier signal was found to consist of a stream of discrete pulses as described in Section 4.1.1.6. These pulses are subject to various amplitude distributions as discussed in the following paragraphs.

Each pulse observed at the anode is due to at least one photo-electron at the photo-cathode and signifies the existence of a discrete event in the stressed region of the gap.

Typical life time of excited molecules are of the order of $10^{-8}$ to $10^{-9}$ seconds and the duration of the resultant photon about $10^{-9}$ seconds (134). These times are much shorter than the photomultiplier transit time spread which is about 20 ns, so that the observed pulse shape will be determined by detecting circuit time constants.

**Relationship between the number of photo-electrons at the photo-cathode and the mean anode current**

With a mean quantum efficiency of 15% (see Fig. 20) approximately 7 photons will produce 1 photo-electron at the photo-cathode and a pulse of Ge coulombs at the anode of the photomultiplier.

so $\frac{\text{Photo-electrons/sec}}{\text{sec}} = \frac{G}{Ge}$ where $G = 4 \times 10^6$

Hence, 1600 photo-electrons per second at the photo-cathode will give a mean anode current of 1 m\(\mu\)A

**Anode current pulse amplitude distribution**

Each photo-electron produces on average $G$ electrons at the anode. Due to the time dispersion of electrons brought about by
variations in interdynode transit times, the electrons do not arrive
at the anode simultaneously. The rate of arrival varies in an
approximately Gaussian Distribution with a time spread of about 10 n
seconds.

Since the time constant of the detecting circuitry is large
compared with the time spread, the mean height of the resultant output
voltage pulse due to 'n' photo-electrons will be proportional to Gn.
Since n is an integer, the output pulses might be expected to have
amplitudes proportional to n.

However due to variations in the value of secondary emission in
the tube, the value of G will vary pulse by pulse introducing an amplitude
distribution. The variation in G arises mainly at the first dynodes
where the secondary electron population due to the original primary
electron is still small. The secondary emission coefficient is known
to vary appreciably about the mean value event by event (138). This will
result in large variations in the number of dynodes respective avalanches
traverse before their population increases sufficiently for the conditions
e.g. when n \( \sim 100 \), \( \delta \sim 10\% \) for the remaining stages so that
of a normal distribution to apply, the height of the anode pulse will
be proportional to \( \delta^n \) where n is the number of remaining stages to be
traversed by the avalanche before reaching the anode. Thus if n differs
by 1 for successive pulses their amplitudes would differ by the value of
\( \delta \) (about 5). The anode current pulses will therefore vary appreciably
in amplitude due to the statistical variations of the secondary emission
phenomena.

Photomultiplier dark current

The photomultiplier was operated under calibrated conditions
requiring an E.H.T. voltage of 1260V, for which the dark current was as
calibrated, 0.4 μA. This current is equivalent to 640 photo-electrons/sec. Most of the dark current is due to thermal electrons from the emission surfaces. Many of these will originate from the dynode surfaces resulting in variations of gain dependent on the originating dynode position. Such electrons will therefore suffer less than the total gain G of the tube producing anode current pulses distributed in amplitude and of mean value less than those associated with pulses due to photo-electrons.

3.1.5. **Visual observation of electroluminescence**

The sensation of brightness in the human eye due to light of constant power will depend on the wavelength of the light, rising from zero for wavelengths shorter than about 4,000 Å to a peak about 5,500 Å and falling to zero around 7,600 Å. Under these conditions the central or Foveal region of the eye is employed (see Fig. 23).

Under conditions of very low intensity, such as occur on the limits of visual perception, Rod perceptors located in the peripheral regions of the eye are used rather than Foveal vision. Rod vision gives rise to the "Purkinje" effect which is typified by the 'blue centred' appearance of objects lit by moonlight. Rod vision is approximately 100 times more sensitive to low intensity light than Foveal and has a spectral response as shown in Fig. 23.

Much of the electroluminescence was viewed under Rod vision conditions due to its low intensity. This fact made observation of the electroluminescence location difficult to establish due to the necessity in many cases to orientate the eye so that the electroluminescence fell
on peripheral regions of the retina making focussing and resolution of
the image difficult. Colour assessment of the electroluminescence
under these conditions will be subject to the blue centred response
of the eye.

3.1.6. Spurious light output

Considerable difficulty was encountered throughout the
preliminary tests with spurious luminescent effects.

The stress shield shown in Fig. 28 was fitted to relieve the
stress in the region of the sharp metal edge embedded in the glass-metal
seal at the anode. This reduced the spurious effects considerably but
did not eliminate them. Two further effects were identified, the first
(reproducible) effect was caused by the cell applied field at the photo-
cathode producing spurious photo-electrons. This was eliminated by
electrostatic shielding as shown in Fig. 22. The second effect
(irreproducible) was found to be due to air humidity on the cell window,
patches of water vapour causing local intensification of the stress
distribution along the surface and in the glass wall of the cell. The
leakage current along the cell surface probably causing discharges due to
local discontinuities in the vapour film. These were reduced to a

negligible level by closing a glass boat containing \( \text{P}_2\text{O}_5 \) for the duration
of a test within the light and air tight shield around the cell as shown
in Fig. 22.

The spurious light output level was checked after the completion
of every test and was always less than 1 \( \mu \text{A} \) with the gap set to 2,500 \( \mu \)
with the highest voltage used in the test applied.
3.1.7. **Determination of spectra**

All spectra were obtained with a liquid sample optical path of 1 cm. A Unicam S.P. 800 ultra-violet spectrometer was used for the extinction spectra. The absorption spectra were obtained on a Zeiss recording spectrometer type RPQ 20 and the emission spectra using the above with a fluorescence attachment ZFM20.

Spectroscopic grade n-hexane was used throughout in the blank cell for the extinction and absorption spectra and all the solutions tested without dilution.

The Unicam extinction spectra are plotted to a linear base of wavelength increasing to the right, whereas the Zeiss absorption and emission spectra are plotted linearly to a base of wavenumber increasing to the left.

\[
\text{Where Wavenumber, (cm}^{-1} = \frac{10^8}{\text{Wavelength, (\AA)}}
\]
and \(1 \text{ m\AA} = 10^2\)

The extinction, \(\varepsilon = \log_{10} \frac{1}{T}\) where \(T\) is the per-unit transmission. The absorption \(A, = 1-T\). The two scales \(\varepsilon\) and \(T\) can be seen plotted vertically at each side of the Unicam extinction spectra, as in Fig. 108.

The arrangement of the Zeiss spectrometer gave the absorption plotted linearly, increasing downwards from the top of the record and the emission increasing linearity upwards from the bottom. The emission scale is arbitrary, but all the spectra shown in Section 4 were obtained with the same sensitivity and slot settings so that amplitudes may be directly compared in accordance with the scales shown. The slot widths for irradiation at 3650\(\text{\AA}\) and 3130\(\text{\AA}\) were adjusted to give the same irradiation intensity at each wavelength (see Appendix C).
All the emission spectra shown in Section 4 are uncorrected for the detector response, which is the same as that for the electroluminescence photomultiplier shown in Fig. 20. The spectral response of the detector extends to 6500Å and reference to the emission spectra of Section 4 shows that this extends beyond the emission bands of the solutions tested. Thus the rapid fall in emission intensity is not due to the shape of the detector response, though some attenuation of the emission spectra will result for wavelengths beyond 4500Å.

The emission spectra were obtained with the sample cell in each of two positions, termed the 'oblique' and 'perpendicular' cell arrangements respectively. Fig. 24 shows the cell arranged in each of the positions, the emission being detected in a plane perpendicular to that of irradiation. With the cell in the perpendicular position emission is detected from the bulk of the liquid (mean path length about 1 cm). The oblique cell arrangement allows the emission from the surface to be detected. This emission is less subject to the effects of quenching and self-absorption. Oblique cell spectra are subject to reflection errors from the glass at wavelengths just longer than that of irradiation, this error is deducted by obtaining the reflection from the empty cell, suitably adjusted to allow for the double surface reflection.

3.2. The oil purification system

A general view of the apparatus is shown in Fig. 18, the oil purification and vacuum system being shown in greater detail in Fig. 25:

A 600 ml degassing flask was arranged as shown in Fig. 26 so that degassing could proceed using the magnetic stirrer with both the Bl4
Rod vision

Foveal vision

Variation in eye intensity (average)

FIG: (23).

PERPENDICULAR CELL

Oblique Cell.

FIG: (24).
Fig. (25). Oil purification and vacuum system.
cone and socket entry and the \( \frac{1}{4} \)" bore nylon exit tube above the liquid level.

The flask was arranged so that after degassing was completed it could be tilted to pass the sample out of the exit tube and down to the sintered glass filter.

All cone joints used in the apparatus were sealed with neoprene O-rings in the vacuum system and Viton-A O-rings in the oil purification system.

Nylon 66 tubing was used throughout in the oil and vacuum systems (18) where relative movement between parts of the system was such as to preclude the use of glass tubing. Where this movement was large such as at the degassing flask, the nylon-glass nipple joints were reinforced externally with araldite and bound with wire to prevent the joint working. Greaseless stop cocks with Viton-A diaphragms were used throughout the oil purification system.

A reservoir was connected between the filter and the test cell to collect the filtered oil. Both the reservoir and the test cell could be connected to the vacuum line by stop cocks 4 and 6 respectively.

The cell was emptied by gravity into a collecting flask via stop cocks 8 and 9, the spur between the cocks being provided in case connection to an aneroid or pressure transducer was required.

The oil system was terminated with a B14 cone to allow the collecting flask to be emptied and replaced by the hexane refluxing system used for cleaning the oil system between tests.

Joints were incorporated in the oil purification system to allow
the sintered glass filter to be changed for each type of liquid sample, this was found necessary to reduce the possibility of contamination from the previous sample. The joint was designed to minimise the possibility of trapping contamination and to allow liquid flushing under gravity with the axis of the filter vertical. The filter arrangement is shown in Fig. 27.

3.3. Vacuum system

Two rotary pumps each with a P₂O₅ moisture trap and a liquid air trap were connected to the vacuum system as shown in Fig. 26. One pump, reserved for rough degassing of the sample and pumping off hexane after flushing the system, was connected directly to the entry cone of the degassing flask via stop cock 11. Access to the pirani gauge was obtained via stop cock 3. The other pump, kept for degassing the cell and final degassing of the sample, was connected via stop cock 17 to the main vacuum line; which was equipped with various greaseless stop cocks arranged to allow vacuum or gas to be supplied to any part of the system. The position of the pirani remote from the final degassing pump prevents a pressure less than that in the cell and other parts of the system being measured.

The provision of the rough degassing pump arrangement prevented the remainder of the apparatus suffering from oil vapour absorption in the walls of the vacuum line and oil purification system below stop cock 1. Oil was not permitted past stop cock 1 until its vapour pressure had been reduced to about 1 x 10⁻³ mm Hg and stop cock 3 was only opened for a minute or so towards the end of the degassing period (with cocks 4, 7 and
Fig. (26). General arrangement of Apparatus
Fig.: (27) Details of exchangeable filter.
12 closed), to monitor the degassed state of the liquid sample. As a consequence of the above arrangement it was possible to obtain a vapour pressure of $10^{-3}$ mm Hg in the oil purification and vacuum system enabling the cell and electrodes to degas whilst the degassing of the liquid sample proceeded independently in the degassing flask. Also this arrangement prevented surface contamination of the pirani element which would result in some inaccuracies of the pressure calibration. Vapour condensing on the elements causes their dissipation to rise giving a pessimistic value for the state of vacuum.

3.4. **The test cell**

The test cell constructed as shown in Fig. 28 consisted of a glass tube made from two glass metal seals, the liquid volume being approximately 20 ml. Two 'Spectrosil B' optical flat windows were provided for viewing the gap. The front flat to allow microscopic examination of the gap and the back flat to allow the gap to be illuminated from the rear and provide optical access for the photomultiplier cathode which was placed approximately 1 cm from the flat. This distance was maintained constant throughout the experiments.

The low voltage electrode was insulated from the adjacent glass-metal seal to exclude leakage currents flowing via the cell walls during the conduction current measurement. As can be seen in the drawing this was effected by attaching the electrode to a glass hermetic seal (Cathodean Ltd. type 3124) which was soldered into a stainless steel tube, the electrode connection being brought out by welding a 0.036 Nickel-chrome wire to the Kovar wire of the seal, the connection being insulated from the stainless steel tube by P.T.F.E. tubing.
Fig.(28) Glass Test Cell
The electrode connection was taken to a coaxial lead and was completely screened by an earthed enclosure.

The high voltage electrode was connected directly to the glass-metal seal at the high voltage end of the cell, the spring loaded solid stainless steel shank butting on to the ball bearing against the micrometer anvil. The spring was strong enough to return the high-voltage electrode against the vacuum pressure and O-ring friction.

The cell was made vacuum tight by means of the Viton-A O-rings sealed between the electrode stems and the brass ends of the cell.

A photograph of the cell arrangement is shown in Fig. 29.  

3.5. Measurement and observation of the electrode spacing

Adjustment of the inter-electrode gap was affected by means of a spring loaded micrometer. In all cases the gap was set by reducing the gap setting, this ensured that the micrometer anvil was always firmly against the electrode end.

The micrometer was calibrated in thousandths of an inch (about 25 micron) with a vernier allowing the calibration to be further subdivided by ten.

'Zero gap' was adjusted using a detector in which the gap is inserted in series with the grid of a pentode such that when contact is made the pentode anode current indicated on an ammeter is cut off. This arrangement, due to Lewis (14), is very sensitive to change of resistance in the grid circuit. The apparent gap setting at near contact varying from full anode current to cut off with the lightest touch on the end of the micrometer. It was never possible to obtain a mid-scale reading. The
Fig. (29). The test cell.
required spacing was then added to the 'zero' micrometer reading, the electrode retracted and fed back by the micrometer to the setting required.

Visual observation of the gap

Microscopic observation of the gap was possible with the assistance of a tungsten-filament light source at the rear of the cell (in place of the photomultiplier) either directly behind for silhouette illumination of the gap, or inclined at approximately $30^\circ$ to the microscope axis for dark field illumination, this allowed small particles to be detected by the presence of diffraction patterns.

The microscope was generally used with a magnification of 100 using a 1.2 inch objective and an x25 eye piece.

3.6. The gas system

The system was supplied from a gas cylinder feeding through a pressure reducing valve via a silica-gel system to dry and remove ionic impurities from the gas. A mercury U-tube allowed the pressure to be monitored over the range ±1 atmosphere, the gas finally passing to the equipment via a No. 4 porosity filter.

The gas was then passed into the apparatus gas system shown in Fig. 26 where it successively passed through No. 4 sintered glass filter, further silica-gel columns and finally a No. 5 sintered glass filter; the gas being admitted to the vacuum line via stop cocks 14 and 12 or 13.

Before allowing gas to enter the vacuum system a steady flow of gas was passed to atmosphere via stopcocks 14 and 16 until it was felt
that any air included in the gas system had passed to atmosphere. The stop cock between the U-tube and the gas line and stop cock 16 were then closed and 15 opened to the rough vacuum, the gas supply was then restored and the rough vacuum removed. Gas was then admitted to the vacuum system where required. This procedure ensured that only dry gas entered the oil and vacuum system.

3.7. Preparation of electrodes

In common with previous workers (18, 19, 22, 26, 27) the electrode surfaces were polished using a high speed mop impregnated in hexane, one side of the mop having a small amount of buffing compound added to remove deep scratches or breakdown sites.

Darveniza (19) found that the scatter in breakdown values was smaller with mechanically polished electrodes than for electrolytically polished ones.

El-Dine et alia (95) have recently confirmed Darveniza's conclusions.

After the initial polishing very little subsequent polishing was necessary to remove the breakdown craters of the previous test, but much more care had to be taken to avoid scratches appearing whilst polishing. So far as was possible the electrode was always kept in an atmosphere of hexane, by keeping the mop well saturated with hexane and storing the electrodes under hexane.

A microscope of 100 magnification was used to inspect the electrodes which consisted of 5 mm diameter spheres made from spectroscopic grade nickel.
The electrodes were secured in place on the stainless steel electrode holders in the cell by means of 12 BA grub screws as shown in Fig. 28. During polishing and reassembling into the cell the electrodes were immersed in hexane or its atmosphere and were not touched by hand. The electrode was polished on a mandrel which replaced the cell electrode holder and was transferred to the electrode holder by means of a tool which threaded into the continuation of the 12 BA grub screw hole. After polishing, both electrodes on their holders were held in a hexane filled polythene bag and cleaned in an ultra-sonic bath.

In the test cell the electrodes were subjected to a further vigorous flushing in hexane as described in the next section.

3.8. Cleaning the liquid system and the test cell

Whenever the apparatus was opened to the atmosphere, nitrogen was admitted to the system at above atmospheric pressure to prevent the ingress of air and water vapour.

Immediately following a test the sample was removed and the collecting flask replaced. The electrodes were also removed for inspection and stored on their mandrels under hexane. The electrode shanks were replaced in the apparatus to seal the cell apertures. The degassing flask cone was opened and 40 ml of distilled and filtered hexane poured into the flask with nitrogen entering the flask via the exit tube. The cone and O-ring were then replaced and the nitrogen in the flask sealed off by closing valves 1, 3, 11 and 14. (Fig. 25). Valve 15 was then opened to admit the rough vacuum to the oil reservoir with 5, 7, 13 and 16 closed and valves 4 and 12 open. With the vacuum in the reservoir 4 and 15 were
closed and 14 opened. The hexane was swilled vigorously around the degassing flask whilst in the tilted position and valve 1 opened to draw the hexane through the filter thus flushing the filter and upper part of the oil system. Valves 3 and 4 were then opened to equalise the gas pressure and all the remaining stop cocks opened to allow the hexane to drain to the collecting flask.

The above procedure was then repeated with a further 40 ml of distilled hexane.

If the next sample was of different composition to that previously tested the filter was changed as follows:

The replacement filter was flushed with hexane in the 'reverse flow' direction and then in its forward flow direction. The entry of the filter was identified by the tag describing the filter liquid tied around it. The clamps on the existing filter joints were removed and the filter and O-rings removed, nitrogen passing to the atmosphere from each of the system orifices. The replacement filter was immediately put in position with fresh O-rings and the clamps replaced, care being taken to see that the filter bedded satisfactorily in position.

After polishing and cleaning the electrodes were replaced using new O-ring seals and the cleaning of the system continued.

The collecting flask was removed and flushed with hexane, and put aside whilst its place was taken by the hexane refluxing apparatus. The degassing flask was placed in the tilted position and the refluxing column connected. Stop cocks 3 and 11 being closed and the cone flushed with hexane and covered with a blanking socket with O-ring.
The apparatus used for refluxing the hexane consisted of a 300 ml flask provided with two B14 sockets. An electric heating mantle on the flask warmed the hexane to about 40°C. One B14 socket was placed with O-ring into the bottom B14 cone of the oil purification system and the glass refluxing-column cone placed with O-ring in the other B14 socket. The B14 cone and O-ring at the top of the refluxing column was placed in the degassing flask entry socket. Stop cocks 6, 7, 10 and 13 were then closed leaving an access between the gas supply and oil purification system via stop cocks 1, 2 and 4.

The first stage of the final cleaning of the system using refluxed hexane flushed the oil system above the reservoir. Stop cock 5 was closed to isolate the upper portion of the oil system and the gas supply cock 14 was closed and the rough vacuum admitted to the oil reservoir via cock 15, the pressure in the oil reservoir dropping rapidly well below the vapour pressure of hexane at 40°C. Stop cock 4 was then closed before the pressure differential had disappeared across the filter and the hexane allowed to boil, refluxed hexane would then distill in the degassing flask whilst the latter was still cool and pass down to the filter. The hexane being drawn through the filter by the pressure differential into the oil reservoir.

Stop cock 15 was then closed and gas re-admitted to the reservoir via stop cock 4. Stop cock 5 was then opened allowing the hexane to return to the refluxing flask. 5 was then reclosed and the whole process repeated several times.

The last stage in the cleaning process was to flush the lower
part of the system up to the oil reservoir, to do this stop cock 5 was left open and 4, 14 and 15 manipulated as detailed in the previous paragraph, the hexane jetting up first as vapour then progressively as condensation as the vacuum in the reservoir disappeared, the whole of the reservoir, under side of the filter, cell and lower part of the system being vigorously flushed whilst a smaller quantity of refluxed hexane still circulated via the refluxing column and down through the filter. As the process was continued the pressure differential was slowly reduced so that the final flushing of the cell was done gently. Nitrogen was again restored to all parts of the apparatus, all greaseless stop cocks apart from 17 and 18 being opened, the refluxing apparatus removed and the collecting flask replaced with a new O-ring seal. The B14 entry cone was replaced in its socket in the degassing flask also with a new O-ring seal. 14 was closed and the rough vacuum applied to the whole of the system for several hours removing most of the remaining hexane. The pirani gauge was heated with the hot air blower to accelerate evaporation of absorbed hexane vapour. The system vapour pressure at this stage being about 5 mm Hg. By this means most of the hexane vapour was removed by the rough vacuum pump so avoiding contamination of the final degassing pump oil. Whilst the hexane was being removed from the apparatus the next test sample was prefiltred as described in Section 3.9.

The apparatus was now ready for adding the test sample and for the final degassing of the system and cell.

Cock 11 was closed, both degassing pumps started and 18 opened. 1, 4, 7 and 13 were closed and 17 opened so that final degassing of the
cell and oil purification systems could proceed whilst the sample was degassed.

The new sample was then quickly added to the degassing flask through the B14 entry socket, nitrogen still flowing via 14, 12 and 3 to the B14 cone. The cone was then replaced with its O-ring seal and the degassing flask clamped over the magnetic stirrer. Valves 3, 12 and 14 were then closed, 7 opened and the vacuum checked on the pirani, the pressure now approaching 1 mm Hg. Pumping continued during the system degassing period, liquid air being added to the trap when the vapour pressure had fallen to 0.1 mm Hg or less. The final vacuum of $1 \times 10^{-3}$ mm Hg was obtained fairly rapidly and maintained until the final degassing stage of the sample was reached.

3.9. Preparation of test liquids

All the solvents and solutions were stored in a light-tight cupboard. All the glassware was cleaned as described in Appendix A and flushed several times with liquid paraffin before admitting the solution. The transformer oil was collected from Gulf Oil (Gt. Britain) Ltd. and kept in $2\frac{1}{2}$ litre flasks previously used for hexane and flushed several times with clean oil at the suppliers premises before filling.

Preliminary filtering of samples

The glassware used to pre-filter the sample was first cleaned as described in Appendix A. The 1µm pore size filter appropriate to the sample under test was then flushed, first in the reversed flow direction and finally in the forward flow direction; a partial vacuum being applied to ensure a vigorous cleaning action. The apparatus was then assembled
comprising, a filter funnel open to the atmosphere, the filter, a 2 socket collecting flask kept exclusively for pre-filtering and the rough vacuum and nitrogen line; all joints were B14 cone and socket with O-rings. The complete assembly was then given a final flushing with hexane, pumped and warmed with the hot air blower. About 50 ml of the sample was then added and the rough vacuum applied to the collecting flask. As the filtrate passed through the filter it was partially degassed, and collected in the flask.

The first portion of the sample to be filtered was always poured off, the flask then being replaced and filtering continued until the liquid fell into the upper side of the filter, when dry nitrogen was admitted to the flask to stop the filtering action and to allow the sample to be transferred to the apparatus. Again the first portion of the sample was poured away to flush the neck of the flask and a residue left after pouring the sample into the degassing flask in the apparatus.

3.10. Degassing the sample

The pre-filtered and partially degassed sample was transferred to the degassing flask as described in Section (3.8.) and vigorously stirred with the magnetic stirrer whilst the pressure was reduced by the rough degassing pumps via 11 and 18 (2 closed). The remainder of the system including the test cell receiving its final degassing to $1 \times 10^{-3}$ mm Hg using the final degassing pump. After some 2 days of degassing the liquid vapour pressure would fall to about $3 \times 10^{-1}$ mm Hg at which pressure liquid air was added to the rough degassing pump trap. Degassing then continued for a further 8 to 10 days by which time the vapour pressure
over the liquid had usually fallen to $2 \times 10^{-3}$ Hg. As mentioned in Section 3.3., monitoring of the liquid vapour pressure was done as infrequently as possible before the liquid was in its final degassed state to prevent contamination of the pirani gauge and vacuum system, oil impregnated glass surfaces requiring a much longer period of degassing than when impregnated by hexane.

When the liquid vapour pressure had fallen to $2 \times 10^{-3}$ mm Hg, 4, 6 and 8 were closed and 3 and 7 opened, the two pumps working in tandem. This reduced the pressure over the sample to $1 \times 10^{-3}$ mm Hg, and after several hours 11 and 18 were closed and the rough degassing pump shut down.

During the course of the experimental work contamination of the sample due to back streaming from the rough degassing cold trap was found to occur when the vacuum pumps were connected in tandem. The degassing procedure was therefore modified in subsequent tests to avoid tandem operation.

Pumping continued with the final degassing pump until the pressure of $1 \times 10^{-3}$ mm had been maintained over the liquid for 48 hours. Stop cock 7 was then closed and the pressure rise noted on the pirani. Provided the pressure did not exceed $5 \times 10^{-3}$ after several minutes the liquid was regarded as sufficiently degassed. Liquid paraffin was found to require several more days degassing than transformer oil. Stop cock 3 was then closed and 7 opened to restore the vacuum at the pirani. 7 was closed and 4 opened to check the test cell vacuum. 6 was then opened to restore the vacuum. The stirrer was switched off and the degassing flask tilted to allow the test liquid to flow down the exit tube. 1 was then
opened and the filter filled with test liquid. Stop cock 4 was closed and 3, 12 and 14 opened to admit dry nitrogen above the liquid in the degassing flask so applying a differential pressure across the filter of approximately 1 Atmosphere. 3, 6 and 12 were then closed (6 to prevent nitrogen entering the degassed cell) and 7 opened to restore the vacuum on the pirani. When full vacuum had been obtained 7 was closed and 6 opened. The pirani was then used to monitor the rise in vapour pressure in the oil reservoir as filtering proceeded by opening stop cock 4. Provided the pressure did not rise to more than $6 \times 10^{-3} \text{ mm Hg}$ the sample was accepted. This pressure rise was always carefully watched, particularly as the liquid level above the filter entered the nylon exit tube, to detect the diffusion of nitrogen into the test liquid. Had this occurred the sample would have been rejected. It was found that the pressure rise in the oil reservoir was the most reliable test of adequate degassing. As the liquid level entered the exit tube of the degassing flask, 2 was shut and 7 opened to maintain the vacuum above the liquid.

Stop cock 5 was then opened and about 5 mL of liquid allowed to flow into the cell, 8 was then opened to drain the cell. Stop cock 5 was closed slightly to allow the liquid to enter the cell slowly and 8 and 10 closed. Care being taken to see that the liquid surface tension wetted the glass completely as the cell filled. Stop cock 5 was closed as the liquid started to rise in the inlet tube giving a hydrostatic head of liquid of about 1.5 cm (18 mm Hg). Pumping continued for a further 18 hours ready for
electrical testing the following morning.

3.11. Test procedure

After setting the gap and adjusting the microscope, the equipment was rendered light-tight and the photomultiplier dark current and E.H.T. voltage checked to see that they agreed with the calibration values. The dark current figure ensured that no extraneous light was being detected.

The electrometer zeros and pen recorder were checked and a continuous pen recording taken for the whole period of the test.

As reported by Kambamonda (20) and succeeding workers (18,27) it was found necessary on applying the stress to increase its value steadily up to 250 kV/cm and then fairly rapidly over the range 250 - 500 kV/cm maintaining the stress at 600 kV/cm for some two hours. This period is termed the stress conditioning period.

The stress was then varied in 100 kV/cm steps, generating the electroluminescence and conduction characteristics. This procedure is described in greater detail in Section 4.

3.12. Gap settings and electrical stress range

The major part of the electrical experimental work was concerned with measurement of the electroluminescence and conduction current as a function of the nominal stress in the highly stressed region of the spheresphere gap. Gap settings of 125, 81, 51 and 28 μ were used with 5 mm diameter polished nickel spheres. The choice of gap setting and sphere material and size was arranged to allow direct comparison with the work of Gosling (18), Angerer (22), Nossier (26) and Megahed (27).
The stresses quoted are estimated on the assumption that the sphere diameter to gap ratio is large enough to allow an approximation to a parallel electrode uniform field configuration to be made for the highly stressed region, the curvature due to the spherical form serving to localise the highly stressed region.

The possibility of the appearance of particle activity and the rapid fall in the conduction current value at stresses below 300 kV/cm usually determined the lower limit of the stress range. The upper stress limit is that set by the breakdown strength of the sample. In most tests it was necessary to spend an appreciable proportion of the time the liquid was stressed at high values of stress to allow observation of the electroluminescence phenomena.
4. EXPERIMENTAL RESULTS

4.1. Introduction

The experimental work covered in this section is mainly concerned with the continuance of the study of conduction current and electroluminescence phenomena first observed by Darveniza and Tropper (19,120).

In the following section some results are presented from preliminary tests. These tests were made to check the experimental apparatus and instruments and to evolve a standard procedure which could be adhered to throughout the remainder of the work.

The test liquids used for the work described in this section were liquid paraffin, 1-methyl-naphthalene and transformer oil. Most of the tests were conducted using liquid paraffin as the solvent with 1-methyl-naphthalene, anthracene and Popop respectively as the solute. Transformer oil was also tested to allow correlation with the results of the other workers mentioned in the text. In general only low concentrations of solute could be tested due to the low solubility of anthracene or Popop in liquid paraffin. 1-methyl-naphthalene was tested with liquid paraffin from 0 to 100% concentration by volume.

Relevant data regarding the physical properties and specification of the above solvents and additives are given in Appendix B.

4.1.1. Phenomena noted during the preliminary tests

4.1.1.1. Particle activity

Very little, if any, particle activity was observed in the liquid under stress in any of the tests reported in this work; however considerable particle activity was noted in a preliminary test using liquid paraffin.
Similar activity has also been observed by the author and by Gosling (18) in transformer oil.

Using dark field illumination and a x100 microscope, the gap was watched continuously for over thirty minutes and the phenomena illustrated in Fig. 30 observed.

Large uncorrelated fluctuations in the conduction current and electroluminescence signals were generally found to be associated with particle activity in the stressed region of the gap (see section 4.1.1.3).

4.1.1.2. **Wax formation on electrodes.**

In a test on liquid paraffin the liquid was stressed continuously for over eight hours between 600 and 700 kV/cm. No breakdown occurred during the whole of the test. The electrodes were inspected immediately after the test using a x100 magnification microscope and no wax could be detected on either electrode. The electrode surfaces appeared to be in the same condition as they were after polishing.

4.1.1.3. **Effect of prolonged stressing of sample on the electroluminescence**

The electroluminescence and conduction current were almost invariably very erratic at the commencement of the stress conditioning period. Usually most of the breakdowns recorded during stress conditioning occurred during this period.

Provided no breakdown occurred, the electroluminescence signal settled to a steady value after some thirty minutes of stress conditioning. A further period would be required to re-stabilise the electroluminescence if a breakdown occurred.

In one of the preliminary tests on liquid paraffin the stress was
Occasional particles climb up at the electrode centre as though to form a bridge and then rapidly move off into the liquid.

'Comet tail' along stress line.

Particle rotates in outer orbit for some time then moves into the inner orbit with an increased angular velocity. The particle then returns to the outer orbit several minutes later, the velocity reducing to approximately the original value.

No correlation was observed between the radius of the orbit and the conduction current fluctuations associated with particle activity.

Fig. (30). Particle activity.
maintained at 600 kV/cm for more than eight hours during which time the
electroluminescence and conduction current values decreased by about 30%.
No breakdowns occurred in the last seven hours of this period. This result
demonstrates that the electroluminescence and conduction current processes
can be assumed to be stationary during the time taken to generate the
conduction and electroluminescence characteristics.

4.1.1.4. Use of soda glass filter

During a test on a sample of \(5 \times 10^{-6}\) M/100g anthracene in liquid
paraffin, a soda glass filter was inserted between the cell window and the
photomultiplier. This filter having a cut-off between 3,000 and 3,500°C.

No change in photomultiplier signal was noted other than a slight
reduction due to the filter transmission in the visible range of the spectrum.
This suggests that the spectral range of the electroluminescence is
consistent with the emission spectral range of the solution when irradiated
with ultra-violet light, as given in Fig. 138.

4.1.1.5. Conduction current characteristics under repeated stress cycling
conditions

Fig. 31 shows the characteristics obtained for the 125\(\mu\) gap setting
from \(1 \times 10^{-5}\) M/100g anthracene in liquid paraffin. The figure demonstrates
the reproducibility of the phenomena when the liquid is fully stress
conditioned after the last breakdown and when breakdown does not occur during
stress cycling.

4.1.1.6. Photomultiplier anode current pulses

Using the circuitry described in section 3.1.4.3, the electroluminescence signal was displayed on an oscilloscope. The photographs
Fig. (31)

**Repeated stress cycling conduction current against stress characteristic.**

125 μm gap.

Key to plots:
- * descending values 1st stress cycle
- × ascending “ 2nd.
- ○ descending “ 3rd.
- △ ascending “ 4th.

Graph shows the relationship between mean stress (kV/cm) and conduction current (Amperes) for different stress cycles.
shown in Fig. 32 are typical of the phenomena observed with various test liquids.

It would be of considerable importance to demonstrate whether or not multi-photon events occur in the stressed region of the gap. Unfortunately, the amplitude distributions of the pulses shown in Fig. 32 are subject to too many factors to allow any such demonstration to be readily made. Some of the factors affecting the detection of multi-photon events are given below.

(a) The spatial distribution of photons emitted from the stressed region is such that only a small fraction of the photons emitted by a multi-photon event will be intercepted by the photo-cathode of the multiplier.

(b) The quantum efficiency of the photo-cathode will result in a similar effect on photo-electrons to (a) above.

However (a) and (b) will still result in occasional multi-photo-electron events occurring (discounting the probability of time coincidence of independent single-photon events)

(c) The variations in pulse amplitude discussed in Section 3.1.4.3. due to the statistics of secondary emission result in amplitude distributions as shown in the adjacent figure, (155) similar in form to those obtained in avalanche phenomena (156).

Factor (c) can produce an amplitude distribution such as to mask the existence of multi-photo-electron events, the probability of which is greatly reduced by factors (a) and (b).
Anode current 1mµA

Anode current 10mµA

Anode current 100mµA

Anode current 1000mµA

Anode current 10000mµA

Time scales: Figs: (a)(b)(c)(d)and(f), lcm = 1ms; Fig(e), lcm = 2µs.

Fig: (32)

Photomultiplier anode current pulse distributions
for various mean anode current values
An I.D.L. Type 1700 Scaler was used to count the anode current pulses and a count rate approximately proportional to the anode current was observed. It was not possible to count and measure the mean anode current simultaneously. Due to the limited counting rate and the relatively long counting time constant of 1.5 seconds, it was decided to record the fluctuations in the mean anode current, rather than those of the pulse count rate.

4.1.2. Stress conditioning

As found by previous workers (18,19,22), the liquid required stress-conditioning for a considerable time to minimise the occurrence of particle activity during the generation of the conduction-current against stress characteristic. The stress-conditioning period was standardised at two hours at a stress of 600 kV/cm before any readings of conduction-current against stress were taken. In the event of a breakdown occurring, the liquid was stress-conditioned for approximately ten minutes before the stress was changed. Often at stresses greater than 900 kV/cm this period was shortened due to the increased probability of a further breakdown. All the tests described in this work were conducted using a sphere-sphere electrode configuration.

4.1.3. Stress-cycling

After the two hour stress-conditioning period at 600 kV/cm the conduction-current against stress characteristic was obtained by reducing the stress in 100 kV/cm steps, the stress being held constant for approximately two minutes, whilst the electroluminescence and conduction current were monitored on the pen recorder. If either of the latter showed strong
fluctuations the stress was held for a longer period until stable conditions were obtained. After reducing the stress from 600 kV/cm to about 200 kV/cm the stress was then increased in 100 kV/cm steps following the method used in decreasing the stress. The stress was then steadily increased in steps to a value approaching that typical of the liquid breakdown value; this procedure generated the first stress cycle.

The procedure was then continued once again decreasing the stress in 100 kV/cm steps to 100-200 kV/cm and then increasing the stress in similar steps up to the maximum obtainable without successive breakdowns occurring. This procedure completed the second stress cycle.

A similar procedure was followed for each gap setting. The stress-conditioning period for any gap setting smaller than the previous setting was about ten to thirty minutes at a stress of 600 kV/cm. The time depending on the stability of the electroluminescence and conduction current.

4.2. Tests using neat liquid paraffin

4.2.1. General

Four tests on liquid paraffin are described below. For convenience these tests are identified as samples 'a', 'b', 'c' and 'd' respectively. Tests 'a' and 'b' were successive tests using different samples degassed for one week from the same bottle of liquid paraffin. Tests 'c' and 'd' were successive tests carried out a year later from a second bottle of liquid paraffin. Test 'c' was degassed for one week and test 'd' for two weeks.
4.2.2. Conduction current against stress characteristics

4.2.2.1. Comparison with previous workers

Fig. 33 shows the conduction-current/stress relationships obtained by Angerer (22), Nossier (26) and Megahed (27) for degassed liquid paraffin using the same gap, 125 μ and 5 mm diameter nickel, sphere-sphere electrodes. The present work can be seen to give good agreement with previous work.

4.2.2.2. Effect of breakdown on conduction characteristics

It was found that the conduction-current for a given stress was usually greater after a breakdown even after the post breakdown stress conditioning period. The effect was most marked with the first few breakdowns and less so as the number of breakdowns increased. The effect is illustrated in Fig. 34.

4.2.2.3. Reproducibility of conduction-current characteristics

Two characteristics for pre-first breakdown conditions were obtained for the 125 μ gaps for samples 'a' and 'b' respectively. See Fig. 35. Slight particle activity was present in sample 'a' and only the 125 μ gap was tested before a breakdown occurred. With sample 'b' however the 125 μ, 81 μ, 51 μ and 26 μ gap settings were tested before the first breakdown occurred.

Several breakdowns occurred during the stress conditioning periods by samples 'c' and 'd'.

Previous workers have found the conduction-current characteristics difficult to reproduce and the present work is no exception. The characteristics for sample 'b' is almost a straight line but that of
sample 'a' shows a pronounced curvature.

Fig. 36 shows that even after two breakdowns, the conduction-current in sample 'c' was still less than the pre-first breakdown values for sample 'b'.

Comparing the conduction-currents after two breakdowns in samples 'b' and 'c' shows that of sample 'b' to be approximately in order and a half greater than that of sample 'c'. Both curves have a similar curvature despite the relative displacement already mentioned. Similar effects to the above have also been noted by Zaky, House and Tropper (88) - see section 2.3.4.

4.2.2.4. Effect of number of breakdowns on reproducibility

Fig. 37 shows that the reproducibility improves as the number of breakdowns increase. In this comparison each sample had several breakdowns prior to the generation of the characteristics plotted. Agreement between the characteristics is closer and suggests that further conditioning of the liquid and electrodes occurs. Darveniza (19) found that reproducibility was improved by breakdown conditioning of the electrodes.

4.2.2.5. Gap dependence

It was observed that the conduction-current for a given stress decreased with gap size for pre-first breakdown conditions as shown in Fig. 38.

As the number of breakdowns increase the gap dependence becomes less marked. Fig. 39 demonstrates the reduced gap dependence after 6 breakdowns and the curvature typical of the post breakdown characteristic.
Conduction Current (Amperes)

| Sample | Degassed Liquid Paraffin 125\(\mu\) Gap Breakdown Dependence | Sample 'b'
<table>
<thead>
<tr>
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<th></th>
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</thead>
<tbody>
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</table>

**Fig. (33)**

**Fig. (34)**

**Fig. (35)**

**Fig. (36)**
The pre-first breakdown conduction characteristics for sample 'b' in Fig. 38 show an approximately exponential relationship for each gap Fig. 40 demonstrates the increased curvature of the conduction-current characteristic after four breakdowns. The transposition of the 28 \( \mu \) characteristic above that of the 125 \( \mu \) setting is difficult to account for, no additional breakdown between the 51 \( \mu \) and 28 \( \mu \) gap settings being apparent on the pen recordings. A similar effect was obtained after several breakdowns with sample 'a', the 81 \( \mu \) and 28 \( \mu \) gap characteristics being coincident. Similar transpositions have been noted by Gosling (18) and Angerer (22).

It is often difficult to compare gap settings in a given test since a breakdown will invariably result at the highest stresses* reached at the first or some subsequent gap setting. The breakdown disturbs the gap dependence relationships and produces a permanent change in the conduction-current characteristic consequent to the breakdown.

4.2.2.6. Hysteresis effects

The generation of the conduction-current characteristic over the whole of the stress cycle would occasionally produce a hysteresis loop. Hysteresis effects were sometimes pronounced but had little obvious consistency, although in general the conduction-current was found to be slightly higher for descending values of stress than for ascending values. The effect becoming more noticeable as the number

* High stresses were necessary throughout this work to obtain measurable electroluminescence yields.
Effect of breakdowns on reproducibility.

Fig: (37)

Fig: (38)

Fig: (39)

Fig: (40)
of breakdowns occurring in the sample increased. Fig. 41 illustrates
a particularly clean loop effect obtained from sample 'c'.

4.2.2.7. Electrode inspection

After each test the electrodes were examined under a microscope
which had a magnification of 100.

A thin layer of wax was observed over the active area on the anode,
the thickness being roughly dependent on the number of breakdowns
occurring in the sample. In the case of samples 'c' and 'd' several
dark smudges each of similar size to a breakdown site were noted.
Cleaning off the wax with stockinette soaked in hexane removed the
carbonised patches leaving a polished and apparently undamaged electrode
surface apart from the breakdown damage. As will be noted in later
tests, the hysteresis effects noted in the previous paragraph were more
obvious when carbon was present in the electrode wax layers.

The cathode appeared to be clean, little if any wax being
present on the surface.

The breakdown sites were fairly centrally placed in the active
area of each electrode, being of typical 'rim and crater' type (18).

4.2.2.8. Observation of the illuminated gap

The gap was inspected during each test using dark field
illumination as described in section 3.5.

Only in the case of sample 'a' were one or two particles seen
on the electrodes. These occasionally moved over the surface in a manner
similar to that already described in section 4.1.1.1.

The layers were of very soft wax. It was not possible to measure the layer thickness
with any precision, but the correspondence between the layer thickness and the
number of breakdown sites on the electrode was evident throughout the tests.
The thickest layer was obtained in a preliminary test using liquid paraffin.
In this test over 100 breakdowns occurred, producing a layer about 20 μ thick.
The visual absence of particles however, does not preclude the existence of particles of smaller size, which would produce diffraction patterns at shorter wavelengths beyond the spectral range of the tungsten filament source illumination and of the eye.

4.2.3. **Electroluminescence against conduction current characteristics**

4.2.3.1. **General**

The characteristics shown in the following graphs are from the same tests previously described in section 4.2.2. Attempts were made to plot the electroluminescence as a function of stress, but, as will be seen later, due to the very strong dependence of the electroluminescence on conduction current, and electrode conditions, the scatter in the plots was too large to allow meaningful curves to be drawn. However, the conduction current appears to be a function of stress and electrode conditions, and independent of the electroluminescence. Consequently plots of electroluminescence against conduction current are more consistent and have much less scatter.

It can be seen from sections of the recordings shown in later figures that the electroluminescence phenomena were subject to apparently erratic fluctuations. As mentioned in section 4.1.3., the stress was maintained at a constant value for a period long enough to allow consistent minima to appear in the signal variations. And it was from these values that the characteristics were plotted.

4.2.3.2. **Pre-first breakdown characteristics**

Fig. 44 shows the electroluminescence plotted against conduction current (both to a logarithmic scale) for the 125 μ gap sample 'b'. The
Liquid Paraffin

Sample c

Stress Cycle Hysteresis

Key to plots for curves:
- Descending values 1st stress cycle
- Ascending values 1st stress cycle
- Descending values 2nd stress cycle
- Ascending values 2nd stress cycle

Degassed Liquid Paraffin Sample c

Stress (kV/cm)

Conduction Current (Amperes)

Fig: (4-1)

Degassed Liquid Paraffin 125 μm Sample d

Stress (kV/cm)

Conduction Current (Amperes)

Fig: (4-2)

Degassed Liquid Paraffin Sample a

Debreakdown

Key to plot symbols as Fig: (4-1)

Number against plot denotes stress in kV/cm.

Degassed Liquid Paraffin Sample b

Debreakdown

Key to plot symbols as Fig: (4-1)

Number against plot denotes stress in kV/cm.

Plate multiplier Anode Current (mA)

Conduction Current (Amperes)

Fig: (4-3)

Conduction Current (Amperes)

Fig: (4-4)
electroluminescence is plotted in arbitrary units, (milli-micro-amperes of photomultiplier anode current). The slope can be seen to approximate to $45^\circ$ suggesting a linear law. It should be noted however that the scatter in the plots is such that a slight curvature of the characteristic is possible. Towards the end of the first stress cycle the characteristic shifted downwards by approximately half an order giving a characteristic of the same slope for the second stress cycle.

This break in the characteristic is indicative of a permanent change in the conditions in the gap.

The relevant section of the pen recordings of electroluminescence and conduction current where the break in the characteristic occurred is shown in Fig. 45.

The pre-breakdown characteristic for sample 'a' is shown in Fig. 43; a similar slope being obtained for the characteristic.

4.2.3.3. Gap dependence (pre-first breakdown)

The corresponding electroluminescence characteristics for the $125 \, \mu$, $81 \, \mu$, $51 \, \mu$ and $28 \, \mu$ gaps for sample 'b' are shown in Figs 44, 46 to 48.

Fig. 49 shows that for a given conduction current the electroluminescence is independent of gap setting. This suggests that the electroluminescence is mainly due to an electrode-liquid interface effect rather than volume effect. The increased electroluminescence for the same stress at larger gap setting is due to the increase in conduction current with gap setting (see Fig.38).
Conduction Current

600 kV/cm

700 kV/cm

Electroluminescence

Time: 0 → ½ mins

Liquid Paraffin sample 'b': Pre-breakdown stress cycling.

Electroluminescence

Conduction Current

fall in current and abrupt rise in electroluminescence

Continued
Below

FIG: (45)
Hundreds of kV/cm
degassed:
Liquid Paraffin
PRE-BREAKDOWN
Sample 'b'
28 µm gap
Plot symbols as
Fig (44)

Fig. (46)

Fig. (47)

Fig. (48)

Fig. (49)

Degassed Liquid Par.
PRE-BREAKDOWN
Sample 'b'
51 µm gap

Degassed Liquid Par.
PRE-BREAKDOWN
GAP DEPENDENCE
Numbers denote stress in hundreds of kV/cm.

Conduction Current (Ampere)

Phosphomultiplier Anode Current (mA)

Conduction Current (Ampere)

Conduction Current (Ampere)
The electroluminescence characteristic for sample 'a' (125 μ gap, pre-first breakdown shown in Fig. 43) is coincident with that for sample 'b' under the same conditions, despite the non-characteristic conduction current characteristic shown dotted in Fig. (35). This demonstrates the dependence of the electroluminescence on the conduction current.

4.2.3.4. Gap dependence (post-breakdown)

The characteristics obtained following breakdown are shown in Figs. 50 to 53. If plotted on a common graph, the characteristics can be made to almost coincide; the scatter in the experimental results is such that no gap dependence is evident.

Comparing Fig. 43 (125 μ gap pre-breakdown) with Fig. 50 (81 μ after 3 breakdowns) at similar values of stress shows that the electroluminescence is approximately one order greater with a corresponding increase in conduction current; demonstrating that breakdown effects can eclipse gap dependence effects.

The characteristics obtained from samples 'c' and 'd' also give approximately 45° slopes for the 125 μ gap as shown in Fig. 54 and 55. Several breakdowns occurred during the stress conditioning period for each of these samples and this probably accounts for the increased scatter in the plots. A similar effect was noted in the post-breakdown tests for samples 'a' and 'b'.

Superposition of the 125 μ gap characteristics for samples 'c' and 'd' (Figs. 54 and 55) shows a nearly coincident, the electro-
luminescence being roughly one order greater than for samples 'a' and 'b' at a given conduction current.

A post breakdown electroluminescence characteristic for the 51 μ gap, sample 'c' is shown in Fig. 56, the electroluminescence being slightly greater than that for the 125 μ gap for the same conduction current or stress.

4.2.4. Electroluminescence against stress characteristics

These have not been plotted, as already mentioned in section 4.2.3.1. The strong dependence of the electroluminescence on the conduction current makes an electroluminescence against stress plot misleading without reference to the conduction current obtained for the particular stress under consideration. However the existence in most cases of a straight line log-electroluminescence against log-conduction current characteristic suggests that the electroluminescence against stress characteristic will be of similar shape to the conduction current against stress characteristic.

4.2.5. Visible observation of electroluminescence

During the preliminary tests it was found that the threshold of visual perception of the electroluminescence occurred when viewed through the microscope for measured values of electroluminescence in excess of 3,000 mμA.

This value was not reached in any of the tests so far described, within the range of stress used to generate the characteristics.

However, the intensity in the 51μ gap test on sample 'c' was just sufficient to allow occasional filamentary channels to be seen. The filaments appeared to lie along the stress lines in the gap.
Sample c' after 5 break downs
125 μm GAP
Symbols as on Fig. (24).

Conduction Current

Fig. (54)

Degassed Liquid Par
Sample 'd'
After 6 break downs
125 μm GAP

Fig. (55)

Degassed Liquid Par
Sample 'c'
After 5 break downs
51 μm GAP

Fig. (56)
Sometimes a transient spot, which slowly waxed and waned in intensity, could be seen at the root of a filament.

4.2.6. Recorded fluctuations of electroluminescence and conduction current

4.2.6.1. General

As described in section 3.1.3, the outputs from the electrometers metering the electroluminescence and conduction current were fed to a pen recorder. The time constants of the current and electroluminescence channels were of the order of 30 msec.

4.2.6.2. Particle activity during stress conditioning

Fig. 57 shows a section from the recording of sample 'd' illustrating the fluctuations in the conduction current associated with particle activity. The abrupt steps and violent fluctuation of the conduction current are accompanied by very erratic variations in the electroluminescence signal. This part of the record occurred approximately 30 minutes into the stress conditioning period after the occurrence of three breakdowns. The clearance of the particles probably by ejection from the gap (16) was followed by more quiescent conditions as indicated by the latter part of the figure. Both the conduction current and electroluminescence decreased in value as the particle activity disappeared.

4.2.6.3. Effects of stress conditioning and breakdown

It can also be seen from Fig. 57 that the correlation between electroluminescence and conduction current is not direct; though a change in conduction current is accompanied by a change in the electroluminescence. Improved correlation can be seen in Fig. 58 which is a later part of the
record taken between the first and second stress cycles.

Figs. 59 and 60 are successive sections of the record for sample 'c' taken after 45 minutes of stress conditioning. Particle activity was less marked in this test and the correlation between the two signals is clearer.

Figs. 61, 62 and 63 were taken five minutes later when three breakdowns occurred. No obvious reason for the breakdowns can be detected from the record, both the conduction current and electroluminescence being very steady before the event. The electroluminescence pattern is more erratic after, than before breakdown, but steadily settled, the correlation growing steadily towards the end of the figure. In the twenty minute period following the above the electroluminescence and conduction current steadily decreased to the pre-breakdown values as seen at the beginning of Fig. 64 which also shows the sixth breakdown to occur in this sample during the stress conditioning period.

4.2.7. Liquid paraffin spectra

4.2.7.1. General

As described in section 3.1.7. extinction, absorption and emission spectra were obtained for the samples, before degassing, after degassing and after testing.

4.2.7.2. Absorption and emission spectra before degassing

The absorption and emission spectra for the original liquid paraffin samples are shown in Fig. 65 for samples 'a' and 'b' and Fig. 66 for samples 'c' and 'd'.

Electroluminescence

600 kV/cm.

Conduction Current

\[ 3 \times 10^{-7} \text{A} \]

FIG: (59) Continued below

LIQUID PAR.
Sample 'c'.

STRESS 46 CONDITIONING 47 TIME

3,000 n\(\mu\)A

Electroluminescence

Conduction Current

\[ 3 \times 10^{-7} \text{A} \]

FIG: (60)

STRESS 48 CONDITIONING 49 TIME 50
Sample 'c': 600kV/cm Stress conditioning

Electroluminescence

3000 µA

Conduction Current

breakdowns

3x10^7 A

STRESS, CONDITIONING, TIME (MIN)

3000 µA

Electroluminescence

Stress conditioning

3x10^7 A

Conduction Current

Sample 'c'

1.3x10^7 A

Conduction Current

b.d.
The spectra show that the liquid paraffin from the first bottle, used for samples 'a' and 'b', has a lower absorption in the near ultraviolet range at 3,650 Å than that of the second bottle, used for samples 'c' and 'd'.

This difference in the absorption spectra is reflected in the emission spectra of Figs. 65 and 66.

Considering the emission spectra due to the 3,130 Å irradiation, the increased emission in Fig. 66 is a consequence of the greater absorption occurring in this sample at the irradiation wavelength. The slight difference in the spectral distributions is due to the steeper absorption front of Fig. 66. The increased absorption attenuating the higher of the two energy peaks apparent in Fig. 65.

4.2.7.3. Liquid paraffin sample spectra

Spectra were obtained for samples 'c' and 'd' after degassing and after testing. No change could be detected in the degassed and tested samples.

Absorption spectra

The respective absorption spectra for samples 'c' and 'd' are shown in Fig. 67 and 68. The effect of degassing on the absorption spectra is apparent in the case of sample 'd' and was found later to be due to 'back streaming' from the cold trap of the rough degassing pump. (The corrective measures taken to avoid this re-occurring were described in section 3.10)
Emission spectra

The absorption and 'perpendicular' cell emission spectra for samples 'c' and 'd' are shown in Figs. 67 and 68. These emission spectra are also shown with those of the oblique cell in Fig. 69.

The similarity in the spectral forms of the oblique and perpendicular spectra at both irradiation wavelengths for sample 'c' indicates that little self-absorption is taking place. The greater emission resulting from the 3,130 Å irradiation reflects the greater absorption at this wavelength.

Similar arguments apply to sample 'd' when irradiated at 3,650 Å. The emission intensity due to the 3,130 Å irradiation however, only reflects the absorption at 3,130 Å for wavelengths longer than 4,000 Å; at shorter wavelengths the emission is heavily attenuated by absorption processes. This applies to both perpendicular and oblique spectra.

The spectral forms have approximately the same proportions for the 3,130 Å irradiation with sample 'c' and the 3,650 Å irradiation with sample 'd'.

* See page 70
Fig: (67)
 Sample 'c'

Fig: (68)
 Sample 'd'

UPPER SCALE (linear): Wave Number in 10^3/cm
LOWER SCALE (reciprocal): Wavelength in m\(\mu\)
4.2.8. **Summary of liquid paraffin results**

The sketches shown in Fig. 71 compare the various conduction currents against stress characteristics, and those in Figure.72 the electroluminescence against conduction current characteristics.

All the pre-breakdown electroluminescence characteristics give a linear relationship without a break in the characteristic.

The electroluminescence is quite low in value and decreased with gap for a given stress, but is independent of gap setting for the same conduction current.

After breakdown the plots show increased scatter and the straight line relationship still holds for the 125 μ gap, but as the gap is reduced the slope of the characteristic suggests either a steeper slope straight line or a slightly curved line.

The conduction current and electroluminescence are greater after breakdown than before, the effect becoming more marked as the stress is increased. Reducing the gap now has less effect on the conduction current or electroluminescence for a given stress, due to the reduced gap dependence of conduction current mentioned in section 4.2.2.5.

Samples 'a' and 'b' gave approximately one order less electroluminescence for the same conduction current than samples 'c' and 'd'. This reduced yield can be correlated to some extent with the respective absorption and emission spectra, the greater absorption of 'c' and 'd' accounting for their greater yield.

The similar electroluminescence yields of samples 'c' and 'd' are compatible with their respective emission yields. The yield from
125 µ gap Pre-breakdown Conductance current Characteristics.

125 µ gap Effect of breakdown on Conductance Current Characteristic.

125 µ gap Post-breakdown gap dependence Sample 'c'.

Fig: (71)
Sample 'b' pre-breakdown.
Virtually no gap dependence

40 mA → 750 kV/cm
Log. Electroluminescence

Sample 'a' pre-breakdown
fits over 125 µ sample 'b'.

40 mA → 750 kV/cm
Log. Cond. Current →

Sample 'a' after
3 break downs

300 mA → 700 kV/cm

81 µ gap two tests 12 hours apart same curve. Also curve for 51 µ and 28 µ gaps. Same peak lumien.

Sample 'e' and 'd'
125 µ gap. Curves coincident.

1500 mA → 750
300 Sample 'e'
2 × 10^7 A

Comparison Samples
a, b and c, d.
sample 'c' being centred around 3,500 Å and is equivalent to irradiation in the band 3,300 - 3,000 Å e.g. irradiation in this wavelength region coinciding with the steep slope of the absorption front. The corresponding band for sample 'd' being in the region 3,800 - 3,500 Å.

4.3. Tests on 1-methyl-naphthalene and methyl-naphthalene and liquid paraffin mixtures

4.3.1. General

1-methyl-naphthalene (appendix B) was chosen as a convenient aromatic hydrocarbon, closely related to anthracene which is well known for its fluorescent properties. The vapour pressure and viscosity of this liquid are of similar values to those of liquid paraffin and transformer oil, so that a similar degree of degassing is possible.

The following paragraphs describe the test results obtained using 0.01% and 1% by volume methyl-naphthalene in liquid paraffin and also for neat methyl-naphthalene.

The above mixtures correspond to 2.5 x 10^{-4} and 2.5 x 10^{-2} molar fractions. Methyl-naphthalene appears to be fully miscible in liquid paraffin. The liquid paraffin solvent was the same as that used for samples 'c' and 'd'.

4.3.2. Tests on 0.01% by volume methyl-naphthalene in liquid paraffin

The sample was degassed for 2 weeks to a pressure of 2 x 10^{-3} mmHg and stress conditioned at 600 kV/cm for 2 hours prior to taking measurements.
4.3.2.1. Stress conditioning

Seven breakdowns occurred during the stress conditioning period. Six of these occurred as the stress was being established at the beginning of the test. Figs. 73 to 75 show the portion of the record illustrating the incidence of the 4th, 5th and 6th breakdowns. These were followed by a reduction in the conduction current and electroluminescence fluctuations; typical of the phenomena reported by the author (116) (see appendix D). Some correlation between conduction current and electroluminescence can be detected, this steadily increased as stress conditioning proceeded. Ten minutes later the electroluminescence rose fairly rapidly as shown in Fig. 76 accompanied by a rise in current value. The steadier nature of the conduction current in this figure should be contrasted with that fifteen minutes before in Fig. 74.

4.3.2.2. Conduction current against stress characteristics

Fig. 77 shows the characteristic obtained for the 125 μ gap. Three breakdowns occurred during this part of the test, the first at the end of the first stress cycle at 750 kV/cm. Prior to this breakdown considerable fluctuation in the conduction current occurred as seen in Fig. 80 the electroluminescence showing some correlation with the envelope of the conduction current signal. This suggests that the superimposed conduction current fluctuations may be attributable to the presence of particle activity, probably resulting in the breakdown at 750 kV/cm. After the breakdown (Fig. 81) the conduction current fluctuations are much steadier suggesting clearance of the particle from the gap or its disintegration.
Electroluminescence range 0.01% by volume Methy-Nap. in Lig. Paraffin.

**Fig: (73)**

Conduction Current

STRESS 7 CONDITIONING 8 TIME (MINUTES) *

**Fig: (74)**

Stress conditioning

**Fig: (75)**

**Fig: (76)**

Conduction Current
Fig. 82 shows the following section of the record where a steady growth in conduction current and electroluminescence at constant stress can be discerned (an effect which was also noted in the 51 µ gap characteristic).

The second breakdown occurred at 700 kV/cm at the end of the second stress cycle and Fig. 83 shows the strong correlation between immediately conduction current and electroluminescence even/after breakdown. No significant change in conduction current or electroluminescence followed this breakdown but stressing at 750 kV/cm for nearly ten minutes again produced a slow growth in conduction current and electroluminescence.

The gap was inspected, at this point and a diffuse glow more intense at the anode but without electrode spots, was seen extending into the gap.

The third breakdown occurred at 1000 kV/cm, the current increased slightly but showed very little fluctuation after the event, whilst the electroluminescence decreased slightly as shown in Figs 84 and 85.

The fluctuations were very small at high values of electroluminescence and conduction current as shown in Fig. 86. It is possible that the 'breakdown' shown on the figure is mal-operation of the diverter due to the high conduction current.

The 51 µ gap conduction current against stress characteristic is shown in Fig. 78. Superposition of those portions of the 125 µ and 51 µ gap characteristics generated for a similar number of breakdowns shows that the 51µ setting gives a larger current for the same stress.

* This anomalous increase in conduction current with time was not typical and a similar phenomenon was not observed in other tests. The increases shown in Fig. 78 occurred in each case over a period of 20 minutes during which time the current ceased to increase further. This effect was not apparent at lower stresses.
Conduction Current (Amperes)

Steady growth of current at constant stress

2nd b.d.

3rd b.d.

DEGASSED 0.01\% by Volume Methyl-Naphthalene in LIQU. PAR. 125\mu GAP

SYMBOLS AS ON FIG: (41)

DEGASSSED 0.01\% METH.-NAPHTHALENE IN LIQU. PAR. 51\mu GAP

SYMBOLS AS ON FIG: (41)

FIG: (78)

FIG: (77)
4.3.2.3. **Inspection of electrodes**

The cathode appeared to be clean and free of wax, the breakdown sites were grouped closely together; this factor could increase the probability of breakdown craters overlapping so that the emission from the cathode is not markedly effected.

The anode had a fairly thick layer of clean wax and compared with the cathode the breakdown sites covered approximately twice the area.

4.3.2.4. **Visual observation of electroluminescence**

During the test the electroluminescence for both gap settings appeared to be a medium blue. No spots were observed on the electrodes, the glow though faint, being diffuse and steady, more intense at the anode and appearing to extend well into the gap.

4.3.2.5. **Electroluminescence against conduction current characteristics**

The 125 μ gap characteristic is shown in Figs 87 to 89. Fig. 87 illustrates the first stress cycle, Fig. 88 the second stress cycle and Fig. 89 the combined characteristic.

The slope of the characteristic is greater than 45°; the displacement in the characteristic at 700 kV/cm can be located on the record at 'a' in Fig. 80. This displacement also took place in the second stress cycle but more gradually as seen in Fig. 88 which also shows that the third breakdown caused a further displacement of the characteristic.

Fig. 89 shows the characteristic for both cycles the superposition indicating a close relationship between electroluminescence and conduction current. The reproducibility of the break in the characteristic indicates
a current dependent change in gap conditions (note that the stress is not the same for each cycle). The incidence of the first breakdown after the transition has taken place suggests that gap conditions are unstable in the vicinity of the transition.

The $51 \mu$ gap characteristic is shown in Fig. 79. Several values taken from the stress conditioning period are also plotted on the characteristic as also are the range of values taken during the time spent at 700 and 800 kV/cm when both the electroluminescence and conduction current progressively increased. Superposition of the characteristics shows no significant gap dependence.

The lack of gap dependence indicates that the electroluminescence-conduction current mechanism may be primarily an electrode surface effect. The presence of wax on the anode and the observation of luminescence against this electrode supports this conclusion.

The break in the electroluminescence characteristic at the same value of current in each stress cycle suggests that the break may be due to a change in electrode surface conditions which is current dependent.

The continuity of the electroluminescence characteristic despite breaks in the conduction current characteristic supports the conclusion that the electroluminescence is strongly current dependent.
DEGASED 0.01% METHYL-NAPHTHALENE IN LIQUID PARAFFIN 125 µ GAP.
1st. Stress cycle.

Fig: (87)

DEGASED 0.01% METHYL-NAPHTHALENE IN LIQUID PARAFFIN 125 µ GAP.
2nd. Stress cycle.

Fig: (88)

FIRST AND SECOND STRESS CYCLES SUPERIMPOSED

Fig: (89)

Symbols as on Fig: (41).
4.3.3. Tests on 1% by volume 1-methyl-naphthalene in liquid paraffin

Two samples 'a' and 'b' were tested using the above concentration (2% molar fraction). In each case many breakdowns occurred during the stress conditioning period. Graphs plotted of conduction current and electroluminescence showed a great deal of scatter.

4.3.3.1. Sample 'a'

4.3.3.1.1. Stress conditioning

Sample 'a' was degassed for one week to $2 \times 10^{-2}$ mmHg. Since the vapour pressure of this solution is not significantly affected by the addition of the methyl-naphthalene it is possible that this sample was not thoroughly degassed. 25 breakdowns occurred during the stress conditioning period. The conduction current was erratic even at the end of the stress conditioning period as can be seen from Fig. 90, though the strong correlation between electroluminescence and conduction current is obvious.

4.3.3.1.2. Conduction current against stress characteristics

The conduction current against stress curves shown in Fig. 93 are similar in shape and magnitude to those for liquid paraffin after 25 breakdowns, illustrated in Fig. 33.

4.3.3.1.3. Electroluminescence against conduction current characteristic

Figs. 91 and 92 illustrate the difficulty in assigning a particular value of conduction current and electroluminescence for a given stress in order to plot Fig. 94. Under these circumstances the characteristics should be regarded with some caution. No breakdowns occurred during the generation of the characteristics.
Electroluminescence

Conduction Current

600kV/cm

Sample 'a'

Fig: (90)

100 nA

Electroluminescence

Conduction Current

Fig: 500kV/cm. 1% by volume Methyl-Naphthalene in Liq.Par.

Fig: (91)

1000 nA

Electroluminescence

Conduction Current

Fig: (92)
4.3.3.1.4. **Visual observation of electroluminescence and illuminated gap**

Due to the lower breakdown strength of the liquid the stress and conduction current could not be raised sufficiently to obtain electroluminescence levels perceptible to the eye.

The gap was inspected at the completion of the test, no opaque particles could be seen but several diffraction patterns resembling 'bubbles' were present with occasional movement on the surface of each electrode.

4.3.3.1.5. **Electrode inspection**

A very thin wax coating was detected on the cathode when inspected under the microscope. The anode had a moderately thick wax covering with some semi-opaque smudges on the surface of the wax suggestive of carbon deposits.

4.3.3.2. **Sample 'b'**

This sample was degassed for two weeks, the vapour pressure being reduced to $5 \times 10^{-3}$ mmHg.

4.3.3.2.1. **Stress conditioning**

In an attempt to reduce the number of breakdowns during the stress conditioning period the stress was maintained for one hour at 500 kV/cm and then raised to 600 kV/cm for the remainder of the period. Several breakdowns occurred on application of stress and continued intermittently for approximately 25 minutes. Occasional but less frequent breakdowns occurred for the remainder of the period. 12 breakdowns occurred during the
stress conditioning period. The initially erratic electroluminescence fluctuations steadily decreased as conditioning proceeded becoming very steady and of low amplitude by the end of the period.

4.3.3.2.2. Conduction current against stress characteristic

The conduction current characteristic has been drawn in Fig. 95 the scatter in the plots is such that no attempt has been made to separate the first and second cycle characteristics. No breakdowns occurred during the stress cycling. The conduction current for a given stress was approximately half an order less than for sample 'a'.

4.3.3.2.3. Electroluminescence against conduction current characteristic

As with sample 'a' erratic variations in electroluminescence and conduction current gave poor correlation between the two quantities and the comments made in paragraph 4.3.3.1.3 also apply here. The characteristic is shown in Fig. 96.

4.3.3.2.4. Inspection of electrodes

The electrode damage was consistent with the number of breakdowns, the breakdown craters being noticeably centralised in the active region of each electrode. The wax layer on the anode was fairly thick and appeared to be composed of clean wax. The cathode was slightly dirty suggesting a thin layer of carbon and wax.
Fig: (93)
Symbols as on Fig: (41)

Fig: (94)

Fig: (95)

Fig: (96)
4.3.4. Test on neat 1-methyl-naphthalene

Due to the relatively high vapour pressure of methyl-naphthalene (appendix B) it was only possible to degass the liquid to $3 \times 10^{-2}$ mmHg.

The sample was stress conditioned for two hours during which time 15 breakdowns occurred. The electroluminescence level was very high during this test and visual inspection of the gap showed considerable electroluminesence activity.

4.3.4.1. Stress conditioning

Five breakdowns occurred whilst establishing the 600 kV/cm conditioning stress. Fig. 97 shows a portion of the recording after five minutes of stress conditioning. The lack of correlation between electroluminescence and conduction current after each breakdown is evident. On several occasions a growth in the electroluminescence fluctuation occurred prior to a breakdown, as reported by Darvensza (19), such an occurrence is shown in Fig. 98. The majority of the conduction current record discontinuities do not produce full scale deflection of the recorder pen, whereas a few do. This suggests the possibility of partial breakdowns or discharges in the gap. The increasing correlation between the electroluminescence and conduction current as conditioning proceeds can be seen in Fig. 99 which shows conditions after six breakdowns and 45 minutes of stress conditioning. Several breakdowns followed shortly after this and are shown in Fig. 100. The post breakdown phenomena with the longer decay times shown in this figure should be contrasted with the very short decay times in Fig. 97.
Electroluminescence

Conduction Current

Fig: (97)

Stress Conditioning 6 Time (Minutes)

Conduction Current

Fig: (98)

Stress Conditioning 8 Time (Minutes)

Stress Conditioning

Fig: (99)

Stress 46 Conditioning 47 Time
The correlation at the end of the stress conditioning period though present, shows the electroluminescence to be very sensitive to changes in current, see Figs. 101 and 102. The fluctuations now being approximately one order less and varying at a much slower rate than at the beginning of the stress conditioning. Compare Figs. 97 and 102.

The lengthening of the post-breakdown decay times and the increased stability and correlation of the signals are thought to be associated with the formation of wax on the electrodes. Visual inspection of the gap showed strong electrode electroluminescence.

4.3.4.2. Conduction current against stress characteristic

As can be seen by inspection of Fig. 103 the low stress conduction currents were generally erratic and apart from the ascent of the second stress cycle, reproducibility was good. The conduction current is some two decades greater than that for liquid paraffin or the other methyl-naphthalene mixtures.

4.3.4.3. Electroluminescence against conduction current characteristics

Considerable fluctuation occurred in the electroluminescence signal whilst stress cycling which, whilst reflected to some extent in the conduction current, did not give a correlation as obvious or simple as that in the tests on liquid paraffin. Since the fluctuations were often erratic the stress had to be maintained at each value for considerable periods of time until consistent minima, or correlation in the fluctuations could be detected. Fig. 104 shows the characteristics, the relative displacements being due to the occurrence of breakdowns at the extreme values of stress.
El ec trum nesence

600 kV/cm 1-Methyl-Naphthalene

Break-down effects

Conduction Current

3,000 mµA

600 kV/cm Stress conditioning

Conduction Current

3 x 10^5 A

600 kV/cm

Conduction Current

3,000 mµA

Electroluminescence

600 kV/cm

Electroluminescence

3 x 10^5 A

Conduction Current

3,000 mµA

600 kV/cm

Conduction Current

3 x 10^5 A
Neat methyl-naphthalene gives a larger conduction current for a given stress, and the electroluminescence characteristic lies to the right of that for liquid paraffin as shown in Fig. 114.

4.3.4.4. Visual observations of electroluminescence

Considerable electroluminescent activity was observed in the gap at the higher stresses in this test. Several features of interest were noted and are illustrated in Fig. 105.

The anode patch existed continuously with slight slow movement at the periphery. Odd spots occasionally appeared around the patch on the anode and were usually paired with an existing cathode spot. These anode spots were fairly stable and lasted one to ten seconds. The cathode spots moved around more vigorously, but followed the occasional movement of the anode spot.

Under quiescent current conditions the anode patch was stable and stationary. Apart from the few transient cathode spots, little electroluminescence on the cathode was observed. The cathode spots were not numerous nor of long lifetime, typically a few seconds. The
variation in cathode spot lifetime was less than that of the less numerous anode spots.

The cathode 'flares' might be due to cathode spots out of the depth of focus of the microscope. The fewer, less bright anode spots would then be virtually undetectable under these conditions.

The electroluminescence signal remained steady whilst the anode patch was stable. Cathode or cathode-anode spots produced fluctuations on the recording for the period of their existence.

After a breakdown the whole gap was disturbed with violent agitation of the liquid. Many bright spots appeared on the anode, the gap being diffusely but brightly illuminated, possibly by myriads of small vapour bubbles due to gaseous products of the breakdown scattering the or
electroluminescence radiating from the electrodes from electroluminescence produced in the bubbles. Little activity was noted on the cathode following a breakdown, but as already mentioned, many spots appeared on the anode. Within 10-20 seconds of the breakdown the occasional cathode spot would return and the anode spots would coalesce to reform the anode patch.

N.B. In a later test on POPOP in liquid paraffin an intense sharply defined cathode electroluminescence was observed. The clean resolution of this line and the contrast in intensity with the adjacent liquid showed the scattering effect referred to above, would be too slight to account for the glow in the gap. Therefore the diffuse glow seen in the gap in many of the tests can be attributed to a volume effect, rather than scattering of the more intense electrode electroluminescence.
4.3.4.5. Inspection of electrodes

The following notes describe the electrode conditions observed through a microscope having a magnification of 100.

Anode

The wax layers surrounding the bright clean central area were thick and dark brown in colour. The breakdown sites were concentrated and all lay in the centre of the bright anode area. The deposit was easily removed by wiping with stockinette impregnated with hexane.

Cathode: This electrode was covered with a thin layer of semi-opaque, dirty wax. Several small areas of thinner wax through which the glint of the electrode could be seen, were dispersed around the centre portion of the electrode area.

The breakdown sites appeared to be covered by the thicker deposit and were very scattered, more so than in tests where the cathode was clean, suggesting that the cathode deposit prevented localisation of the breakdown sites.
4.3.5. Spectra

4.3.5.1. General

The spectra shown in this section are those obtained for the original sample (before degassing), the degassed but untested sample, and the tested sample.

4.3.5.2. 0.01% by volume methyl-naphthalene in liquid paraffin

Absorption spectra

The absorption spectra for the original sample, degassed sample and the sample after degassing and testing are shown in Fig. 107. The spectra for the degassed and the tested samples were identical. No significant differences due to the effects of electrical stressing and breakdown could be detected.

The shift in the absorption front due to the presence of methyl-naphthalene in the solvent can be clearly seen.

Slight contamination of a similar nature to that detected in the liquid paraffin samples was also present, the much reduced level of contamination showing that the corrective measures taken were becoming increasingly effective.

Emission spectra

The effect of degassing and of testing on the emission characteristics can also be seen in Fig. 107.

The optical activity of methyl-naphthalene is apparent in the spectra shown in Fig. 107. For, with 2 molecules of methyl-naphthalene to $10^4$ of liquid paraffin, the extinction at $3130\, \AA$ has increased by 60% and the emission by 90%, relative to that of the solvent alone.

* See page 122
The absorption at 3650 Å is almost entirely due to the solvent (see the extinction spectrum for methyl-naphthalene shown in Fig. 108). Consequently the emission when irradiated at this wavelength is similar to that obtained for the solvent alone. This can be confirmed by reference to Fig. 66.

The degassed and the tested samples both show increased emission at longer wavelengths, a second peak occurring at 27,000 cm⁻¹ (3700 Å).

The reduced probability of self-absorption occurring at 3650 Å and longer wavelengths is demonstrated by the similarity of the oblique and perpendicular cell spectral distributions when irradiated at 3650 Å, in keeping with the lower absorption at this and longer wavelengths.

Comparison with Fig. 69 liquid paraffin sample 'c', shows the spectra to be of similar form, the greater intensity of the short wavelength emission peak being due to the methyl-naphthalene, adding to that of the liquid paraffin.

It is well known (126) that with certain aromatic compounds the extinction and emission spectra show a mirror symmetry, and this can be seen by comparing the oblique cell 3130 Å irradiation of the original sample with the extinction spectrum for methyl-naphthalene shown in Fig. 108. This symmetry obtains when the concentration quenching is not excessive, the extinction small and the irradiation wavelength short.
FIG: (107)

0.01% by volume
1-Methyl-Naphthalene in Liquid Paraffin

DEGASSED AND TESTED SAMPLES

UPPER SCALE (linear): Wave Number in 10^3 cm
LOWER SCALE (reciprocal): Wavelength in μm
1-Methyl-Naphthalene diluted 1 part in 50,000 in Chloroform against Chloroform.

FIG: (108)
4.3.5.3. Spectra for 1% methyl-naphthalene in liquid paraffin

These are shown in the following figures. No difference in the degassed and the tested samples was detected.

Absorption spectra

Two samples were tested; sample 'a' degassed for one week, and sample 'b' degassed for two weeks. The absorption spectra shown in Fig. 109 show the effect of methyl-naphthalene and slight degassing contamination.

The shift in the absorption front to longer wavelengths due to the methyl-naphthalene can be seen when compared with that for the liquid paraffin solvent.

Emission spectra

The emission spectra for the original, degassed and tested samples ('a' and 'b') are shown in Figs. 110 to 112.

The similarity of the perpendicular and oblique spectra when irradiated at 3650Å suggest that concentration quenching is not appreciable, despite the 100 fold increase in concentration to 0.02 molar fraction (143). Due to the low emission attributable to methyl-naphthalene in the 0.01% solution, it is difficult to estimate if the emission is in proportion to the increase in concentration.

Assuming no change in the degree of quenching occurs when irradiated at 3130Å the effect of self-absorption is obvious in the different forms of the oblique and perpendicular spectra.

The modification to the degassing procedure to prevent back streaming from the rough degassing cold trap (as described in section 3.10)
Figure (111)
Sample 'a'

Figure (112)
Sample 'b'

Upper scale (linear): Wave number in 10\(^3\)/cm.
Lower scale (reciprocal): Wavelength in μm.
was put into effect earlier, in the test on the 0.01% methyl-naphthalene sample. This resulted in much lower contamination levels during degassing. However a new source of contamination was evident in sample 'b' and was found to be due to slight deterioration and swelling of the neoprene diaphragm on the greaseless stopcock above the test cell. This was remedied by replacing all the diaphragms in the oil system with ones made of 'Viton-A'.

Neoprene and Viton-A 'O'-rings were tested for deterioration by immersing for several weeks in methyl-naphthalene, liquid paraffin and transformer oil solvents. Only the neoprene in the methyl-naphthalene solvent showed any signs of deterioration.

4.3.5.4. Neat methyl-naphthalene spectra

Absorption

Figs. 113 shows the absorption spectra for neat methyl-naphthalene. The figure also shows the absorption spectra for 0.01% and 1% methyl-naphthalene mixtures, illustrating how the absorption front steadily moves to the longer wavelengths with increasing concentration.

Emission spectra

The effect on the emission spectra of the shift of the absorption front to longer wavelengths, due to the 100-fold increase in concentration, is very marked.

The emission due to 3130Å irrigation is greater in the long wave half of the spectra than that for the 1% solution, though concentration effects limit the ratio of increase to 1/5th of the concentration ratio. The high absorption present in the short wave half of the spectra attenuates the emission amplitude due to self-absorption processes.
The figure below illustrates the effect of increasing concentration competing with increasing self-absorption and concentration quenching.

![](image)

**Fig. (114).** Emission spectra for two concentrations, $c_2 > c_1$

Similar arguments apply to the 3650Å irradiation, though the emission process is much more efficient here due to the close proximity of the 3650Å irradiation wavelength to the absorption front.

The absorption front suppresses the shorter wavelength peaks evident in Fig.110. But the longer wavelength peak free of the absorption front, is 30 times the magnitude; confirming that concentration quenching is not of predominant importance in methyl-naphthalene (148).

Thus as suggested for the 1% emission spectra, methyl-naphthalene emission is dominated by the absorption front.

4.3.6. **Summary of methyl-naphthalene results**

As with the liquid paraffin results, the correlation between the electroluminescence and conduction current increased with both the stress conditioning time and the number of breakdowns. The breakdown voltage of the gap also increased with the number of breakdowns, provided the breakdowns were infrequent and of limited number. This effect was less obvious as the methyl-naphthalene concentration was increased to 1%...
Fig: (113)
Neat Methyl-Naphthalene
Absorption Spectra

Fig: (113)
Neat Methyl-Naphthalene
(tested sample)

3130Å Irradiation
oblique cell
perpendicular cell
Absorption

3650Å Irradiation
perpendicular cell
oblique cell

UPPER SCALE (linear): WAVE NUMBER IN 10^9/cm.
LOWER SCALE (reciprocal): WAVELENGTH IN µm.
and higher. The breakdown strength appeared to be increased for small 
methyl-naphthalene concentrations and then rapidly fell to that of methyl-
naphthalene (~ 600 kV/cm) for higher concentrations.

A summary of the characteristics obtained is shown in Fig. 114.

The addition of 0.01% methyl-naphthalene appeared to have little 
effect on the conduction characteristic, which virtually coincided with that 
for liquid paraffin sample 'c', the same solvent as used in the methyl-
naphthalene solutions. A similar comment applies to the electroluminescence 
characteristic. The extension of both the conduction current and electro-
luminescence characteristics would appear to be solely due to the enhanced 
breakdown strength of this particular sample.

The conduction current characteristics for the 1% methyl-
naphthalene samples showed similar dependence on the number of breakdowns to 
that noted for liquid paraffin. The general effect of increasing 
concentration was to increase the electroluminescence for a given stress. 
However, due to the reduction in breakdown strength at higher concentrations, 
the maximum electroluminescent yield obtainable was not increased 
significantly; that of the 0.01% solution at 1250 kV/cm being similar 
in value to that of the neat solution at 700 kV/cm. The conduction 
current in the latter case was one order greater at 700 kV/cm and showed 
similar conduction current characteristics at low stresses to those of 
benzene (19).
0.01% M-Naphthalene and Liquid Paraffin Conduction Current.

Effect of Concentration and number of breakdowns on conduction current characteristic.

Log. Electronov.  
10,000  
100  
1  
Comparison with Liquid Paraffin solvent.

Log. Electronov.  
10,000  
100  
1  
Effect of Concentration on Electroluminescence.
4.4. Tests using anthracene in liquid paraffin

4.4.1. General

Puriss grade anthracene was used and supplied in powder form under the following description:

'Puriss Scintillation grade' C$_6$H$_4$:CH:C$_6$H$_4$:CH

Molecular weight 178.23, green fluorescence. Supplied by Koch-Light Laboratory Chemicals Ltd.

A solution of maximum solubility was obtained by adding anthracene to liquid paraffin heated to 75°C and vigorously stirring for several hours. The solution was then diluted in known ratio until no precipitate could be observed in the flask after storing for extended periods.

Two concentrations were tested, 5 x 10$^{-6}$M/100 g and 1 x 10$^{-4}$M/100 g, corresponding to approximate molar fractions of 1.5 x 10$^{-5}$ and 3 x 10$^{-4}$ respectively.

4.4.2. Test on 5 x 10$^{-6}$M/100 g anthracene in liquid paraffin

This sample was degassed for ten days to 4 x 10$^{-3}$ mmHg and the normal test procedure followed, the liquid was stress conditioned for two hours at 600 kV/cm.

4.4.2.1. Stress conditioning

Three of the four breakdowns that occurred during the stress conditioning period occurred on applying the stress and establishing the conditioning value of 600 kV/cm. The electroluminescence fluctuated very erratically for a considerable period showing a general slow decrease with time and accompanied by large conduction current fluctuations. No direct correlation existed as can be seen in Fig.115 though in
general, an increase in conduction current resulted in a larger value of electroluminescence.

The correlation improved as stress conditioning proceeded, but the fluctuations were still very marked at the end of the period — see Fig. 116.

4.4.2.2. Conduction current against stress characteristics

The fluctuations continued during the first test on the 125 μ gap, the erratic nature of the phenomena being such that the conduction current showed considerable scatter. A breakdown occurred during the second stress cycle of this test, the form of the characteristic changing as shown in Fig. 119. Three breakdowns at 1300 kV/cm terminated this test, after which the gap was closed to 51 μ and the liquid stress conditioned for 15 minutes. These breakdowns may be responsible for the increased current obtained for the 51 μ gap (characteristic shown in Fig. 119 as the upper dotted curve).

Fig. 117 illustrates the strong correlation between the electroluminescence and conduction current during the generation of the 51 μ characteristic.

The upper full line characteristics in Fig. 119 show the results obtained from the second test on the 125 μ gap. A tendency for the conduction current and electroluminescence to increase with time on ascending regions of the stress cycle, and the converse on descending regions, was noted for both gap settings.
Electroluminescence range change Stress conditioning

Fig: (115)

Conduction Current

STRESS IS CONDITIONING 10 TIME (MIN) 20

Electroluminescence range change

5 x 10^-8 M/100g Anthracene in Liq. Paraffin

Conduction Current

Fig: (116)

STRESS IS CONDITIONING 17 TIME (MIN) 118

Electroluminescence range change

500 kV/cm 400 kV/cm Stress cycling

Conduction Current

Fig: (117)

STRESS IS CONDITIONING 11 TIME (MIN) 115

Electroluminescence range change

400 kV/cm 600 kV/cm

Conduction Current

Fig: (118)
4.4.2.3. Electroluminescence against conduction current characteristics

The characteristics obtained for the 51 \( \mu \) and the second 125 \( \mu \) gap test are shown in Figs. 120 and 121 respectively.

The slope for the 51 \( \mu \) gap is slightly greater than that for the 125 \( \mu \) gap which approximates to 45°. The wider spacing of the plots for the 51 \( \mu \) gap characteristic at low stresses is due to the increased curvature of the conduction current characteristic. No breakdown occurred during the 51 \( \mu \) gap test.

The gap was then reset to 125 \( \mu \) and the liquid stress-conditioned for 30 minutes to allow the electroluminescence to settle to a steady value. The upper line in Fig. 121 shows values for the first stress cycle, the ascending characteristics abruptly changing between 400 and 500 kV/cm to the lower line. This transition is shown on the record at point 'A' in Fig. 118. The reason for this transition is not apparent on the record.

4.4.2.4. Visual observation of electroluminescence

At high stresses during the first test with the 125 \( \mu \) gap, observation of the electroluminescence was possible and was as indicated in Fig. 122 below:

A deep blue glow was observed on the anode surface and a fainter glow seen extending into the liquid. This distribution remained unaltered as the stress was raised but increased in intensity.

Following the three breakdowns at 1300 kV/cm that terminated the first 125 \( \mu \) gap test, the anode glow became irregular and a faint glow appeared at the cathode at high stresses.
Fig: (119)
Symbols as in Fig: (103)

Fig: (120)

Fig: (121)

Degassed
$5 \times 10^{-6} \text{ M/100g}$
ANTHRACENE IN LIQ. PAR. 5$\mu$ GAP
Fig. 123 below illustrates the distribution of the electroluminescence observed during the 51 μ gap test and the second 125 μ gap test.

The anode surface effect in this test was much more diffuse and intense than the cathode effect.

At higher stresses the multiplier was switched off and the gap illuminated with dark field illumination. This allowed the electrode faces to be located to verify that the cathode glow was not anode reflection, the electroluminescence being bright enough to be visible against the illumination. Under these conditions the glow was pronounced and strongly indicative of a glow from the liquid adjacent to the electrodes, rather than a scattering effect from sources on the electrode itself. A single stationary diffraction pattern on the anode produced no local change in the electroluminescence in the vicinity of the particle.
4.4.2.5. **Inspection of electrodes**

The electrodes were inspected in a similar manner to that described in previous tests using a x100 magnification microscope.

A thin layer of clear wax was observed on the cathode. This covered the breakdown sites which were of the usual rim and crater form.

The anode had a more complex covering of wax, a small area enclosing several breakdown sites, and in the centre of the active area of the electrode, was observed to be free of wax, the surrounding edge of the wax layer being discoloured.

The discoloured regions smudged when wiped suggesting the presence of carbon. A slight scratch on the anode surface had no breakdown site on it despite its proximity to the breakdown site region.

4.4.3. **Test on 1 x 10^{-4} M/100g anthracene in liquid paraffin**

This sample was degassed for two weeks to 3 x 10^{-3} mmHg. Stress conditioning took place at 600 kV/cm for two hours and both the 125 µ and 51 µ gaps were tested.

4.4.3.1. **Stress conditioning**

The conduction current and electroluminescence fluctuated erratically following the application of the stress. Fig. 124 shows a portion of the record where the lack of direct correlation and the very abrupt changes in both the conduction current and electroluminescence are obvious. Ten minutes later the rare occurrence of direct negative correlation occurs in Fig. 125 at 'A' and 'B'. Fig. 126 shows a section of the record after 35 minutes of conditioning, where in region 'C'
little correlation occurs followed by 'D' where very marked correlation is apparent. As will be discussed in section 5.9, 600 kV/cm appears to fall in a transition stress region for this sample. The phenomena below 600 kV/cm being somewhat different from those above.

The conduction current and electroluminescence levels fell steadily during the stress conditioning period accompanied by a slowly increasing correlation similar to that noted in previous tests. Fig. 127 shows the record 20 minutes before the end of the stress conditioning period, the correlation is apparent despite the conduction current fluctuation. Fig. 128 shows the conditions at the end of the period. The now larger fluctuations mask the correlation apart from the section 'A', where for some 20 seconds the current fluctuation subsides, disclosing a slower fluctuation very strongly correlated to the electroluminescence. This portion of the record suggests the existence of two superimposed current processes at least partially independent.

4.4.3.2. Conduction current against stress characteristics

The values of conduction current and electroluminescence were very low below 600 kV/cm. As can be seen Fig. 130 very high values of stress were obtained.

The upper dotted characteristic shows ascending values for the first stress cycle during which three breakdowns occurred at 900 kV/cm, producing a break in the characteristic. These breakdowns resulted in the disappearance of the erratic current fluctuation observed during the stress conditioning period.

At 1200 kV/cm and above, during the ascending region of the stress cycle, both the electroluminescence and the conduction current
Stress conditioning

Electroluminescence

Conduction Current

Stress 121 conditioning 122 time (mins) 123

Electroluminescence

Conduction Current

Stress cycling
increased slowly with time at each value of stress. The converse was noted during descending regions of the stress cycle. The correlation was also less marked at lower stresses, the conduction current fluctuations noted during stress conditioning slowly reappearing as the stress was reduced. The lower dotted curve in Fig. 130 was generated by ascending values of the second stress cycle, the curvature of this characteristic being similar to that obtained for the 51 μ gap. The 51 μ gap characteristic is shown in Fig. 131.

4.4.3.3. **Electroluminescence against conduction current characteristics**

As can be seen from Fig. 129 and 132 the electroluminescence was of very low value even at 600 kV/cm so that the characteristics could only be plotted for stresses above 600 kV/cm.

The three breakdowns at 900 kV/cm already referred to in section 4.4.3.2. also produced a break in this characteristic, the rate of increase of conduction current with increase in stress being reduced by the stress conditioning process, causing the characteristic to return to its previous orientation. The increases of electroluminescence and conduction current for ascending values of stress (and the converse for descending values) are shown by the multiple plots for single stress values on the characteristics. A similar characteristic was obtained for the 51 μ gap and is shown in Fig. 133.

4.4.3.4. **Visible observation of electroluminescence and illuminated gap**

The gap was illuminated at the end of the stress conditioning period and appeared to be almost completely clear of spherical diffraction patterns on the electrodes. No trace of filamentary patterns along stress lines could be detected.
Degassed $1 \times 10^{-4} \text{M/100g Anthracene in Liquid Paraffin}$

125 $\mu$GAP.

Fig: (130)

Degassed $1 \times 10^{-4} \text{M/100g Anthracene in Liquid Paraffin}$

51 $\mu$GAP.

Symbols as in Fig: (109)

Fig: (131)
Degassed $1 \times 10^{-4}$ M/100g.
Anthracene in Liq. Par. 125 $\mu$GAP.

Fig: (132)

Degassed $1 \times 10^{-4}$ M/100g.
Anthracene in Liquid Paraffin.
51 $\mu$GAP

Fig: (133)
The electroluminescence was observed when the stress exceeded 1200 kV/cm and was an extremely deep purple. The faintness of the intensity relative to the photomultiplier reading suggested that the electroluminescence spectrum was on the upper energy limit of the visible spectrum.

At 1400 kV/cm with the 125 μ gap a breakdown occurred (see Fig. 132) producing a large increase in both the electroluminescence and conduction current. The change in the visible electroluminescence pattern during this event is shown in the figure below.

Before breakdown

very faint patches on anode

After breakdown

bright purple patches

more uniform and diffuse glow than at patches

Slight glow in the gap

The bright anode patches graded off in intensity into the gap, the glow extending with diminishing intensity to the cathode. At higher stresses a well defined glow (less intense than that at the anode) appeared at the cathode.

At the highest stresses (about 1600 kV/cm) the gap luminosity tended to become more uniform approaching that of the electrodes, the effect being similar to that reported by Darveniza (19) at very high stresses.
4.4.3.5. Inspection of electrodes and irradiation with ultra-violet light

Before cleaning, the electrodes were exposed to ultra-violet irradiation to detect the presence of anthracene on the electrode surfaces. The electrodes were inspected under the light from a U.V. source with filters for the 2540Å and 3500Å lines. These filters allowed a slight amount of visible purple to pass which was reflected from the polished surfaces.

Inspection of cathode gave no suggestion of the green fluorescence typical of solid anthracene.

Fig. (135).

Fig. 135 illustrates the appearance of the anode, the 'cap' observed over the active region of the electrode subtending approximately 90° of arc, the diffuse reflection of this area revealing the presence of the wax layer. No change in colour was apparent on the wax. Rinsing the liquid paraffin coating and with hexane removed the fluorescent area and rendered the wax layer less obvious. No green fluorescence typical of solid anthracene could be detected.

Electrode inspection

The cathode surface was coated with a thin layer of slightly discoloured wax.

Lightly rubbing with stockinette impregnated with hexane smeared and removed discoloured wax from the breakdown site region, suggesting that carbonised wax existed around the rims and in the craters of the sites.
The active area of the anode surface was covered with a slightly discoloured layer of wax, apart from a small area clear of wax containing a number of breakdown sites. Fig. 136 shows the appearance of the electrode as seen through the microscope. The 'edges' suggesting an abrupt thickening of the wax. This coating was thicker than that on the cathode.

External to the second edge the layer appeared perfectly smooth and uniform. A few breakdown sites were dispersed outside the clear patch. The anode sites were also of the rim and crater type.

Fig. (136).

4.4.4. Spectra

4.4.4.1. \(5 \times 10^{-6} \text{ M/100g anthracene in liquid paraffin}\)

Absorption spectra

Fig. 137 shows the absorption spectra for the sample and solvent, the triple absorption bands due to the presence of the anthracene being apparent in the spectrum of the sample.

Emission spectra

Little difference was found in the emission spectra of the degassed and tested samples, that of the latter being shown in Fig. 138. The spectra indicate that the emission is due to the anthracene present in the solution.

The virtually transparent absorption spectrum at longer wavelengths indicates why anthracene is a good scintillator particularly when irradiated just within the absorption front of 3650 Å.
Most of the emission occurs between 3850Å and 4550Å, the main emission peak lying in the deep purple and purple-blue bands, as observed in the visual observation of electroluminescence (section 4.4.2.4.). The oblique and perpendicular cell spectra are in the same ratio for each irradiation suggesting that quenching or self-absorption processes below the absorption front are not significant. Due to the heavy absorption at higher energies above the absorption front at 3850Å, the emission between 3130 and 3850Å is quite small, the low emission intensity following the absorption spectral form in this region. Due to the high degree of self-absorption in this region the total emission for 3130Å irradiation is much less than that when irradiated at 3650Å.

4.4.4.2. \[1 \times 10^{-4} \text{ M/100g anthracene in liquid paraffin}\]

Absorption spectra

Fig. 139 shows the absorption spectrum of this sample. The most noticeable feature is the very steep absorption front at 3850Å, the transmission being virtually zero beyond this wavelength. This can be contrasted with the previous concentration where some 30% transmission occurred up to 3000Å.

Emission spectra

The emission spectra in Fig. 140 demonstrate the opaqueness of the solution at wavelengths shorter than 3850Å. Apart from the reduced intensity, the 3130Å irradiation produces a very similar spectrum to the 3650Å irradiation.

The oblique cell arrangement produces a similar effect. A slight change in spectrum results in the high energy emission front consistent
Fig: (137)
Absorption Curves
For 5\times10^{-6} M/100g
Anthracene in
Liquid Paraffin
(e-Hexane blank)

Fig: (138)
5\times10^{-6} M/100g
Anthracene in
Liquid Paraffin
(tested sample)
with the heavy absorption in this region. The similarity in the oblique and perpendicular cell spectral distributions suggests that little self absorption is taking place at wavelengths longer than 3850Å.

In the anthracene solutions no shift in spectra takes place, only the intensity changing as the irradiation wavelength is varied. The spectral distribution would change if the irradiation wavelengths were longer than about 3850Å, but in this event the emission would be relatively small due to the lower values of absorption at longer wavelengths.

4.4.5. **Summary of anthracene test results**

As in previous tests the correlation between conduction current and electroluminescence increased with the stress conditioning time and was progressively enhanced by each breakdown.

The conduction current gap dependence shown in Fig.130 was obtained without the complication of an intermediate breakdown, suggesting that the slightly greater current and curvature of the characteristic in the 51 μ gap case is a gap dependence effect.

The breakdown strength at very high stresses improved when the interval between breakdowns lengthened. This effect has also been noted by Gosling (18).

The characteristics obtained in the previous sections are summarised in sketch form in Fig.141.
**Fig: (139)**
Absorption Curves for $1 \times 10^{-4} \text{M}/100\text{g}$ Anthracene in Liquid Paraffin (n-Hexane blank)

**Fig: (140)**
$I \times 10^{-4} \text{M}/100\text{g}$ Anthracene in Liquid Paraffin (tested sample)

3650Å Irradiation
perpendicular cell
oblique cell

3130Å Irradiation
perpendicular cell
oblique cell

**Upper Scale (Linear):** Wave Number in $10^3 \text{cm}^{-1}$

**Lower Scale (Reciprocal):** Wavelength in $\mu\text{m}$
5 \times 10^{-6} \text{ M/100g Anthracene in Liquid Paraffin}

Conduction current-stress characteristics

1 \times 10^{-4} \text{ M/100g Anthracene in Liquid Paraffin}

Conduction current-stress characteristics

FIG: (141)
4.5. Tests with Popop in liquid paraffin

4.5.1. General

A solution of maximum solubility was mixed using Popop (1,4-bis-(2-(5-phenyl-oxazolyl-benzene))) with the structural formula:

\[
\begin{align*}
\text{N} & \text{O} \\
\text{N} & \text{O} \\
\end{align*}
\]

Molecular Wt 324. Supplied by Kodak Ltd.
Pollen like powder, green fluorescence.
The solution was heated at approximately 50°C and vigorously stirred for several hours, it was then allowed to stand for several months, the solution being diluted until no precipitate formed over a six month period, this solution was then diluted fivefold to form the stock maximum concentration solution for the tests described below. All solutions were kept in a light tight cupboard.

Three concentrations were tested; 2 \times 10^{-7} \text{M}/100\text{g}, 2 \times 10^{-6} \text{M}/100\text{g} and 2 \times 10^{-5} \text{M}/100\text{g}.

The above concentrations correspond to molar fractions of 6 \times 10^{-7}, 6 \times 10^{-6} and 6 \times 10^{-5} respectively.

4.5.2. Test using 2 \times 10^{-7} \text{M}/100\text{g Popop in liquid paraffin}

The sample was degassed for eight days to 2 \times 10^{-3} \text{mmHg}. The liquid was stress conditioned for 2\frac{1}{2} hours at 600 \text{kV/cm} using the 125 \mu gap. Both the 125 \mu and 51 \mu gap settings were tested.
4.5.2.1. **Stress conditioning**

As in the anthracene tests, both the electroluminescence and conduction current showed erratic fluctuations at the start of the stress conditioning period (see Fig. 142). During the first twenty minutes three breakdowns occurred, the two signals increasing very slowly in the period following each breakdown. The correlation between electroluminescence and current was quite marked after the third breakdown as shown in Fig. 143. During the remainder of the stress conditioning period a further seven breakdowns occurred at irregular intervals, the final breakdown appearing to have little effect on either conduction current or electroluminescence - Fig. 144.

4.5.2.2. **Conduction current characteristics**

A marked feature of this test was the stability of the electroluminescence and conduction current at each value of stress. As can be seen from Fig. 145, the conduction current remained at a high value even with low values of stress. At high values of stress a breakdown usually resulted in an increase in conduction current, producing a step in the characteristic. The second stress cycle yielded higher conduction currents than the first, probably due to the breakdown at high stresses toward the end of the first stress cycle. It is difficult to assess any gap dependence effect due to the breakdown at 900 and 1000 kV/cm during the 125 μ stress cycling. The 125 μ and 51 μ characteristics however are of similar shape.
Electroluminescence

$600 \text{ kV/cm. (125} \mu \text{m gap)}$

$3 \times 10^{-7} \text{A}$

Conduction Current

1 STRESS CONDITIONING 2 TIME (MINS) 3 4

$1,000 \text{mA}$

Electroluminescence

Stress conditioning $2 \times 10^{-7} \text{M/100g POP/POP}$ Fig: (143)

$3 \times 10^{-7} \text{A}$

Conduction Current

21 23 24

$3,000 \text{mA}$

Electroluminescence

$3 \times 10^{-7} \text{A}$

Conduction Current

196 199 200

Fig: (144)
4.5.2.3. **Electroluminescence against conduction current characteristic**

These are shown in Figs. 146 and 147. The strong correlation between electroluminescence and current even after a breakdown results in only small departures from the characteristic. The breakdown at 900 kV/cm (see Fig. 145) during the ascending portion of the second stress cycle for the 125 μ gap resulted in an increase in conduction current without a corresponding increase in electroluminescence. As post breakdown conditioning proceeded at the higher stresses of the cycle the original characteristic was rejoined.

No gap dependence is apparent, the 51 μ and 125 μ characteristics superimposing almost exactly. The larger gap characteristic giving a greater variation in electroluminescence and current with stress.

4.5.2.4. **Visual observation of electroluminescence**

The high electroluminescence yield during this test allowed observation of the gap at various values of stress, the colour being a deep purple-blue. Electroluminescence was noted at both electrodes, that at the cathode being intense and confined to the surface,* whereas the anode glow was more diffuse and extended with diminishing intensity into the gap.

Fig. 148 shows the distribution of the electroluminescence in the gap at various stresses. At the very highest stresses the glow in the gap was so bright that the anode glow could not be distinguished, the cathode 'line' being just perceptible.

* This suggests that the electroluminescence glow observed in the liquid is not merely scattered light from the electrodes.
Degassed
$2 \times 10^{-7} \text{M/100g POPOP}$
in liquid paraffin

Fig: (145)

---

Degassed
$2 \times 10^{-7} \text{M/100g POPOP}$
in liquid paraffin

Symbols as on

Fig: (103)

---

Degassed
$2 \times 10^{-7} \text{M/100g POPOP}$
in liquid paraffin

Symbols as on

Fig: (103)

---

Degassed
$2 \times 10^{-7} \text{M/100g POPOP}$
in liquid paraffin

Symbols as on

Fig: (103)
Visible observation of electroluminescence

A 800 kV/cm  1000 kV/cm  1200 kV/cm
Anode  Cathode  A  C  A  C

Thin intense line on Cathode, more dispersed region against Anode.

As 800 kV/cm but more intense and sharp cathode glow. Anode glow extends into the gap.

Gap glows brightly. Anode glow is stronger. Cathode line very bright.

125 μ Gap.

A  C  A  C  A  C

Electroluminescence higher value than for same stress in 125 μ Gap. (Fig 4.5.24)

Small gap appears in Anode and Cathode glows following a break-down.

Anode glow almost completely merged into very bright glow across gap. Cathode line extremely bright.

51 μ Gap.

Fig: 148
4.5.2.5. **Inspection of electrodes**

The electrodes were inspected under an ultra-violet lamp in a similar manner to that described in section 4.4.3.5. No fluorescence typical of Popop in the solid state could be detected on the electrodes.

Inspection of the anode under the microscope showed the anode active surface to be covered with a clean unbroken layer of wax. The breakdown sites appeared to decrease in size as discoloured wax, probably carbonised, was wiped from them suggesting the rims of the sites were coated with carbon. A few of the breakdown sites were grouped closely together, the sites being of the usual rim and crater form.

The cathode sites appeared to be nearly all double or grouped formations due to overlapping of craters (as noted by Gosling (18)). The cathode surface was clean apart from a very thin wax patch over and around groups of breakdown sites, this wax was clean and wiped off very easily. The cathode sites were also of rim and crater form.

4.5.3. **Test using 2 x 100^-6 M/100g Popop in liquid paraffin**

This sample was degassed for eight days to 2 x 10^-3 mmHg, and stress conditioned for two hours at 600 kV/cm using the 125 μ gap. No breakdowns occurred during the stress conditioning period. Both 125 μ and 51 μ gap settings were tested.

4.5.3.1. **Stress conditioning**

A correlation existed between the electroluminescence and the conduction current throughout the whole of the stress conditioning period as can be seen in Figs 149, 150 and 151 which show the fluctuations...
at the beginning, after ten minutes and at the end of the stress conditioning period. Only rarely did non-correlated phenomena occur, one such event is shown in Fig. 150. The abrupt fluctuations in conduction current and electroluminescence slowly decreased in amplitude and occurred less frequently whilst the correlation became more direct as stress conditioning proceeded. Fig. 151 shows the stable conditions attained by the end of the stress conditioning period.

The effect of breakdown on the fluctuations can be seen by comparing Figs. 152 and 153 the former showing pre-first breakdown phenomena and the latter post breakdown phenomena. The conduction current has slightly more fluctuation content and was lower in value after breakdown. The for the same stress electroluminescence was also lower in value and contained a less correlated and more erratic fluctuation.

The effect of closing the gap can be seen in Fig. 154 which shows the stress conditioning fluctuations for the 51 μ gap setting. Both the electroluminescence and conduction current showed quite erratic variations at the beginning, those in the current tending to disappear towards the end of the period. Both the conduction current and electroluminescence increased slowly as conditioning proceeded. Correlation was present throughout, but as the current fluctuation decreased the electroluminescence fluctuation became more sensitive to current fluctuations.

4.5.3.2. Conduction current against stress characteristics

The pre-first breakdown characteristic for the 125 μ gap setting is shown by the upper curve in Fig. 156, the first breakdown in the sample occurring at 900 kV/cm. After five minutes stress conditioning at 800 kV/cm,
Electroluminescence

\[ \frac{600 \text{ kV/cm}}{125 \mu \text{gap}} \times 2 \times 10^{-6} \text{M/100g POP POP} \quad \text{Fig: (149)} \]

in LIQUID PARAFFIN

Conduction Current

4 STRESS CONDITIONING 5 TIME (MINUTES) 6

3 \times 10^{-7} \text{A}

Electroluminescence

Stress conditioning

FIG: (150)

3 \times 10^{-7} \text{A}

Conduction Current

FIG: (151)

300 \mu \text{A}

Electroluminescence

3 \times 10^{-7} \text{A}

Conduction Current
the current fell to its pre-breakdown value and the second stress cycle was completed producing the lower characteristic for the 125 μ gap.

The 51 μ gap characteristic is shown as the dotted curve in Fig. 156 the current is apparently greater than for the 125 μ gap, but as in other tests, the breakdowns terminating the 125 μ gap test may produce this apparent gap dependence.

4.5.3.3. Electroluminescence against conduction current characteristics

The lower of the two curves in Fig. 157 shows the pre-breakdown characteristic corresponding to the upper conduction current plot in Fig. 156. The post-breakdown characteristic is parallel to that for pre-breakdown conditions and reflects the decrease in conduction current following breakdown for a given stress by its displacement to the left of the pre-breakdown curve.

The 51 μ gap characteristic is also plotted on Fig. 157 yielding a steeper slope than for the 125 μ gap settings. Both the electroluminescence and conduction current fluctuated more for this gap setting than for the 125 μ gap test.

4.5.3.4. Visual observation of the electroluminescence

The intensity of the luminescence in the gap was more uniform than that noted in previous tests, the intensity being greatest against the anode. A faint cathode glow could be seen at the highest stresses.

The effect of stress (or conduction current) and breakdown on the electroluminescence distribution in the gap is shown in Fig. 158.
DEGASSED
2x10^-6 M/100g POPOP
IN LIQUID PARAFFIN

FIG: (156)

DEGASSED
2x10^-6 M/100g POPOP
IN LIQUID PARAFFIN
Symbols as in
FIG: (193)

FIG: (157)
Visual observation of electroluminescence.

(none observed before breakdown).

After 4 breakdowns.

<table>
<thead>
<tr>
<th>Voltage (kV/cm)</th>
<th>Anode</th>
<th>Cath.</th>
<th>Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1300</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1400</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Faint glow on anode, very faint glow in gap.

Anode glow more obvious, faint glow across gap.

Distribution as at 1300kV/cm, glow more intense.

Electroluminescence

\(~ 1500\mu A\) \(\sim 3500\mu A\) \(\sim 4500\mu A\)

After 6 breakdowns

<table>
<thead>
<tr>
<th>Voltage (kV/cm)</th>
<th>Post breakdown</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100</td>
<td></td>
</tr>
<tr>
<td>1300</td>
<td></td>
</tr>
</tbody>
</table>

Extremely intense glow across whole of gap just after breakdown.

\(~ 250,000\mu A\)

Ten minutes later.

Electroluminescence

\(~ 30,000\mu A\)

Deep purple-blue colour electroluminescence.

Fig.(158).
4.5.3.5. **Inspection of electrodes**

A strong medium blue fluorescence typical of Popop in solution was observed on the anode under the ultra-violet lamp. This fluorescence disappeared when the anode was rinsed with hexane and appeared to be more intense in the region of the wax coating covering the active area of the electrode.

The wax layer appeared to be of uniform thickness and to contain carbon throughout its depth.

The cathode showed no fluorescence under the ultra-violet lamp, and appeared to be clean. The breakdown sites were of rim and crater type. Three double crater sites were observed.

4.5.4. **Test using $2 \times 10^{-5} \text{ M/100g Popop in liquid paraffin}$**

The sample was degassed for ten days to $1.5 \times 10^{-3} \text{ mmHg}$ and the liquid was stress conditioned for two hours at 600 kV/cm using the 125 $\mu$ gap. Both the 125 $\mu$ and 51 $\mu$ gap were tested.

4.5.4.1. **Stress conditioning**

Three breakdowns occurred at the onset of the conditioning stress, the electroluminescence and conduction current fluctuations being more marked than for the previous test with the lower concentration. During the two hour period six breakdowns occurred, all in the first thirty minutes. Figs. 159 and 160 show the first ten minutes of the conditioning period during which the first five breakdowns occurred. The electroluminescence fluctuations steadily subsided while at the same time becoming more sensitive to the current fluctuation. Fig. 161 shows the fifth breakdown.
to occur in the sample after thirty minutes of conditioning, the electroluminescence being strongly correlated to the current and much steadier. The erratic fluctuations present at the commencement of the period have disappeared accompanied by a twofold increase in the mean value. As stress conditioning proceeded and the correlation increased a slow drift in the value of the conduction current and electroluminescence appeared lasting for periods of several minutes. The mean value of the signals increased by a factor of two to three during the drift, before falling again. This effect is illustrated in Fig. 162 which shows conditions at the end of the conditioning period.

The fluctuations during the stress conditioning of the 51 μ gap were similar to those already described above for the 125 μ gap.

4.5.4.2. Conduction current characteristics

The characteristics for both the 125 μ and 51 μ gaps are shown on Fig. 163. The 51 μ gap characteristic lies above that for the 125 μ gap. This may be due to the four breakdowns occurring at 1200 kV/cm, terminating the 125 μ gap test.

4.5.4.3. Electroluminescence against conduction current characteristic

Fig. 164 shows the characteristics for both the 125 μ and 51 μ gaps. The 125 μ gap characteristic shifted with each stress cycle, the displacement between the first and second stress cycles (uppermost and adjacent characteristics of the figure), is not due to a breakdown but to a gradual fall in electroluminescence at 900 kV/cm without a corresponding change in current. At stresses up to this value the correlation between electroluminescence and conduction current can be seen by the presence of
I 9 3 >
300 mμA
Electroluminescence

600 kV/cm (125 μ gap) 2×10⁻⁵ M/100g POP in Liq. Par.

0                  STRESS | CONDITIONING 2 TIME (MINUTES) 3 4

300 mμA
Stress conditioning

3×10⁻⁷ A
4 th. b.d

Electroluminescence

3×10⁻⁷ A
Conduction Current

29 30 31 32 33

300 mμA

Electroluminescence

3×10⁻⁷ A

Conduction Current

120 121 122 123 124
multiple plots for a given stress.

The second stress cycle showed greater stability, both signals being subject to less fluctuation, resulting in single plots at each stress. The third characteristic for the 125 μ gap was due to a further fall in electroluminescence, this time at 200 kV/cm in the second stress cycle, the electroluminescence yield for each current being lower than previously. The dotted characteristic at the top of Fig.164 was obtained towards the end of the second stress cycle when four breakdowns occurred at 900 kV/cm. The characteristic was plotted over the period of the post-breakdown exponential decay and subsequent stress conditioning.

The portion of the curve parallel with main characteristic occurred within minutes of the breakdown. The non-parallel curve shows the effect of stress conditioning over the remainder of the fifteen minutes post-breakdown conditioning period.

The 51 μ characteristic is of similar slope, the yield being lower than for the 125 μ gap for a given current.

4.5.4.4. Visual observation of the electroluminescence

Due to the lower yield in this test, opportunities for observation were very limited. Faint, deep blue electroluminescence was observed against the anode and so far as could be judged, was similar to that of the previous tests.

4.5.4.5. Inspection of electrodes

As in the previous test, inspection of the electrodes under the ultra-violet lamp produced fluorescence on the anode typical of Popop in solution over the wax layer on the anode. Little fluorescence was observed on the cathode surface.
Conduction Current (Ampere)

\[ 10^{-8} \leq \text{Conduction Current} \leq 10^4 \]

Stress (kV/cm)

\[ 500, 600, 700, 800, 900, 1,000, 1,100, 1,200 \]

\[ (kV/cm) \]

Fig: (163)

DEGASED

\[ 2 \times 10^{-5} M/100g, \text{ POPC in Liquid Paraffin} \]

Symbols as in Fig: (103)

Fig: (164)
The cathode was covered with a thin layer of clean wax. Carbonised deposits were found over the cathode breakdown sites.

The anode wax layer was also clean, the layer being thicker than that on the cathode. No carbon could be detected on the breakdown sites.

4.5.5. Spectra

4.5.5.1. $2 \times 10^{-7}$ M/100g Popop in liquid paraffin

Absorption and extinction spectra

The extinction spectra for the original sample is shown in Fig. 165. Comparison with the liquid paraffin solvent shows that the solution is extremely dilute. Fig. 166 shows the corresponding spectra for the sample in its degassed and tested state, the difference in the spectra in the degassed and tested cases was too small to be significant, but it can be seen that either due to filtering or the degassing process the concentration of Popop in solution has halved. The small increase in extinction at shorter wavelengths (around $2500\AA$) is due to degassing contamination, now of negligible proportions.

Emission spectra

These are shown in Figs. 169 and 170. No significant difference in the degassed and tested samples could be detected. The effect of the reduced Popop concentration is reflected in the emission intensities. An interesting feature is the emission between $3130\AA$ and $3750\AA$ which is the same for each sample and identical to that of the original liquid paraffin
solvent. The quadruple peak at longer wavelengths is that of the Popop in solution. As with anthracene, the Popop emission spectra are similar in form for both irradiation wavelengths, although in this sample the liquid paraffin emission spectrum at the shorter wavelengths makes an increasing contribution to the total emission as the irradiating wavelength is reduced. The corresponding fall in Popop emission shows that although some energy is absorbed by the Popop (either by 'direct absorption at irradiating wavelengths, or energy transfer, (131)) much of the energy is being dissipated by self-absorption processes before it degenerates into the Popop absorption bands.

4.5.5.2. $2 \times 10^{-6}$ M/100g Popop in liquid paraffin

Absorption and extinction spectra

The extinction spectra shown in Fig. 167 for the original, degassed and the tested samples respectively, show that the concentration of Popop in solution progressively decreased in each sample in the ratios 1 : 0.7 : 0.45. The 'tested sample' of the solution was the first portion of the degassed liquid to be filtered and might thus lose most Popop to the clean filter. The 'degassed sample' is the latter portion and consequently will pass through a possibly already partly 'loaded' filter and so be of greater concentration. To investigate this possibility a sample of the original solution was passed several times through a filter of similar pore size and extinction spectra obtained as shown in Fig. 168.

The source of the 'contamination' present around 2900Å (and also noted in the previous test) is now apparent and is due to some residue from a previous sample (despite vigorous and thorough cleaning of the filter.
Fig: (169)

3,50Å Irradiation
perpendicular cell
oblique cell

Fig: (170)

2×10⁻⁷ M/100g POPP in Liquid Paraffin
(Original sample)

2×10⁻⁷ M/100g POPP in Liquid Paraffin
(Degassed and Baked samples)

UPPER SCALE (linear)-WAVE NUMBER IN 10⁶/cm
LOWER SCALE (reciprocal)-WAVE LENGTH IN μm.
before use on the Popop samples. The filtering, however, does not appear to change the concentration.

Popop is a large molecule and retention in the filter seems to be the obvious explanation despite the negative result of the filtering test. Possibly the retentivity in the filter is enhanced when the liquid is in a degassed state. Since both the degassed and tested portions of the solution are degassed together and stirred whilst degassing proceeds, degassing alone would not account for the change in concentration unless a further coincidental change resulted due to electrical testing. After each test, since hexane flushed Popop from the filter without difficulty, retention of the Popop when in solution with liquid paraffin would suggest the existence of liquid paraffin - Popop complexes of sufficient size to cause retention in the filter membrane.

Emission spectra

Comparison of the three sets of emission spectra (that for the tested sample in shown in Fig. 172) showed that apart from the different emission intensities, the spectral distributions were apparently identical for each sample. The emission ratios corresponding to the above absorptions were 1 : 0.81 : 0.66. The slight increase in emission ratio with falling concentration is probably due to a reduction in self-absorption. The emission spectra are typical of Popop and show that apart from the slight emission between 3130 and 3850\AA the spectra distributions are independent of irradiation wavelength. The emission intensity however, falls as the irradiation wavelength moves into the more heavily absorbing wavelengths.
Absorption Spectra
$2 \times 10^{-6} \text{ M/100g}$
POPOP in Liquid Paraffin

Absorption
Liquid Paraffin Solvent
tested sample
degassed sample
original sample

20 Wave Number $10^3$/cm

Emission Spectra
$2 \times 10^{-6} \text{ M/100g}$
POPOP in Liquid Paraffin (tested sample)

3650Å
Irradiation perpendicular cell
oblique cell

3130Å
Irradiation perpendicular cell, oblique cell

UPPER SCALE (linear): Wave Number in $10^3$/cm
LOWER SCALE (reciprocal): Wave Length in m.μ
The deep blue-purple colour of the electroluminescence observed in the test (section 4.3.3.4) is consistent with the main emission band of Popop in the visible region 4000-4600 Å. The fact that the emission spectral distribution does not change significantly with irradiation wavelength is consistent with the absence of any apparent change in the colour of the electroluminescence with change in current or stress.

4.5.5.3. $2 \times 10^{-5}$ M/100g Popop in liquid paraffin

Absorption spectra

The absorption spectrum given in Fig. 173 shows that the concentration is now sufficiently heavy to produce very heavy absorption beyond 3900 Å. The absorption front is in a similar position to that of the $1 \times 10^{-4}$ M/100g. anthracene in liquid paraffin solution. The Popop samples however have virtually no absorption at wavelengths longer than 3900 Å giving an almost rectangular absorption characteristic. No degassing or testing effects can be detected from the spectra.

Emission spectra

The emission spectra shown in Fig. 173 were found to be the same for the original, degassed and tested samples. Filtering and degassing had no obvious effect at this concentration. The effect of the absorption front on the spectral distribution can be seen by comparison with Fig. 170 and 172 where the short wavelength peak is greater in amplitude than the long wave peak (less so in the latter figure, due to the heavier absorption). In the case of the present sample the short wave peak has been suppressed in the perpendicular spectra by the overlapping
absorption front. The presence of heavy self-absorption is also evident in the relatively larger amplitudes of the oblique spectra, these are less susceptible to self-absorption effects and reflect the increase in concentration more than do the perpendicular cell spectra. The amplitudes of the perpendicular cell spectra peaks are less than those of the previous concentration and indicates the existence of concentration quenching effects (127).

The spectral width of the emission is quite narrow and lies in the purple-blue. The observed electroluminescence though faint, was slightly less in the violet than for the previous test. The reduced yield is also consistent with the reduced emission obtained from the samples when irradiated.

4.5.6. Summary of test results for Popop solutions

In a similar manner to that already reported in previous tests the correlation between the electroluminescence and conduction current increased with the length of stress conditioning.

The conduction and electroluminescence characteristics are summarised in Fig. 174.

As in the anthracene tests, the effect of the concentration on the conduction current is complicated by breakdown effects and the resultant deposition of wax on the electrodes. If the greater conduction current for the lowest concentration is ascribed to the increased number of breakdowns, then increasing the concentration has little effect on the current. The effect of breakdown on the conduction current characteristic in the case of the intermediate concentration is not typical in that the conduction current was less after breakdown of the sample.
FIG: (173)

$2 \times 10^{-5} \text{M/100g}$

POPOP in

Liquid Paraffin.

3650Å Irradiation
perpendicular cell
oblique cell

3130Å Irradiation
perpendicular cell
oblique cell

UPPER SCALE (linear): Wave Number in $10^3$/cm
LOWER SCALE (reciprocal): Wavelength in μm
In all cases, as with the anthracene solutions, the 51 \( \mu \) gap gave slightly greater currents than the 125 \( \mu \) gap.

The electroluminescence shows a decreasing yield for a given conduction current as the concentration increases, a similar effect occurring with both the 125 \( \mu \) and 51 \( \mu \) gaps. The greater yield for the lowest concentration is possibly due to the strong cathode emission present in this particular test, in addition to the anode emission which occurs in the other tests. Allowing for this additional cathode emission the electroluminescence yields correspond to the emission spectra intensities for each concentration.

4.6. **Test on transformer oil**

4.6.1. **General**

As is well known, transformer oil is used for insulation and cooling purposes in a large range of electrical equipment. It has been tested extensively by other workers (18,19,22,26,27), and in order to allow some comparison with the present work on liquid paraffin, the following test on transformer oil is included. Many tests were made during the preliminary work of the author (116) giving similar results and phenomena to those described below.

As will be seen, transformer oil is not as satisfactory a solvent as liquid paraffin for this work due to its optical opacity.
51\mu current relationships shown in Figure, but larger for given stress than for 125\mu gap.

Effect of concentration on Conduction Current.

Effect of breakdown.

Comparison with Liq. Par. Sample c' after 6 breakdowns.

Electroluminescence 125\mu gap.

Electroluminescence 51\mu gap.

Fig: (174)
4.6.2. Test on degassed transformer oil

The sample was degassed to $1 \times 10^{-3}$ mmHg for ten days, the vacuum being maintained over the liquid whilst under test. The liquid was stress conditioned for 2 hours at 600 kV/cm using $125 \mu$ gap setting. Both the 125 $\mu$ and 51 $\mu$ gaps were tested.

4.6.2.1. Stress conditioning

No breakdowns occurred until the end of the stress conditioning period. Both the electroluminescence and conduction current were low in value and fairly steady from the onset of stress. Fig. 175 shows the record at the beginning of stress conditioning. After about ten minutes, large fluctuations in the conduction current correlated with fluctuations in the electroluminescent signal occurred. These would disappear only to return later. Fig. 176 shows events after some 20 minutes of stress conditioning. The fluctuations at the end of Fig. 176 represent the state of affairs existing for the rest of the stress conditioning period apart from small short-lived variations.

Two breakdowns occurred just as stress cycling was about to commence, so the sample was stress conditioned for a further 15 minutes. Fig. 177 shows the breakdowns and their effect on the conduction current and electroluminescence (which increased 30 fold). Fig. 178 shows the fluctuations 20 minutes later, after stress conditioning.

4.6.2.2. Conduction current against stress characteristics

During stress cycling the fluctuation was an approximately constant proportion of the signal irrespective of the order or magnitude of the current. This is consistent with the work of Megahed (27) who found
that the amplitude and population of the pulse distributions increased with stress. The conduction current characteristics for the 125 μ and 51 μ gap settings are shown in Fig. 179. These characteristics and the gap dependence show almost exact correspondence with those obtained by Gosling (18).

4.6.2.3. Electroluminescence against conduction current

The electroluminescence characteristics are shown in Figs. 180 and 181. Due to variations of conduction current and electroluminescence at constant stress more than one plot is shown for a given stress. The correlation between the current and electroluminescence is not as strong as much of the earlier work making the identification of consistent minima in the two signals more difficult than hitherto and resulting in greater scatter in the plots. The conduction current against stress plots in Fig. 179 represents the median of the current fluctuation at a given stress and therefore lie within the multiple plots for a given stress on the electroluminescence characteristic.

4.6.2.4. Visual observation of electroluminescence and the illuminated gap

No electroluminescence could be observed during the stress conditioning or stress cycling periods but at the end of the test, after observation of the gap when illuminated, the stress was increased (resulting in further breakdowns) to observe the electroluminescence. This was very faint and appeared only on the electrode surface. The figure shows the approximate distribution observed.
After a breakdown a glow appeared similar to that noted in previous tests but more confined to the liquid adjacent to the electrodes.*

This glow rapidly reduced in several seconds to a few transient spots which disappeared one by one over the following few seconds.

The gap was inspected using dark field illumination and some activity was observed similar to that already described in section 4.1.1.1.

Several diffraction patterns could be seen suggesting that this sample had more particles present than liquid paraffin, where particle activity was noted on very few occasions. The activity was similar to that reported by Gosling and it is significant that the conduction current and electroluminescence should be more erratic in this sample. The gap was observed in a similar way to that used by Gosling, the gap being alternatively illuminated and darkened whilst the particle activity and electroluminescence were observed. No correlation between particle activity and electroluminescence were observed. No correlation between particle activity and electroluminescence were observed.

* This is consistent with the heavier absorption that occurs in transformer oil compared with liquid paraffin. See relevant spectra.
position or movement and the very occasional electroluminescent spots could be detected. This was also the case following a breakdown. It should however be borne in mind that only the larger particles are observable under these conditions and that the electroluminescence events were barely perceptible.

4.6.2.5. Inspection of electrodes

The electrodes were inspected under the microscope immediately after the test was completed.

The cathode was quite clean, no traces of carbon being detectable in the breakdown sites or wax on the electrode surface.

A very thin layer of wax was seen on the anode with slight imperfections in the centre of the active area adjacent to the breakdown sites, which showed very slight traces of carbon around their peripheries.

4.6.3. Spectra

The spectra for the original, degassed and tested samples were found to be identical.

4.6.3.1. Absorption spectrum

Fig. 182 shows the absorption spectrum for transformer oil. The heavy absorption front occurs about 4050Å, the curve differing from those of anthracene or Popop by possessing moderate absorption at wavelengths up to 4800Å. This absorption characteristic in the purple-blue accounts for the yellowish green colour of transformer oil. The absorption of all other samples previously described is at wavelengths less than 3850Å, which is in the near ultra violet; resulting in nearly colourless, transparent solutions.
4.6.3.2. Emission spectra

The effect of the heavy absorption front on the emission spectra shown in Fig. 183 is obvious. The very heavy self-absorption results in very little emission from the perpendicular cell arrangement at wavelengths shorter than 4000Å; the efficiency of energy conversion falling off very rapidly as the irradiation wavelength is shortened to penetrate the absorption front. This effect can be seen by comparing the emission obtained with the perpendicular cell arrangement for each of the irradiation wavelengths.

The relative amplitude of the 3650Å irradiation emission peaks with the shift of the oblique emission to shorter wavelengths shows that self-absorption is heavy even when irradiating at 3650Å. The large value of the oblique emission (relative to previous solutions) shows that transformer oil contains highly efficient scintillating molecules (naphthalene), anthracene and heavier polycyclic molecules) but that self-absorption and possibly quenching dominate the energy transfer process, drastically reducing the emission from the bulk of the liquid. This is probably due to the existence of heavy absorbing bands, which do not result in emission, in the same region as the emission bands of the scintillating molecules.

The foregoing is supported by the relatively high emission mainly above 4000Å obtained with the oblique cell irradiated by 3130Å, the reduction in emission for this spectrum below 3500Å is probably due to the absorption of the quenching bands attenuating emission down to approximately 4000Å, beyond which the relatively high emission of the 3650Å irradiation suggests quenching is not so severe.
Fig. (182)
Absorption Curve
Transformer oil.
(against n-Hexane) blank

Fig. (183)
Emission Spectra
Transformer Oil

3,130Å Irradiation
perpendicular cell
oblique cell

3,650Å Irradiation
perpendicular cell
oblique cell

UPPER SCALE (linear): Wave Number in 10^3 cm⁻¹
LOWER SCALE (reciprocal): Wavelength in mJL.
4.6.4. **Summary of results**

The fluctuations in transformer oil showed a less marked correlation between conduction current and electroluminescence than with the other samples where liquid paraffin was used as the solvent. Correlation nevertheless existed, additional independent (and erratic) phenomena were present to a greater degree than in liquid paraffin. The fluctuations noted might be enhanced by the low hydrostatic pressure and high degree of degassing maintained in the cell during the tests by continuous pumping. Another contributary factor in the case of transformer oil is the inclusion of mineral particles inherent in the oil or introduced during the refining process (e.g. Fuller's earth and cellulose fibres introduced by paper filters).

The similarity in the conduction current and electroluminescence characteristics of liquid paraffin and transformer oil is shown in Fig. 184.

The electroluminescence characteristic for transformer oil shows no gap dependence (as with liquid paraffin) and gives a slightly higher yield for a given stress than liquid paraffin from the first bottle. The yield however is lower than that for liquid paraffin from the second bottle.

The relative positions of the liquid paraffin sample 'c' and transformer oil characteristics are similar to those found by Gosling when comparing the light output from transformer oil with its paraffinic constituents (18).
The spectra suggest that though highly efficient scintillating molecules are present in transformer oil, the existence of heavy self absorption and probably quenching processes reduces the efficiency of the absorption-emission process. This agrees with the low electroluminescence yield, resulting in values similar to those of liquid paraffin.

4.7. Use of transformer oil as a solvent

Solutions were made similar to those described in the liquid paraffin tests, but using transformer oil as the solvent. Maximum solubilities were found to be similar to those using liquid paraffin. The transformer oil solvent absorption spectrum however, overlaps the emission bands of the additives so that the emission spectra of the solutions show little change from that of the solvent.

High concentrations of methyl-naphthalene had little effect on the total emission from the solution, the emission from the methyl-naphthalene replacing that of the transformer oil (compare Figs. 113 and 183).

The emission peaks of anthracene fall in the same wavelength region as that of the transformer oil absorption front, see Figs. 140 and 183. Consequently the addition of anthracene has little effect on the solution emission. It is known (19) that transformer oil contains anthracene and similar polycyclic molecules and that the aromatic constituents comprise some 15% by volume of the oil (Appendix B).

Some slight increase in emission results from the addition of Popop to transformer oil due to the wider emission band width in the wavelength region of the visible spectra (Fig. 173 and 193).
5. DISCUSSION OF RESULTS

5.1. Stress conditioning

The initial low breakdown strengths and fluctuations in conduction current which are uncorrelated with electroluminescence are generally associated with the presence of particles. Other workers (18, 26, 27) have also noted that particles cause current fluctuations in the early stages of stress conditioning. Such fluctuations were generally more noticeable with transformer oil which is known to contain mineral impurities and cellulose fibres after refining (24, 39). In the case of liquid paraffin many tests showed little particle activity after stress conditioning.

Fig. 128 illustrates the erratic current fluctuation associated with particle activity. It can be seen that the fluctuations are marked with large pulses of conduction current (18, 27), the disappearance of the large pulses from the current, portion A of the record, reveals a correlation between the conduction current and the electroluminescence.

As stress conditioning proceeds low permittivity particles (18) and vapour bubbles on the electrode surfaces (81) will be ejected from the gap whilst high permittivity particles or metallic particles resulting from spark damage of the electrodes (153) will remain in the high stress region of the gap and collect on the electrodes. A further mechanism which may give rise to particles is the raising and removal (either by "burning off" or detachment) of asperities produced on the nickel electrode surface by the polishing process (42). Also buffing compound and inherent inclusions in the electrode material may be
released from the surface when an electric stress is applied. However buffing compound was rarely used and great care was taken with the ultrasonic cleaning of the electrodes to minimise the above possibilities.

During a stress conditioning period free from breakdowns little correlation between conduction current and electroluminescence was noted. Following a breakdown however the correlation increased significantly, usually accompanied by an increase in the conduction current and electroluminescence.

The existence of insulating wax layers at the electrodes will lead to a redistribution of stress in the gap \((41,45)\). Thus breakdown during the stress conditioning period will reduce the chance of further breakdowns due to the disintegration or ejection of large particles \((18)\) and the stabilising effect of deposits formed by a breakdown.

As the electrode deposits increase in thickness with the number of breakdowns, the effect of the space charge at each electrode will increase.

5.2. Breakdown deposits

The deposition of wax on the electrodes coupled with the production of gaseous breakdown products are indicative of dissociation of the liquid during the period of the discharge \((28,43,45)\). Recombination of the dissociated products will also take place, wax forming on the electrodes during the conditioning period following the breakdown. During this time the conduction current settles to the post breakdown value as the wax layers consolidate. The fact that the anode wax layer was always found to be much thicker than the cathode layer suggests the possibility that
the majority charge carriers in the conduction mechanism in the liquid are negative. The latter is in agreement with the conclusions of Eldine et al (41) following investigations into the space charge distribution in the stressed region of a gap having coated electrodes.

As reported in Section 3, carbonised regions were found on the electrode layers in some tests and it is suggested that the growth of such regions might be initiated by asperities (42) lifting from the electrode under the action of the high local stress. These asperities could partially or completely puncture the layer and initiate a breakdown.

Another possibility is the inclusion of metallic dust from electrode damage following a breakdown (153). Such particles will form a region of localised stress enhancement so increasing the local conduction current density in the layer and the probability of further dust deposition. By this process, which will be cumulative, a region of weaker dielectric strength will form having a relatively high current density. Dissociation of the wax with the formation of carbon is likely under these conditions.

Using the arguments presented above, a carbonised 'plug' of wax could be produced over a breakdown site as wax and metallic dust heal the breakdown puncture in the layer. The occurrence of carbonised wax over breakdown sites was observed to be more common than elsewhere on the electrode, and the local stress enhancement due to breakdown damage will increase the probability of carbonisation. Successive breakdowns at high stress could result in the appearance of an anode coating puncture, subsequent surface discharges (142) causing carbonisation
of the puncture edge (e.g. in Fig. 119 where two breakdowns occurred at 900 kV/cm followed by six breakdowns in succession at 1300 kV/cm).

Strong electroluminescence was always noted at the anode when a wax coating was present. An intense local non-uniformity in the electroluminescence occurring at the anode whenever a puncture formed in the layer.

Therefore the incidence of a high energy breakdown may result in a permanent change in the conduction current magnitude and the shape of the current-stress characteristic. A permanent shift in the electroluminescence-conduction current characteristic could also result due to the change in electrode conditions. Such changes have been noted and reported in Section 4.

5.3. Effect of aromatics on wax deposits

The effect of aromatic constituents on the quantity of wax deposited has been discussed in Section 2.5 and, in agreement with previous work (43, 92, 96), the electrode coatings formed during the transformer oil tests were thinner than those produced in the liquid paraffin tests.

The large number of breakdowns in the methyl-naphthalene test probably accounts for the thick coatings found on the electrodes. This liquid was stated to be 95% 1-methyl-naphthalene and it is known that 2-methyl-naphthalene forms part of the unspecified 5% of the solution. 2-methyl-naphthalene melts at +34°C and may therefore have contributed to the formation of wax by precipitation during the test.
5.4. Cathode effects

The existence of a thin wax (or oxide) layer at the cathode would prevent positive ions from readily reaching the cathode and giving up their charge. Therefore a positive ion space charge is likely to be formed close to the cathode and this space charge would greatly increase the local field at the cathode thus producing either Schottky or field emission through the layer.

The emitted electrons will enter the liquid with widely differing energies. Electrons of higher energy in the range 3 to 4.5 eV may initiate direct excitation of fluorescent molecules such as anthracene and Popop. Electrons of energies of about 7-10 eV or higher may cause ionisation of the liquid molecules so producing positive ions and local recombination.

The lower values of cathode electroluminescence relative to that at the anode, even when high concentrations of fluorescent molecules exist in the liquid, suggest that charge neutralisation at the cathode by emitted electrons is less than the corresponding processes at the anode. It is possible that most of the emitted electrons will successively collide with liquid molecules, until attachment to a neutral molecule takes place forming a negative ion. It was suggested in Section 5.2. that the conduction current would appear to contain a larger negative ion or electron component than a positive ion component. The latter however must always be sufficiently large to maintain the positive ion space charge at the cathode and thereby the emission.
5.5. Phenomena in the cathode region

The positive space charge on the cathode coating will exert coulomb forces on the negative ions and electrons increasing the local recombination rate in the vicinity of the cathode.

Some direct excitation of fluorescent molecules may also result from energetic electrons entering the liquid. Such excitation would require energies similar to the dissociation energies of the molecular bonds. The lack of wax formation due to prolonged direct stressing (Section 4.1.1.3) suggests that the direct excitation contribution could be quite small.

Both recombination and direct excitation processes will result in a sharply defined electroluminescence region against the cathode in agreement with the experimental observations reported in Section 4.

It is significant that in one test where intense cathode electroluminescence was observed, a Schottky plot of the conduction current-stress characteristic produced a linear relationship (Fig. 185).

When intense electroluminescence is observed at the cathode and a Schottky conduction plot is obtained it would suggest that cathode processes are governing the conduction phenomena. Kalinowski and Dera (114,116) have also reported similar phenomena to the above.

Also shown in Fig. 185 are similar plots for tests where anode electroluminescence was much more pronounced than that at the cathode. It can be seen that these characteristics show a pronounced curvature. Similar plots for all the tests conducted in Section 4 agree with the above observations.
Conduction Current Amperes.

\( 2 \times 10^{-5} \text{M/100g} \)

\( 2 \times 10^{-7} \text{M/100g} \)

\( 2 \times 10^{-5} \text{M/100g} \)

\( 2 \times 10^{-6} \text{M/100g} \)

Figure (185).

Schottky plots
Popop solutions

Nominal Stress kV/cm.
Hence the existence of intense anode electroluminescence
coupled with a non-linear Schottky plot would suggest that processes
at the anode can have a strong influence on the conduction mechanism.

5.6. Anode effect

The existence of an anode wax layer will block the free flow
of negative ions and electrons to the electrode, thus producing a
negative ion region at the wax-liquid interface. This region will
enhance the field in the layer promoting conduction processes through
it (89, 146, 154). It has been suggested by Zein-Eldine (65) that a positive
hole or Zener current mechanism may also be operative, however the
validity of applying band-model arguments dependent on a crystalline
structure to an amorphous wax layer is open to question.

Whatever the mode of conduction in the anode layer the density
of the space charge region will build up until the necessary field exists
in the layer to produce the observed conduction current.

The existence of electroluminescence at the anode over wide
ranges of stress may be regarded as evidence of direct excitation of
fluorescent molecules and recombination processes near the anode. As
described in Section 5.5, the fact that prolonged stressing does not
produce a detectable growth in the electrode layers suggests that direct
excitation of fluorescent molecules due to collisional processes may not be
the only mechanism producing electroluminescence and that recombinational
processes may also exist. For recombination to occur positive ions must
be provided and these are most likely to be produced in the highly stressed
region at the liquid-wax interface.
5.7. **Inter-dependence of anode and cathode processes**

The progression of positive ions to the cathode from the anode will result in recombination with negative carriers proceeding to the anode. The recombination rate and the intensity of the electroluminescence will be proportional to the product of the negative charge carrier and positive ion density. Thus in keeping with experimental observations the electroluminescence intensity in the liquid will be greatest near the anode and diminish steadily towards the cathode.

A state of equilibrium results when the positive ion production in the anode region is sufficient to maintain the positive ion space charge at the cathode, which in turn maintains the cathode emission and hence via the negative charge carriers, the negative space charge in the anode region. The two processes are therefore inter-dependent and will reduce the stress in the liquid to a value consistent with the necessary charge motion across the gap.

The existence of this inter-dependence between the electrodes will render the conduction current sensitive to changes in the space charge densities due to local coating or liquid instabilities. In these circumstances the conduction current may change or drift in value. Such drifts should be more apparent when thick coatings exist on the electrodes. An associated effect will be the increased time taken for the conduction current to stabilise at its new value following an alteration in the nominal applied stress. Both of the above phenomena were evident throughout the tests.
5.8. **Bulk effects and gap dependence**

When electrode coatings and their associated space charges are present the stress in the bulk of the liquid will be less than the nominal value and will depend on the thickness of the coatings. Such a reduction in bulk stress will increase the probability of recombination occurring.

In the tests where thin electrode coatings were observed the conduction current was found to increase with gap setting. Conversely in all the experiments where thick electrode coatings were found, the conduction current increased as the gap setting was reduced. These observations are consistent with the existence of recombination processes in the gap as discussed above.

5.9. **Stress effects**

Eldine and Hawley (62), see Section 2.3. obtained a conduction characteristic for a coated anode and bare cathode configuration as shown in Fig. 3. This characteristic has a similar form to those shown in Figs. 35,119,130 and 131 in the low stress regions.

The above authors suggested that at low stresses the conduction current was mainly due to impurity and ionic products of thermal dissociation and that as the stress was increased ionisation processes occurring at the anode would feed back positive ions so enhancing the cathode field and emission. A similar mechanism has also been proposed by Gallagher and Lewis for liquid argon (44).

Calderwood and Kao (61) obtained similar characteristics at low stresses and also suggest similar components of conduction current.
In the light of the above it is possible that the initial curvature in the characteristics shown in Figs. 130 and 131 occurring around 600 kV/cm is due to the conduction process changing from one due to dissociation of impurity ions to one of Schottky emission or to an electrode dependent charge multiplication process.

It was suggested in Section 5.5. that a linear Schottky conduction plot signifies that emission processes are determining the conduction current phenomena. Fig. 185(a) is such a plot obtained with a very thin cathode coating and thicker anode coating. This would suggest that the anode processes were providing an adequate supply of positive ions at the cathode, the emission being controlled by the cathode coating conditions. Conversely it was suggested that non-linear plots would imply that anode processes were not supplying sufficient ions to the cathode to cause emission limitation of the current. Under these conditions anode processes are also controlling the current. It was observed in many tests that at very high stresses the previously very faint cathode electroluminescence became much more marked and that the Schottky conduction plots (Fig. 185(b) and (c)) became linear suggesting that the anode processes were beginning to provide an adequate supply of positive ions at the cathode and that the emission properties of the cathode surface coating were beginning to limit the current. Thus it does not follow that the balance between the cathode and anode processes remains constant over the stress range or that this balance is the same for each test. Clearly the relative thickness of the coatings on each electrode will affect this balance and hence the conduction current characteristic (see the final paragraphs of Section 5.2.). The effect
of coating thickness on the conduction current will be discussed later in Section 5.11.

5.10. **Electroluminescence phenomena.**

The strong dependence of the electroluminescence on the conduction current phenomena both in the electroluminescence characteristics plotted for each test in Section 4, and in the fluctuational correlation, has been discussed in the previous sections. It has been suggested that electroluminescence is due in the main to recombination and direct excitation effects.

The electroluminescence detected by the photomultiplier will depend on the fluorescent properties of the liquid and the absorption losses in the liquid between the stressed region of the gap and the cell window. Thus due allowance must be made for these optical factors if any electrical significance is to be attached to the relative values of the electroluminescence obtained in the tests.

For the above reasons the absorption spectra given in Section 4 were obtained using a similar depth of liquid to that between the stressed region of the gap and the cell window. The emission spectra obtained with the perpendicular cell arrangement also involved a similar optical path length for the light emitted from the irradiated region.

**Effect of fluorescent characteristics of the liquid**

It is generally accepted that when optical emission occurs from a liquid, similar basic physical processes are involved irrespective of the mode of excitation (91,125,127). Thus recombination and collisional processes may be regarded as providing excitation events distributed in
population and energy and equivalent in effect to irradiating the liquid with energy according to this distribution.

Although it is known that the efficiency of the excitation energy conversion process falls with increasing irradiation energy, it is unlikely that the energy in the excitation distribution due to recombination and collisional events is significant beyond the far ultra-violet region. Thus the data obtained by ultra-violet irradiation may be applied to enable the fluorescent efficiencies of the respective samples to be compared, this comparison allowing the electroluminescence characteristics to be modified so that the effect of the optical properties of each of the samples is eliminated.

By using photomultipliers having the same type of photocathode the electroluminescence and fluorescence data are compatible and allow the data to be compared without the necessity to compensate for the spectral response of the individual photomultipliers.

The emission function

Irradiating a liquid sample with a beam of constant intensity or population \( n_i \) and of wavenumber \( \gamma_i \) will produce an emission spectra the area of which represents the photon population \( N_e(\gamma) \) of the emission.

Plotting \( N_e(\gamma) \) against the irradiating wavenumber \( \gamma_i \) will produce an emission function as shown in Fig.186.
No emission will be detected if $\gamma_i$ is less than the lower wavenumber of the emission spectrum $\gamma_1$. (Infra-red spectra are outside the spectral response of the photomultiplier).

**Effect of the absorption front**

As the irradiation wavenumber is increased from $\gamma_1$ to $\gamma_h$, the emission spectrum will change in form and increase in amplitude, the fully formed spectrum resulting when $\gamma_i$ is greater than $\gamma_h$ (125). Spectra regarded as typical of the liquid or its additive occur when $\gamma_i > \gamma_h$.

The emission spectrum amplitude will continue to grow as $\gamma_i$ is increased reaching its maximum value as $\gamma_i$ enters the shoulder of the absorption front. As $\gamma_i$ is increased further the emission amplitude steadily decreases eventually falling to a negligible value when $\gamma_i$ passes beyond the 100% absorption region.

Thus the value of the emission function $N_e(\gamma)$ will grow from a negligible value when $\gamma_i = \gamma_1$ rising to a maximum as $\gamma_i$ passes the...
absorption front shoulder and dropping to a very low value as $\gamma$ enters the 100% absorption region. This variation is illustrated in Fig. 186.

The effect of the steepness of the absorption front will be affected by the presence of fluorescence absorption bands in the front. The absorption front in the case of the liquid paraffin sample 'd' rapidly reduces the value of $N_e(\gamma)$ as the absorption approaches 100%, whereas in the samples containing Popop the approach to the 100% absorption value does not reduce $N_e(\gamma)$ appreciably until the liquid paraffin front (obscured by the absorption band of Popop) is approached.

The electroluminescence function

The emission function $N_e(\gamma)$ has been derived on the basis of constant irradiation intensity $n_i$ of varying wavenumber $\gamma_i$. With electroluminescence phenomena however, the value of $n$ probably changes with $\gamma$ so that at any value of $\gamma$ the electroluminescence function can be described by

$$N_E(\gamma) = \frac{n}{n_i} N_e(\gamma)$$

as illustrated in Fig. 187.

![Electroluminescence function](image)
The electroluminescence function will only exist over the same wavenumber range as $N_e(\gamma)$ despite the existence of $n$ over wider limits, thus the form of the excitation distribution $n$, at values of $\gamma$ below $\gamma_{el}$ is relatively unimportant.

The electroluminescent yield measured when plotting the electroluminescence against conduction current characteristic is due to the existence of $n$ over the band of wavenumbers $\gamma_{eh}$ to $\gamma_{el}$. Thus the electroluminescence will be proportional to the area under the electroluminescence function $N_E(\gamma)$.

The assumption of linearity is felt to be justified since the electroluminescence observed during the experiments was much less intense than that under irradiation, so that the emission centres available under electroluminescent conditions are unlikely to be saturated.

It is not possible to obtain $N_e(\gamma)$ directly by using a conventional spectrometer, but an approximation to the function may be deduced by using data from the absorption and emission spectra given in Section 4.

The ordinates of the distributions shown in Fig.189 were obtained by measuring the areas under the respective emission spectra. The values of these areas (in arbitrary units) are stated against the ordinates. The extremes of the distribution have been determined from the absorption spectra. The peak of the distribution has been drawn to coincide with wavelengths just within the shoulder of the absorption front (see Fig.186).
Reference to Fig. 189 shows that the width of the distribution at half the peak height is small compared with the wavenumber at which the peak occurs ($\gamma_m$). This allows the variation of $n$ with $\gamma$ within the distribution width to be neglected and taken as $n_m$, the value at $\gamma_m$.

Comparing Fig. 187 with Fig. 188 shows that the electroluminescence

$$\mathcal{E} \propto \int_{\text{el}}^{\text{eh}} N_e(\gamma) \cdot n \cdot d\gamma \text{ (in suitable units)}$$

$$\propto N_e \cdot n_m$$

Where $N_e$ is the area (in arbitrary units) under the sample emission function shown in Fig. 189 and $n_m = n$ at $\gamma_m$, and is a relative factor representing the optical characteristics of the sample.

For a given sample $N_e$ will be constant provided no change occurs in the composition or concentration of the liquid. The value of $\gamma_m$ given in the right column of Fig. 189 shows little variation over the range of samples tested, typical values being 32,000 cm$^{-1}$ for liquid paraffin, 29,000 cm$^{-1}$ for the Popop and the anthracene solutions, 27,000 cm$^{-1}$ for transformer oil and 27,000 cm$^{-1}$ for methyl-naphthalene. So, provided $n$ changes slowly with $\gamma$, the electroluminescence can be assumed to be proportional to $N_e$. 
The variations in $N_e$ sample by sample are somewhat larger, though it is of interest to note that despite the range of scintillators used, the ratio of the extreme values of $N_e$ lie within one decade.

Thus if as indicated above, the electroluminescence is proportional to $N_e$, it can be corrected in value to compensate for the effect of the differing optical characteristics of the respective samples.

**e.g.** The relative value of $N_e$ for the $2 \times 10^{-6}$ Hz/100g Popop solution is 3.3 times that of liquid paraffin sample 'd'. Hence if the excitation of electroluminescence involves similar optical processes to those occurring when the sample is irradiated, compensation for the superior emission characteristics of the Popop solution can be made by dividing the electroluminescence value from the solution by 3.3 at each value of current.

Fig. 190 shows the electroluminescence characteristics for the various samples corrected (or 'normalised') to eliminate the optical factors. It can be seen that large differences exist in the normalised electroluminescence for the various samples. This in turn implies similar differences in the excitation and recombination processes in the samples.

### 5.11. Electrode coatings

Considerable variation in the thickness and condition of the electrode wax coatings was noted in Section 4 where it was observed that the coating thickness increased with the number of breakdowns occurring in the sample.

Table 1 lists the samples in the order of anode coating thickness, the relative value of which was estimated by the following method.
Normalized Electroluminescence

Conduction Current (Amperes)

Figure (190)

Normalised electroluminescence against conduction current characteristics.
The total breakdown energy occurring in the sample was estimated on the assumption that the energy of each breakdown was proportional to the \((\text{breakdown stress})^2\). The information regarding the number of breakdowns and the breakdown stress was taken from the recordings made of each test (see Section 4).

The relative order of the samples given by the total breakdown energy was found to agree with the order obtained from the observed thickness of the anode coatings. The relative thickness of the anode coatings during the generation of the \(125\mu\) characteristic was then estimated from the energy of the preceding breakdowns and this order used to compile the list shown in Table 1.

The table also includes information about the condition of the electrode coatings and the thickness of the cathode coating. The right hand column of the table illustrates the electroluminescence distribution observed during the tests.

5.12. The effect of electrode coatings

It was suggested earlier in the discussion that the conduction processes would be strongly influenced by the existence of electrode layers; in view of these observations an attempt was made to relate the data given by the normalised electroluminescence (Fig. 19), the conduction current (given in Fig. 191) and the electrode coating data given in Table 1. This data has been collated in graphic form in the chart shown in Fig. 192. The structure of this chart is as described below.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Anode coating</th>
<th>Cathode coating</th>
<th>Distribution of the observed electroluminescence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl-naphthalene</td>
<td>Large puncture with carbonised edge in dirty wax coating</td>
<td>Fairly thick dirty wax coating, some carbon in breakdown sites</td>
<td>A [/] C</td>
</tr>
<tr>
<td>5x10^{-6} M/100g anthracene</td>
<td>Small puncture with carbonised edge in clean wax</td>
<td>Thin coating of clean wax</td>
<td>A [/] C</td>
</tr>
<tr>
<td>1% by volume methyl-naphthalene Sample (a)</td>
<td>Clean wax, some carbon in patches on wax surface.</td>
<td>Very thin coating of clean wax</td>
<td></td>
</tr>
<tr>
<td>1% by volume methyl-naphthalene Sample (b)</td>
<td>Clean wax</td>
<td>Thin coating of dirty wax with some carbon in breakdown sites</td>
<td></td>
</tr>
<tr>
<td>1x10^{-4} M/100g anthracene</td>
<td>Large puncture with carbonised edge in slightly dirty wax layer</td>
<td>Thin coating of slightly dirty wax carbon in breakdown sites</td>
<td>A [/] C</td>
</tr>
<tr>
<td>2x10^{-7} M/100g Popop</td>
<td>Clean wax, some carbon in breakdown sites</td>
<td>Extremely thin clean wax coating</td>
<td>A [/] C</td>
</tr>
<tr>
<td>2x10^{-6} M/100g Popop</td>
<td>Dirty wax</td>
<td>No wax observed on electrode</td>
<td>A [/] C</td>
</tr>
<tr>
<td>0.01% by volume methyl naphthalene</td>
<td>Clean wax</td>
<td>No wax observed on electrode</td>
<td>A [/] C</td>
</tr>
<tr>
<td>Liquid Paraffin Samples (c) and (d)</td>
<td>Clean wax, some patches of carbon on wax surface</td>
<td>No wax observed on electrode</td>
<td>A [/] C</td>
</tr>
<tr>
<td>2x10^{-5} M/100g Popop</td>
<td>Clean wax</td>
<td>Very thin clean wax coating, carbon in breakdown sites</td>
<td>A [/] C</td>
</tr>
<tr>
<td>Transformer oil</td>
<td>Very thin layer of clean wax, some carbon in breakdown sites</td>
<td>No wax observed on electrode</td>
<td>A [/] C</td>
</tr>
</tbody>
</table>

Table 1
The left hand column of the chart lists the samples in order of the normalised electroluminescence as given in Fig. 190 at a conduction current of $10^{-7}$ amperes.

The centre-left column indicates the relative thickness of the anode coating from Table 1. Any given line drawn between the two columns relates to the position in each column of that sample.

The centre-right column tabulates the samples according to the stress required to set up a conduction current of $10^{-7}$ amperes (it should be noted from Fig. 191 that if the conduction current at 600 kV/cm is considered the samples will remain in the same order).

The right hand column lists the samples according to the cathode coating thickness.

If the effect of the anode coating thickness is considered, it can be seen from the chart that:

a) As the anode coating thickness is increased it does not result in a significant increase in conduction current until a wax layer is detected on the cathode.

b) Moderately thick anode coatings are accompanied by the formation of thin cathode coatings. A very thin cathode coating results in a marked increase in the conduction current.

c) For anode coatings of greater thickness the cathode coating is correspondingly thicker and the conduction current is of reduced value, the increased cathode thickness having a very marked effect (62).
Considering the individual samples in more detail, Fig. 192 shows four samples (identified by the line code ---) that show little change in current as the anode coating thickness is increased. This suggests that the absence of a detectable cathode coating limits enhancement of emission from the cathode.

The high value of the conduction current obtained with the $2 \times 10^{-7}$ M/100g Popop solution suggests that an extremely thin cathode coating and a moderately thick anode layer provide optimum conditions for enhancing the emission from the cathode (Section 5.5). A less effective current enhancement also occurs with the $2 \times 10^{-6}$ M/100g Popop sample (the cathode layer being slightly thicker in this case).

The four samples identified by the line code ---- in Fig. 192 illustrate the effect of the increased thickness of the cathode layer. This thickness probably being sufficient to inhibit emission despite the possibility of a high rate of positive ion production at the anode implied by the high levels of normalised electroluminescence.

It would appear from Fig. 192 that the conduction mechanism in methyl-naphthalene differs from that in the other samples. Various factors may be involved in the higher conductivity of this liquid. Among them are the effects of viscosity; methyl-naphthalene has a lower viscosity than liquid paraffin or transformer oil and this may allow increased particle (140) or liquid motion (61,71-74). Conduction processes by 'electron hopping' via the orbitals of the conjugated molecular bonding have been proposed by many workers (84,147,148,150,151).
Fig. (192). Chart showing data from Figs. (190) & (191) and from Table 1. in condensed form.

Samples given in the order of increasing normalized electroluminescence at a conduction current of 10^7 A.

Table 1. in condensed form.

Stress to set up a conduction current of 10^7 A.

Increasing Anode coating thickness

Carbon patches

Clean wax

Carbon in wax layer

Stress in KV/cm

Moderately thick Thin Very thin Extremely thin No coating detected

Key to Symbols used on chart:

005 M/lOOg

Anthracene

Methyl naphthalene

2 x 10^-6 M/lOOg

Puncture in wax layer

0% meth. nap. sample (a)

1% meth. nap. sample (b)

Liquid paraffin

Trans. oil

Fig. (192). Chart showing data from Figs. (190) & (191) and from Table 1. in condensed form.

Stress to set up a conduction current of 10^7 A.

Increasing Anode coating thickness

Carbon patches

Clean wax

Carbon in wax layer

Stress in KV/cm

Moderately thick Thin Very thin Extremely thin No coating detected

Key to Symbols used on chart:

005 M/lOOg

Anthracene

Methyl naphthalene

2 x 10^-6 M/lOOg

Puncture in wax layer

0% meth. nap. sample (a)

1% meth. nap. sample (b)

Liquid paraffin

Trans. oil

Fig. (192). Chart showing data from Figs. (190) & (191) and from Table 1. in condensed form.

Stress to set up a conduction current of 10^7 A.

Increasing Anode coating thickness

Carbon patches

Clean wax

Carbon in wax layer

Stress in KV/cm

Moderately thick Thin Very thin Extremely thin No coating detected

Key to Symbols used on chart:

005 M/lOOg

Anthracene

Methyl naphthalene

2 x 10^-6 M/lOOg

Puncture in wax layer

0% meth. nap. sample (a)

1% meth. nap. sample (b)

Liquid paraffin

Trans. oil

Fig. (192). Chart showing data from Figs. (190) & (191) and from Table 1. in condensed form.

Stress to set up a conduction current of 10^7 A.

Increasing Anode coating thickness

Carbon patches

Clean wax

Carbon in wax layer

Stress in KV/cm

Moderately thick Thin Very thin Extremely thin No coating detected

Key to Symbols used on chart:

005 M/lOOg

Anthracene

Methyl naphthalene

2 x 10^-6 M/lOOg

Puncture in wax layer

0% meth. nap. sample (a)

1% meth. nap. sample (b)

Liquid paraffin

Trans. oil

Fig. (192). Chart showing data from Figs. (190) & (191) and from Table 1. in condensed form.

Stress to set up a conduction current of 10^7 A.

Increasing Anode coating thickness

Carbon patches

Clean wax

Carbon in wax layer

Stress in KV/cm

Moderately thick Thin Very thin Extremely thin No coating detected

Key to Symbols used on chart:

005 M/lOOg

Anthracene

Methyl naphthalene

2 x 10^-6 M/lOOg

Puncture in wax layer

0% meth. nap. sample (a)

1% meth. nap. sample (b)

Liquid paraffin

Trans. oil

Fig. (192). Chart showing data from Figs. (190) & (191) and from Table 1. in condensed form.

Stress to set up a conduction current of 10^7 A.

Increasing Anode coating thickness

Carbon patches

Clean wax

Carbon in wax layer

Stress in KV/cm

Moderately thick Thin Very thin Extremely thin No coating detected

Key to Symbols used on chart:

005 M/lOOg

Anthracene

Methyl naphthalene

2 x 10^-6 M/lOOg

Puncture in wax layer

0% meth. nap. sample (a)

1% meth. nap. sample (b)

Liquid paraffin

Trans. oil

Fig. (192). Chart showing data from Figs. (190) & (191) and from Table 1. in condensed form.

Stress to set up a conduction current of 10^7 A.

Increasing Anode coating thickness

Carbon patches

Clean wax

Carbon in wax layer

Stress in KV/cm

Moderately thick Thin Very thin Extremely thin No coating detected

Key to Symbols used on chart:

005 M/lOOg

Anthracene

Methyl naphthalene

2 x 10^-6 M/lOOg

Puncture in wax layer

0% meth. nap. sample (a)

1% meth. nap. sample (b)

Liquid paraffin

Trans. oil

Fig. (192). Chart showing data from Figs. (190) & (191) and from Table 1. in condensed form.

Stress to set up a conduction current of 10^7 A.

Increasing Anode coating thickness

Carbon patches

Clean wax

Carbon in wax layer

Stress in KV/cm

Moderately thick Thin Very thin Extremely thin No coating detected

Key to Symbols used on chart:

005 M/lOOg

Anthracene

Methyl naphthalene

2 x 10^-6 M/lOOg

Puncture in wax layer

0% meth. nap. sample (a)

1% meth. nap. sample (b)

Liquid paraffin

Trans. oil

Fig. (192). Chart showing data from Figs. (190) & (191) and from Table 1. in condensed form.

Stress to set up a conduction current of 10^7 A.

Increasing Anode coating thickness

Carbon patches

Clean wax

Carbon in wax layer

Stress in KV/cm

Moderately thick Thin Very thin Extremely thin No coating detected

Key to Symbols used on chart:

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2 x 10^-6 M/lOOg

Puncture in wax layer

0% meth. nap. sample (a)

1% meth. nap. sample (b)

Liquid paraffin

Trans. oil

Fig. (192). Chart showing data from Figs. (190) & (191) and from Table 1. in condensed form.

Stress to set up a conduction current of 10^7 A.

Increasing Anode coating thickness

Carbon patches

Clean wax

Carbon in wax layer

Stress in KV/cm

Moderately thick Thin Very thin Extremely thin No coating detected

Key to Symbols used on chart:

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Puncture in wax layer

0% meth. nap. sample (a)

1% meth. nap. sample (b)

Liquid paraffin

Trans. oil

Fig. (192). Chart showing data from Figs. (190) & (191) and from Table 1. in condensed form.

Stress to set up a conduction current of 10^7 A.

Increasing Anode coating thickness

Carbon patches

Clean wax

Carbon in wax layer

Stress in KV/cm

Moderately thick Thin Very thin Extremely thin No coating detected

Key to Symbols used on chart:

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Puncture in wax layer

0% meth. nap. sample (a)

1% meth. nap. sample (b)

Liquid paraffin

Trans. oil

Fig. (192). Chart showing data from Figs. (190) & (191) and from Table 1. in condensed form.

Stress to set up a conduction current of 10^7 A.

Increasing Anode coating thickness

Carbon patches

Clean wax

Carbon in wax layer

Stress in KV/cm

Moderately thick Thin Very thin Extremely thin No coating detected

Key to Symbols used on chart:

005 M/lOOg

Anthracene

Methyl naphthalene

2 x 10^-6 M/lOOg

Puncture in wax layer

0% meth. nap. sample (a)

1% meth. nap. sample (b)

Liquid paraffin

Trans. oil

Fig. (192). Chart showing data from Figs. (190) & (191) and from Table 1. in condensed form.

Stress to set up a conduction current of 10^7 A.

Increasing Anode coating thickness

Carbon patches

Clean wax

Carbon in wax layer

Stress in KV/cm

Moderately thick Thin Very thin Extremely thin No coating detected

Key to Symbols used on chart:

005 M/lOOg

Anthracene

Methyl naphthalene

2 x 10^-6 M/lOOg

Puncture in wax layer

0% meth. nap. sample (a)

1% meth. nap. sample (b)

Liquid paraffin

Trans. oil
Kallman et al (147,148) using methyl-naphthalene found a 100-300 fold increase in the conduction current when the anode was irradiated at 31302, and proposed a hole or electron hopping mechanism at the anode surface. He also suggested that positive ion production was possible. Photo-ionisation at the anode may therefore take place at high stresses, contributing to the current.

The isolation of aromatic molecules by the paraffinic constituents in transformer oil could greatly reduce the electron hopping contribution to the current. The data in Fig. 192 suggests that the conduction current in transformer oil is mainly due to conduction mechanisms that are also operative in the paraffinic samples.

5.13. Electroluminescence processes

Reference to Fig. 192 shows that the normalised electroluminescence for the 5 x 10^-6 M/100g anthracene sample is several times that of the 1 x 10^-4 M/100g anthracene, the former sample having a thicker anode layer than the latter and a lower nominal stress. Thus the bulk stress in the former sample will be considerably less than that in the latter sample whilst giving several times the electroluminescence yield.

This indicates that the electroluminescence observed in the liquid (Fig. 122 etc) is not entirely due to direct excitation processes. The increase in gap electroluminescence intensity as the anode is approached suggests that recombination processes due to effects at the anode are also present as proposed in Section 5.6. and 5.7.
Any discharge phenomena in, or at the surface of, the electrode layer could result in a wide spectral emission band due to the excitation, recombination and ionisation processes.

Such processes viewed through a transparent anode electrode or via a virtually transparent liquid such as hexane will result in spectra covering a wide range of wavelengths (113,115,119).

Spectra viewed through the liquid would be subject to its transmission properties resulting in the emitted light being typical of the liquid. Due to its high excitation energy, hexane will produce visible gap electroluminescence, the light signal being primarily due to ionisation processes at the electrodes (115,119). Liquids with lower excitation energies will reveal direct excitation and recombination phenomena in the liquid more readily, giving spectra mainly due to electroluminescence in the gap and typical of the liquid (114,118,120).

Some slight penetration of the liquid by shorter wavelength emission due to processes in the vapour phase could occur provided the liquid absorption was not too dense, and combined with the liquid emission, result in a spectrum slightly displaced to the short wavelength side of the liquid emission spectrum. Kalinowski and Dera (114) noted a slight displacement of the electroluminescence spectrum of benzene, which is difficult to degass adequately, so that the presence of vapour bubbles was more probable than with the present experimental work.
5.14. **Effect of additives**

It has been suggested by Angerer (22,23) that volatile aromatic constituents act directly within any vapour bubbles present in the gap, such action reducing the acceleration of electrons and having a quenching effect on any discrete avalanche phenomena within the bubble.

It is significant that Fig. 193 demonstrates a reduction in the normalised electroluminescence as the concentration of volatile aromatic increases, suggesting that quenching processes may be taking place in the vapour phase reducing the ionisation at the anode and hence the electrode and liquid electroluminescence.

Fig. 194 shows that a similar effect was obtained with the non-volatile aromatics, Popop having a more marked effect than anthracene. The effectiveness of Popop may be due to its oxidised nature, such additives producing surface effects (22). Electrode inspection under ultra-violet light (Section 4.5.3.5) suggested that the concentration of Popop in the liquid against the anode might have been greater than that at the cathode. It is significant that the pre-breakdown characteristic shown in Fig. 156 has considerable curvature, such curvature normally being associated with the existence of an electrode coating (Section 5.9).

If the concentration of Popop against the anode is greater than that in the rest of the liquid in the cell, emission concentration quenching effects will be increased so that the position of the normalised electroluminescence characteristics shown in Fig. 190, normalised on the assumption that the liquid concentration was uniform, may be too low. An upward transition of the lower Popop characteristics would render these
Normalised electroluminescence.

Samples containing volatile aromatic additive.

Fig. (133).

Normalized electroluminescence.

Conduction current (Amperes)
Normalised electroluminescence (arbitrary units)

- $10^5$
- $10^4$
- $10^3$
- $10^2$
- $10^1$
- 1
- $10^{-1}$
- $10^{-2}$
- $10^{-3}$
- $10^{-4}$
- $10^{-5}$
- $10^{-6}$

Conduction current (Amperes)

Fig. (194).

Normalised electroluminescence.

Samples containing non-volatile aromatics.
characteristics more consistent with the electrode coating effects illustrated in Fig. 192.

3.15. Miscellaneous

Gosling (18) noted a quenching effect on the electroluminescence when oxygen was added to the sample (see Section 2.7.8). Oxygen quenching is also found in irradiation work (125) and it has been suggested by Evans (123) that $O_2$ in the presence of aromatics can cause fluorescence quenching. Megahed (27) suggested that this coupled with the trapping effect of $O_2^+$ might explain the continuous quenching effect noted by Gosling (18) as the $O_2$ content in transformer oil was increased. The electronegative properties of oxygen have been associated with electron trapping by Lewis and Sletten (34) to explain the increased breakdown values of liquids containing oxygen. Thus it is possible that due to their electron trapping properties the concentration of oxygen molecules in a gassy liquid may increase towards the anode, the degree of quenching progressively increasing so that anode conduction processes result in little electroluminescence. The oxygen concentration at the cathode, on the other hand, may be reduced so that quenching processes there would be less effective.

It is significant that in other work where cathode electroluminescence has been observed to be as bright as that from the anode the liquids used (such as benzene and hexane (19,114)), were of high vapour pressure and are not easily degassed. Under these conditions the less intense anode electroluminescence may also be explained by the existence of quenching effects due to dissolved oxygen.
A similar effect may result when an electronegative gas such as SF\textsubscript{6} is present in the liquid. Little or no electroluminescence was noted at the anode by Nossier and Clothier (51) with SF\textsubscript{6} in degassed transformer oil. They observed a growth in the cathode electroluminescence and in the conduction current as stress conditioning proceeded, suggesting the growth of surface and charge layers at the electrodes in a similar manner to that noted for the Popop solutions.

5.16. Conclusions

The present work has shown that electroluminescence in a stressed liquid is strongly current dependent. A linear relation between log electroluminescence and log current exists over at least 4 decades with well conditioned samples and electrodes. Current fluctuations and electroluminescence fluctuations are closely linked.

The stress conditioning of a sample following a breakdown is accompanied by the formation of wax layers upon the electrodes. That upon the anode is noticeably thicker than that upon the cathode. The existence of such layers modifies the electric field in the gap and reduces the dependence of current and electroluminescence upon the gap dimensions.

The electroluminescence has been found to be in the form of a series of very short duration pulses. This suggests that the phenomenon may be due to the excitation by discharges in microcavities or recombination in or near such discharges which occur close to the electrodes. The fact that some electroluminescence is detectable (but at reduced amplitude) at some distance into the liquid may be due to positive ions accelerated out of microcavity discharges near the anode.
Measurement of the absorption and emission spectra of the liquids has made it possible to present the electroluminescence data normalised on a basis of the fluorescent properties of the solvent. The normalised characteristics representing the excitation processes that result in electroluminescence.

The measurement of the effects of aromatic additives supports the suggestion that electroluminescence may be due to ionisation in microcavities in the highly stressed regions near the anode. The effect of such additives in quenching ionisation in primary microcavities or in non-volatile secondary cavities (e.g. hydrogen microbubbles) has been previously suggested.\(^1\)

5.17. Suggestions for future work

It was suggested in the discussion that anode electroluminescence might be selectively quenched by the oxygen content of any gas present in the liquid. A cell of reversible polarity equipped with a transparent electrode would increase the probability of detecting discharge phenomena in the electroluminescence pulses and experiments using varying gas contents of oxygen and nitrogen would enable the effect of gas content on the phenomena occurring in the electrode regions to be studied.

If discharge phenomena occur in the vapour phase a pressure dependence should be detected, possibly related to the pressure dependence in the conduction current pulses noted by Megahed (27).
Experiments similar to the above using a spectrometer to analyse the emission spectra under steady and immediate post-breakdown conditions would assist in determining whether electroluminescence occurred in the liquid or vapour phases and would also give information concerning electrode healing processes following a breakdown.

More information could be obtained from the same experiments by a study of the cross-correlation in the electroluminescence and conduction current signals using a tape recording technique similar to that used by Nossier and Megahed (26,27) when studying conduction current fluctuations.

The use of a transparent electrode passing in the 7 to 10 eV energy range should show correlation if, as suggested in the discussion, ionisation at the anode plays a significant role in the conduction process.

During the course of the experimental work for this thesis the author commenced the construction of a spectrometer intended to implement some of the experimental work proposed above. The following paragraphs give a brief description of the apparatus.

**Simple electroluminescence spectrometer**

The apparatus incorporates filtering facilities down to pore sizes of 100 Å using membrane filters, filtering pressure being provided by means of a spring loaded piston, thus avoiding the use of gas pressure above the liquid surface. The test cell has a small volume of about 10cc and incorporates a sensitive pressure transducer to enable pressure and gas content effects to be studied.
The apparatus will be cleaned using refluxed Hexane passed via a 100 Å pore size filter to remove particles from the Hexane as it enters the apparatus. Hexane returning to the flask would do so via a filter by-pass to enable particles to be trapped below the filter.

The spectral determination of the electroluminescence will be obtained by using a rotating optical filter monochromator, two such filters being required to cover the visible and ultra-violet regions of the spectrum respectively. Two photomultipliers are used, one sampling the total electroluminescence signal and the other the emission at the selected wavelength. An electronic circuit (152) forms a quotient of the two photomultiplier signals, the output being applied to the Y plates of a C.R.O. The X deflection is fed from an angular displacement signal taken from the rotating filter shaft giving a deflection proportional to wavelength.

Rotating the filter at about 100 r.p.m. will provide a continuous sweep of the spectrum so that post-breakdown and steady state electroluminescence phenomena can be studied.
APPENDIX A

Preparation of new glassware used in tests

New glassware was first fumed in a solution of methyl-alcohol and nitric acid, thoroughly washed in cold water and stored until required.

All glassware required for a particular test was first rinsed with a dilute solution of 'Teepol' in water to remove any grease, thoroughly washed in water to remove traces of teepol, followed by several rinses with acetone. The acetone rinses were continued until all traces of water vapour disappeared.

Finally the glassware was thoroughly washed in hexane and heated to remove the acetone, the glassware being sealed into polythene bags until required.

Prior to immediate use the glassware was always flushed with hexane to detect traces of water vapour.

Preparation of hexane used for flushing

All hexane was re-distilled prior to use in the laboratory only distillate evaporating between the limits specified on the bottle being retained for use.

Hexane for use in cleaning the apparatus was also filtered and stored in a special bottle in a light tight cupboard.
APPENDIX B

Test liquid characteristics

All data given at 20°C.

Transformer oil  Supplied by Gulf Oil Co. Ltd.
Density 0.88 gram/cc.
Average molecular weight 310.
Relative dielectric constant 2.16.
Vapour pressure $1 \times 10^{-4}$ mmHg
Kinematic viscosity 32 c.s.

The various constituents as separated by Gosling using similar oil are by volume:

- Paraffins 24.6%, Naphthenic-paraffins 16.4%, Aromatic-naphthenics 37.6%
- and Aromatics 21.4%.

Liquid paraffin  Supplied by British Drug Houses Co. Ltd.
Density 0.83 - 0.87 gram/cc.
Average molecular weight 320.
Relative dielectric constant 2.2 (135).
Vapour Pressure $1 \times 10^{-3}$ mmHg.
Kinematic viscosity 40 c.s.

1-methyl-naphthalene $\text{CH}_3 \cdot \text{C}_10 \cdot \text{H}_7$

Density 1.02 gram/cc.
Molecular weight 142.2.
Vapour Pressure $3 \times 10^{-2}$ mmHg (149)
Boiling range 241 - 245°C.
Refractive index 1.616.
APPENDIX C.

Relative values of irradiation intensities

The emission spectra in section 4 were obtained by irradiation from a mercury vapour source using filters passing the $3650\text{\AA}$ Hg triplet and the $3130\text{\AA}$ Hg doublet respectively.

Due to the high intensity of the source it was necessary to reduce the slit setting in order to record the relative irradiation intensities at each wavelength shown in Fig. 195.

The intensity ratio, obtained by taking the ratio of the respective areas $= 6.1$.

The ratio of energies, $\frac{3650\text{\AA}}{3130\text{\AA}} = 6.1 \times \frac{3130}{3650} = 5.15$

Using a fluorescent calibration crystal the emission intensity for the emission spectra peak (proportional to irradiation intensity, at a given irradiation wavelength) was plotted against slit width setting for each irradiation wavelength.

It was found that a slit width of 0.11 mm gave 6.1 times the emission obtained with a slit setting of 0.05 mm at either irradiation wavelength.

A slit width of 0.05 mm for the $3650\text{\AA}$ irradiation and of 0.11 mm for the $3130\text{\AA}$ irradiation, was used throughout the experimental work reported in section 4.
APPENDIX D

(REPRINTED FROM NATURE, VOL. 210, NO. 5042, PP. 1219-1220, JUNE 18, 1966)

ELECTROLUMINESCENCE OF TRANSFORMER OIL AND LIQUID PARAFFIN IN HIGH D.C. FIELDS

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RELATIVELY little information is available regarding the electroluminescence of insulating oils. Darveniza and Tropper1, 2 have described electroluminescence phenomena in transformer oil, its constituents and in simple organic liquids containing fluorescent materials, when they are subjected to high d.c. stresses. Emission of light, conduction current and stress relationships were investigated and also the effect of added impurities on the breakdown voltage of the solutions. The study has been continued, for some time, at this Laboratory and the results presented here give more information about these phenomena. The test liquids used were transformer oil and liquid paraffin. Anthracene and 1,4-bis-(5-phenyloxazolyl)-benzene (POPOP) were used to study their effect on conduction current and light output.

The test samples were prepared by filtering through a No. 5 sintered glass filter and degassing to a pressure of 10⁻³ mm mercury. The test cell had a capacity of about 10 ml. and two nickel electrodes of 5 mm diameter were used to form the test gap. An eleven-stage photomultiplier was placed adjacent to a synthetic quartz window, perpendicular to the common axis of the spheres, and a microscope with a magnification of 100 was used for visual observation.

All tests were preceded by an electrical prestressing period in an attempt to stabilize the conditions during the tests. The effect of prestressing on the conduction current was similar to that reported by other workers3, 4, - 2 h being needed to obtain reproducible measurements. The photomultiplier anode current was much greater at the beginning of the prestressing period and decreased with time in an approximately exponential manner, the mean value of the light output decreasing by several decades. In most cases, reasonable steady values for mean light output could be obtained after a period of 20-30 min of prestressing. Further stressing, for as long as 6 h, resulted in only small further decrease of about 30 per cent in the light output.

The photomultiplier had an S13 cathode with the spectral response covering from 1600 to 7000 Å and was
ACKNOWLEDGMENTS

The author wishes to express his thanks to Professor D.R. Chick for the use of the laboratory facilities in the Department of Electrical and Control Engineering at the University of Surrey and to Professor W.F. Lovering, who supervised the work, for his interest and encouragement. Many discussions with his colleagues L. Angerer and B.W. Ward are also acknowledged and the author is indebted to the former for his help and co-operation in the initial stages of the experimental work.

Acknowledgments are also due to Q.V. Davis and P.K. Warrick for assistance with the electronic circuitry and to the departmental workshops and the glassblower for their help in constructing the apparatus.

The author is also grateful to the library staff for their assistance and to Miss E. Warner for typing the thesis.
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