5. INTRODUCTION

In order to understand the electrical conduction in organic materials one has to understand the process of polarization in them. Thermally stimulated discharge current (TSDC or TSC) is a method used for identifying different modes of polarization. The spontaneous discharge of electrets takes several years at room temperature, Frei and Groetzinger\(^1\) proposed a technique known as TSDC to enhance the mobility of the frozen in dipoles and charges so that the decay experiment could be done within a reasonable time. Gross\(^2\) applied ionic thermally stimulated method and showed a method of calculation
of dipole relaxation times and activation energy. The method of TSC technique is a potentially powerful tool in analysing the molecular relaxation mechanism, trapping parameters and charge storage behaviour of semi-insulators and insulators.

The method involved charge-storage and discharging both. The various processes which set during polarization may be present during discharge. Any interaction between various processes has not been ignored. The direction of specific discharge process can easily be predicted, it should generate a current of polarity opposite to that of charging current. The TSD current which is function of net charge of electret, forming temperature and rate of thermal activation shows current maxima at different temperatures. The current maxima (or peaks) have been taken as evidence corresponding to different processes of polarization under required conditions.

The charge of the thermo-electret usually arises from dipoles and trapped excess charges. In heterogeneous system the charges are trapped at phase boundaries and these charges are supplied by unequal ohmic conduction. The trapped charge-carriers give rise to "Maxwell-Wagner" charging. The excess charges may be injected in the material by Richardson-Schottky emission from metal electrode.

Caserta and Serra tried to clarify about the mechanism of the formation of electret in carnauba wax. He interpreted the results of TSD, I-V characteristics and isothermal current
measurement by proposing the existence of localized levels in between the energy bands and they act as the trapping centres responsible for storage of charge in electret. The polarization present in a molecular material is due to migration of charge carriers over microscopic distances with subsequent trapping.\textsuperscript{9,10} The current peaks are the same as due to molecular rotations except with a difference in the value of activation energy. On the basis of calculated TSD parameters, it is suggested that volume ionic space charge, frozen-in dipoles\textsuperscript{11} and ionic trapping\textsuperscript{12} are the responsible processes. Surface states and deep trapping levels have been reported in mylor films.\textsuperscript{13} Perlman\textsuperscript{14} has pointed out three stage (or level) trapping of charge carriers. Primary one is the atomic site of molecular chain, secondary one is the charge-caging between adjacent molecules and the third trapping occurs in crystalline region and/or in amorphous region and/or at the interfaces of these two.

Recent work on polymers like polyvinyl-chloride,\textsuperscript{15} polypropylene,\textsuperscript{16} teflon,\textsuperscript{17,18} polystyrene,\textsuperscript{19,20} polyvinyl butyral,\textsuperscript{21} polycarbonate\textsuperscript{22} copolymers and their blending show different relaxations.\textsuperscript{23,24} Pillai et al.\textsuperscript{25} have reported five relaxation peaks in TSD thermograms of polypropylene.

Individual atomic motions are responsible for the release of charges from primary levels. Charges released from secondary trappings are due to motion of group of atoms or motion of molecules.
Charges present in deep traps i.e., interfaces are released due to motion of main chain segment. In short the depolarization is realized by several different processes. Two such processes are well known: the relaxation of aligned impurity point-defect complexes and the relaxation of a space charge caused by mobile point defects accumulated at the electrodes. But there are other processes causing TSD peaks which have not yet been identified.

The different current peaks in the TSD thermograms are in general nomenclatured as $\alpha$, $\beta$, $\gamma$ and $\delta$ under specific experimental conditions. In polar substances either any of or all of them may be present but in case of non-polar substances $\alpha$ and $\beta$ are found. However, a trace of impurity in non-polar substance may also give rise to dipolar relaxation peaks. The $\alpha$ relaxation appears below the glass transition-temperature ($T_g$) of polymers and is due to co-operative-reorientation of polar side groups with motion of main-chain. The dipolar $\beta$ peak arises due to local motions of polar side groups which takes place in glassy state of the polymer below $T_g$. $\gamma$ peak is exhibited by some polymers under certain conditions and is due to specific geometrical configuration of the polymer matrix. The $\delta$ peak is due to space-charge or excess charge which is released by drifting of charge from the interface under SCL conditions.
6.2 DEVELOPMENT OF TSD METHOD AS A TECHNIQUE

TSD is used much more than surface charge measurement because the later takes longer time even years and does not give sufficient information about relaxation parameters, whereas electrical spectroscopy the synonymous of TSD provides this information in few hours. The capacity and stability of stored-charge depend on the large number of deep traps and small number of shallow traps. Study of these traps is possible by TSD current measurement. Frei and Groetzinger suggested the method of thermal depolarization by heating to study the electret properties. Gross and Denard tried to get information about dipolar moment by thermal depolarization. Wikstrom used this method to measure the release charge of the thermo-electret.

Dielectric measurement method is inferior to TSC owing to the reason that TSD is more sensitive to additives and impurities and also to other parameters. If more than one relaxations are present in materials then it causes broadening of the Debye curve whereas TSD can identify them separately, even very weak relaxations may be found out using peak cleaning technique. Secondly frequency response processes of dielectric materials are incompetent at lowest frequency range and below room temperature. In such cases analysis can fully be done by TSD technique. Further more losses associated with interfacial polarization do not appear in dielectric measurement.
The presence of large number of localized trapping states both above and below the Fermi level has been justified by Mott and others, on the ground that in insulating material contains large number of structural disorders. These localized levels inside the dielectric material can be characterized by thermally stimulated discharge current method. Thus by this technique we can get valuable information to understand electrical conduction in dielectrics. Jonscher, Muller and Sawa used this technique successfully for this purpose. Thus molecular phenomena of either physical and/or chemical nature giving rise to an electric potential between opposite surfaces of a dielectric can be investigated through this technique.

6.3 TSD AS ELECTRICAL SPECTROSCOPY

TSD is extremely sensitive to surface phenomena which might be necessarily be representation of bulk. TSD spectroscopy can diagnose polarization affects in dielectrics. TSC is a valuable aid in characterization of insulators. The TSC thermograms or as Perlman called electrical spectrum, offers a key to the comprehension of the fundamental microscopic mechanism responsible for charge storage and release such as dipoles, electrons, holes and ionic traps space charge etc. The charge-storage yields valuable information about electrical conduction.

The TSC spectra are unique to the insulators under study. They are finger prints of them and are sensitive to impurities,
additives, discharges, humidity i.e. to any chemical or morphological change. They provide a sensitive analytical tool that could be used to guide production of insulators with fixed electrical properties. TSC eventually can develop into electrical spectroscopy and will have practical applications in electrical quality control.

6.4 PARAMETERS AFFECTING TSD THERMOGRAMS

These parameters and factors are discussed here in brief.

6.4.1 Rate of Heating ($\beta$) - When the heating rate is slow the polymer response sooner giving a current at a lower temperature. Its intensity is lowered by a factor equal to the ratio of the inverse heating rate. The current is decreased because the final charge released is the same. The peak temperature and heating rate are related according to the following equation for dipolar relaxation processes:

$$\text{Relaxation time at the peak temperature} = \frac{kTm^2}{\beta E_a} \quad (6.1)$$

where $k$ - Boltzman's constant, $Tm$ - the peak temperature, $\beta$ - the rate of heating and $E_a$ - is the activation energy.

The shift in peak temperature can be verified by above relation. The shift in peak is toward higher temperature side with increase in rate of heating. Resolution of peaks primarily depends
upon rate of heating. But at lower rate of heating, the peak flattened which looks like isothermal decay of current.

Classification of the SCL drift and ohmic conduction for non-linear homo-electrets is done by parameter heating rate $\beta$. If there is no conduction the ultimate charge release is independent of heating rate but if SCL and ohmic conduction both are temperature dependent then ultimate charge is slightly lower for a tenfold increase in heating rate. This discrepancy arises from different extent to which the responses for SCL drift and ohmic conduction are shifted to higher temperature for higher heating rates. The contribution of unnoticed ohmic charge decay becomes relatively larger at higher heating rates. Such mechanism does not occur in dipole orientation. Gross 40 was the first to come across this phenomena. Another way of classifying SCL drift and ohmic conduction for non-polar homo-electret is by multistage TSD. The decay due to SCL drift is stabilized in later runs whereas it is not the case for ohmic conduction.

6.4.2 Forming Parameters — Polarizing field $E_p$ is much effective than polarizing temperature $T_p$ and polarizing time $t_p$. The variation of $E_p$ may lead to distinction current peaks due to dipoles and space charges. The former increases linearly 41,42 with $E_p$ whereas the later non-linearly.43,44 However, the deviation from linearity is not large. Polarizing temperature $T_p$ is the next to $E_p$ in controlling polarization in dielectrics. The peak temperature and
polarizing temperature variation are very much helpful in identifying decay of hetero-charges whether these are due to detrapping or dipole disorientation. Secondly if the current maxima is due to single dipolar relaxation then the current decreases with $T_p$ and current maxima will remain at the same position but if distributed dipole relaxation is present, the current maxima will shift with $T_p$ unless $T_p$ is chosen above the transition temperature involved i.e. at this temperature neither peak position will be shifted nor the magnitude of the peak current will change. If peak is markedly affected with change in $T_o$.

Obviously at low temperature ($T_o$) the conduction is low, so fewer carriers are available to accumulate which weakens the space-charge peak. Strikingly it's position is not changed which indicates that the carriers are not trapped at different energy levels.

The polarization time to has the same effect as that of polarization temperature. The relaxation time and activation energy increase with increasing $T_p$ but this is not the case when maximum polarization sets in.

5.4.3 Electrode System - The electrode material and system play very important role in charging the specimen. The electrode system decides the type of charging i.e., homo and/or hetero. For different electrode materials, the injection of charge carriers is different hence peak is affected by electrode material. Open circuited and closed circuited TSDC study decides the decay mode of the charging and their difference to each other.
6.4.4 Thickness and Crystallinity — As the thickness of the film increases, the current decreases. The TSC of pellets is different than that of films. Sometimes in case of pellets when laid-on electrodes are used only homo-charging takes place. The production and decay of homo-charge due to effect of crystallization and atmosphere indicate that activation energy decreases with increasing crystallinity which is a function of temperature.

6.4.5 Additives and Impurities — It has been reported that doping activates the charge stability of an electret forming material because of charge transfer complexes. Increase in activation energy with doping has also been reported in few cases.

Presence of polar impurities in non-polar substances may give rise to dipolar polarization and sometimes when these impurities are ionized under the action of field then dipoles are induced in the material. Campos et al. have observed an extra current maxima in TSDC thermogram of naphthalene single crystal when doped with alpha or beta-naphthol. The charge released was also more and the number of dipoles were found to be proportional to the impurity concentration.

6.4.6 Other Factors — Thermal sampling, humidity and preservation of thermo-electrets also affect the TSD thermograms.
Under unshielded conditions, the external charge decay due to ion deposition can be very severe. The rapid decay of the unshielded sample is attributed to compensation of electret charges by atmosphere ions attracted by the electret (this happens in corona-charged electret). Making the storage volume small by shielding, the external decay can be diminished. The charge stability can also be increased by annealing after charging. By repeatedly charging and annealing, the original charge density may be increased and at the same time charge stability is improved.

Recent experimental results indicate that even heating prior to charging improve electret stability. Improved stability has also been reported by thermal quenching prior to charging. Due to the heat treatment degree of crystallinity changes which accounts for creation of deeper traps.

6.5 THEORY

There are different theories about the polarization picture of an electret. The main contribution to this field is by Gross, Gemant, Baldus, Gerson and Rohrbaugh, Wiseman and Feaster and Gubkin. The modified Gross theory explains the charge storage phenomena. The homo-charges have been explained on the basis of surface effects. Townsend breakdown, ion-deposition on surface and bombardment of the materials are the main causes responsible for homo-charge. The hetero-charge is
developed due to bulk or internal polarization i.e., orientation of dipoles and charges trapped at deeper levels. Both the charges coexist at a time. Ultimate charge released is the combined decay of both types of charging.

In 1959, Perlman 60 and Tilly 61 reviewed the phenomenological theories of electrets. They have pointed out that qualitative prediction can thus be made for electrets polarized at one temperature and made to decay at another temperature i.e., made to decay non-isothermally. Van Turnhout 39 has given complete theory of thermally stimulated discharge current method as applied to an electret, considering the electret as Maxwell model with an equivalent capacitance and reactance. The discharge current as a function of temperature is derived as:

\[
I(T) = I_0 \exp \left[ - \frac{E_a}{kT} \right] \left( \frac{R}{\sigma_0} \right)^{-1} \int_{T_0}^{T} \exp \left( - \frac{E_a}{kT} \right) dT
\]

(6.2)

\(I_0\) - current due to initial charge stored in the equivalent capacitance of the electret, \(E_a\) - activation energy, \(k\) - Boltzmann's constant, \(\beta\) - rate of heating, \(T_0\) - room temperature, \(\sigma_0\) - the relaxation parameter (time), characteristic of the material and is expressed by the equation:

\[\sigma(T) = \sigma_0 \exp \left( \frac{E_a}{kT} \right)\]

(6.3)

where \((T)\) is the relaxation time at temperature \(T\) and

\[\sigma_0 = \frac{k T_m^2}{\beta E_a \exp \left( \frac{E_a}{kT_m} \right)}\]

(6.4)

where \(T_m\) is peak temperature.
Equation (6.3) is special condition of Equation (6.1) for maximum value of current. The total charge released is given by,

\[ Q = \int_0^\infty I(t) \, dt \]  

(6.5)

The area under the TSD curve is proportional to the charge released. The activation energy can be calculated from the low temperature tail of Equation (6.2), using equation –

\[ \log I(t) = \log I_0 - \frac{E_a}{kT} \]  

(6.6)

Thus a plot of \( \log I(T) \) Vs. \( \frac{1000}{T} \) gives a straight line where slope gives the value of \( E_a \). This is called initial rise method of Garlick and Gibson. 62

6.6 PRESENT INVESTIGATION

Thermally stimulated discharge current measurement of naphthalene, ferrocene and their mixture have been carried out. These two substances when mixed together do not react with each other but forms a organic complex compound which gives additive effect. The measurements are made on thick films as pellets of uniform thickness. The current measurement with different parameters within experimental limitations have been made. Some interesting results have been observed.

6.7 EXPERIMENTAL

Thin pellets of naphthalene, ferrocene and their mixture in rectangular shape of the order of 600 microns were prepared by
pouring melted substances in mica frames. The tin foil electrodes are used by fixing them on brass plate fixed in a brass stand as described in Chapter III. The electrodes are of blocking type. The lower electrode can be considered as metallized because melted substances are poured on it; this becomes cathode when connected to negative of the battery terminal. The upper electrode is pressed with the help of a long screw as shown in Fig. 3.1. Thus anode is positively a laid-on electrode. The electrets are prepared as described in Chapter III.

The electrets were poled at different fields and temperatures. The field is applied for five hours and then the specimen is cooled in half an hour to temperatures 35°C, 20°C and 0°C respectively with three rates of cooling. The field was kept on during cooling. The electrets were heated with different linear rates of heating to observe TSD currents. The current was recorded with the help of 500B Keithley Electrometer. The electrets were short-circuited for five minutes before heating, to avoid stray effect due to surface charges. The DC field was applied by 90 volts eveready batteries. The thickness was measured with the help of micrometer screw. In most of the cases it is kept constant. For each measurement a fresh sample is used. Shielded chamber is used for cooling and thermal treatment to avoid humidity effects which might be possible due to surroundings. Shielded wire are used for circuit connections and shieldings are earthed.
6.8 RESULTS AND DISCUSSIONS

6.8.1 Naphthalene - The electrets are poled at 72°C with two fields and stimulated with two rate of heatings. The thermograms are shown in Fig. 6.1. The peak current increases with field and rate of heating but the peak position is independent of field and shifts to higher temperature side with rate of heating. The log I Vs. \( \frac{1000}{T} \) plots are shown in Fig. 6.2 and the corresponding relaxation parameters are given in Table 6.1.

The three curves of Fig. 6.1 indicate that the released charge increases non-linearly with field and increases with higher rate of heating. It is suspected that the charging is due to carriers trapping. The sharpness of the peak increases with higher rate of heating whereas for lower rate of heating the rise of current near peak temperature is curved. It can be said that the emission or decay of charging is controlled. Peak temperature shifts with rate of stimulation. In case of curve 3 an extra small current maxima is present after that current rise is controlled. All the three curves are obtained from electrets when cooled below room temperature. It is found that for every curve current decreases around 20°C and then increases which indicates that a low relaxation time phenomenon has already been discharged below 20°C. The current peak of curve 3 may be due to homo-charge deposition as the field is sufficient to do so. Such deposition is possible because the surface resistivity of naphthalene is very
FIG 6:1 TSC SPECTRA OF NAPHTHALENE
FIG. 6.2  INITIAL RISE PLOTS FOR CURVE OF FIG. 1
Two current maxima were reported in naphthalene crystals by Campos et al.\textsuperscript{53} The processes of polarization is dipole's orientation and carrier trapping to form Schottky barrier polarization. The dipoles present may be intrinsic or/and extrinsic. Baldus\textsuperscript{54} admitted the existence of dipoles in such crystals. In recent papers of Campos et al.\textsuperscript{55} observed a slow decay of surface potential of corona-charged crystals of naphthalene. They explained it by proposing deep exponential distribution of traps.\textsuperscript{56} These electron traps are discrete one according to Campos and Mergulhao.\textsuperscript{51} They observed three current maxima with activation energies 0.5, 0.79 and 1.1 eV and explained them by proposing discrete electron-trapping levels present in naphthalene crystals.

Campos et al.\textsuperscript{51} stated that if the polarization is uniform but due to migration of charges over microscopic distances with subsequent trapping then the glow peak has exactly the same shape as those for dipole-orientation. In both these cases the temperature at maximum of the current occurs independent of polarization field and polarization temperature but depends on space-charge. In such cases it is difficult to name process of polarization as due to SCL drift and diffusion or dipole-orientation. If total stored charge increases linearly with the applied field, the dipole-orientation is present and if non-linearity then space-charge polarization is present. Thus polarization is due to SCL diffusion
and drift on the basis of above mentioned facts. The excess charges originate by dissociation of impurity centres. As the naphthalene used in present investigation is commercially supplied therefore, impurities might be present.

The space-charge polarization must likely to occur at forming temperature near to softening temperature. In this case poling temperature $345^\circ K$ is very near to melting point $359^\circ K$ of naphthalene. Thus conduction $57$ (due to presence of impurities) with SCL drift and diffusion, contribute to space-charge polarization as the ultimate released charge is not independent of heating rate. At the same time the current is mainly carried by injected carriers at higher voltage. Such injection is possible from cathodic side (considered to be ohmic-contact).

A corona-discharge may take place in the air gap between electrode-electret interface at anode side with higher polarization field. Such discharges deposit cations. $58$ The ions arriving on surfaces do not retain their excess electrons which are injected into sample. Such corona-discharge in air can be interpreted in terms of diffusional charge migration and charge trapping. Thus SCL diffusional, drifting of charges with ohmic conduction set polarization by trapping at discrete trapping levels having activation energy in the range 0.39 to 1.62 eV. In case of curve 3, it can be said that the first unresolved maxima is due to trapping of charges from corona-discharge at deeper traps. Few of these traps are filled by diffusional migration. The release of charges from shallow traps is maximum. Sharp decrease of current violates retrapping mechanism.
### TABLE 6.1 (Fig. 6.1) Data for TSC Thermograms of Naphthalene.

<table>
<thead>
<tr>
<th>Curve No.</th>
<th>Pol.Field (kV/cm)</th>
<th>Pol.Temp. (°C)</th>
<th>Rate of stimulation (°K/m)</th>
<th>Peak Temp. (°C)</th>
<th>Peak current in Amp.</th>
<th>Activation energy in eV</th>
<th>$\tau_0$ (in sec. at infinite time)</th>
<th>$\tau_{300}$ (in sec. at 300°K)</th>
<th>$\tau_m$ (in sec. at peak temperature)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.4</td>
<td>72</td>
<td>11</td>
<td>55.55</td>
<td>0.4x10^{-6}</td>
<td>1.62</td>
<td>29.24x10^{-24}</td>
<td>50.57x10^3</td>
<td>37.13</td>
</tr>
<tr>
<td>2</td>
<td>5.8</td>
<td>72</td>
<td>10</td>
<td>53.33</td>
<td>0.4x10^{-7}</td>
<td>1.02</td>
<td>5.91x10^{-15}</td>
<td>1.32x10^3</td>
<td>53.91</td>
</tr>
<tr>
<td>3-I</td>
<td>9.5</td>
<td>72</td>
<td>8</td>
<td>25.55</td>
<td>0.4x10^{-7}</td>
<td>0.37</td>
<td>7.26x10^{-5}</td>
<td>1.52x10^2</td>
<td>155.48</td>
</tr>
<tr>
<td>3-II</td>
<td>9.5</td>
<td>72</td>
<td>8</td>
<td>60.00</td>
<td>0.5x10^{-5}</td>
<td>0.76</td>
<td>2.55x10^{-12}</td>
<td>1.77x10^3</td>
<td>94.58</td>
</tr>
</tbody>
</table>

### TABLE 6.2 (Fig. 6.3) Data for TSC Thermograms of Ferrocene.

<table>
<thead>
<tr>
<th>Curve No.</th>
<th>Pol.Field (kV/cm)</th>
<th>Pol.Temp. (°C)</th>
<th>Rate of stimulation (°K/m)</th>
<th>Peak Temp. (°C)</th>
<th>Peak current in Amp.</th>
<th>Activation energy in eV</th>
<th>$\tau_0$ (in sec. at infinite time)</th>
<th>$\tau_{300}$ (in sec. at 300°K)</th>
<th>$\tau_m$ (in sec. at peak temperature)</th>
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<tbody>
<tr>
<td>1</td>
<td>7.5</td>
<td>72</td>
<td>12</td>
<td>128.00</td>
<td>0.25x10^{-10}</td>
<td>0.16</td>
<td>20.82</td>
<td>1850.87</td>
<td>597.52</td>
</tr>
<tr>
<td>2</td>
<td>9.0</td>
<td>72</td>
<td>8</td>
<td>123.00</td>
<td>0.25x10^{-10}</td>
<td>0.35</td>
<td>1.10x10^{-2}</td>
<td>9052.47</td>
<td>297.33</td>
</tr>
<tr>
<td>4-I</td>
<td>9.0</td>
<td>72</td>
<td>11</td>
<td>51.00</td>
<td>0.27x10^{-10}</td>
<td>0.55</td>
<td>23.59x10^{-8}</td>
<td>9.67x10^2</td>
<td>92.11</td>
</tr>
<tr>
<td>4-II</td>
<td>9.0</td>
<td>72</td>
<td>11</td>
<td>119.00</td>
<td>0.32x10^{-10}</td>
<td>0.35</td>
<td>5.15x10^{-3}</td>
<td>5183.75</td>
<td>292.17</td>
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<tr>
<td>4-III</td>
<td>9.0</td>
<td>72</td>
<td>11</td>
<td>152.00</td>
<td>0.95x10^{-10}</td>
<td>1.67</td>
<td>5.93x10^{-19}</td>
<td>9.69x10^9</td>
<td>91.75</td>
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</table>
5.8.2 Ferrocene — The thermally stimulated discharge current decay characteristics are shown in Fig. 6.2. The electrets are poled at different temperatures with different field strengths. The other conditions are identical to that of naphthalene. The polarization time and preservation time are the same in all cases. Three rates of heatings are taken for stimulation. The electrets are stimulated with uniform rate of heating near the melting point of ferrocene (m.p. $445^\circ$K). Ferrocene shows remarkable stability, it resists heat, catalytic reduction and is not affected by dilute alkali acids even at the boiling point.

In Fig. 6.2, three current maxima are well defined in case of curve 4 poled at higher field (with less thickness) and curve 5 stimulated with lower rate of heating (polarized at higher temperature). When the electret is poled at higher temperature and is also stimulated with higher rate (Curve 3), the first current maxima is well defined whereas remaining two are overlapped. If such electrets are stimulated with higher rate of heating then single current peak with controlled initial decay is observed (Curve 1). If field is increased slightly the area under peak is more but only single current maxima is exhibited (Curve 2). Thus the current maxima are the function of field and temperature both. There is no change in peak position of first peak but the remaining two peaks are affected by rate of heating. The area underlying curves 3 and 5 is almost the same whereas in case of curve 4 it is less than curves 3 and 5. Similarly the area under
Fig. 6.3 TSC SPECTRA OF FERROCENE

<table>
<thead>
<tr>
<th>TEMP °C</th>
<th>FIELD kV/cm</th>
<th>RATE °C/M</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 72</td>
<td>6.9</td>
<td>12</td>
</tr>
<tr>
<td>2. 72</td>
<td>8.9</td>
<td>8</td>
</tr>
<tr>
<td>3. 72</td>
<td>9.0</td>
<td>10</td>
</tr>
<tr>
<td>4. 72</td>
<td>11.76</td>
<td>11</td>
</tr>
<tr>
<td>5. 76</td>
<td>9.2</td>
<td>8</td>
</tr>
</tbody>
</table>

CURRENT AMPS

TEMPERATURE °C

30  60  90  120  150  160

10^-11

Curves 1, 2, 3, 4, 5 represent different conditions or measurements.
curve 1 is less than curve 2. In this way charge released is the function of temperature and field but it does not show a regular variation with rate of heating. In curve 2 there are crests corresponding to first two peaks. It means the polarization corresponding to these relaxation phenomena takes place partially. If we increase field or/and temperature then all the three peaks are prominent and can be resolved by fractional polarization using peak cleaning technique. Thus polarization might have taken place corresponding to each relaxation present therein with field and temperature. If the electrets are cooled either at higher field or at higher temperature or at both simultaneously then the current after third current maxima increases continuously even up to the melting point of the substance.

The log I Vs. \( \frac{1000}{T} \) plots for these curves are shown in Fig. 6.4 and calculated relaxation parameters are shown in Table 6.2.

The area under peak around 60°C does not depend much on rate of heating but is affected by thickness and polarization temperature. This peak does not occur in curves 1 and 2 with field less than 9 kV/cm. The field corresponding to curves 3, 4 and 5 is 9 kV/cm which is sufficient to produce corona-discharge through the air gap in between anode and sample surface. The charge corresponding to it may be due to ion-deposition. These ions may be extrinsic or/and intrinsic. It is also possible that in solids an orientation of dipoles often involves the movement of ions from one equilibrium position to another. Ferrocene is a compound of cyclopentadiene which is a strong acid ( \( K_a = 10^{-13} \) ) indicating that loss of a
Fig. 6.4 Initial rise plot for curves in Fig. 6.3

Ferrocene

1

2

4.1

4.3

4.2

1000/T (°K⁻¹)

Current Amps

10⁻¹¹

10⁻¹⁰

10⁻¹⁰

10⁻¹¹

Current Amps
hydrogen ion gives a particular stable anion. Initially it was formulated with ionic structure (two cations of cyclopentadiene in equilibrium positions around iron anion). Therefore, movement of ions associated with it and/or with ion deposition from corona-discharge together contribute to dipolar-like polarization which on depolarization exhibits current maxima around 60°C. The activation energy corresponding to this peak is 0.37 eV.

The peaks around 120°C and 150°C are due to trapping at various levels. The carriers are produced due to injection, deposition and ionization of impurities. Such trapping occurs during conduction or/and diffusion of these charge carriers. As the current maxima around 120°C is broad for each curve, it may be due to detrapping of charge carriers from shallow trapping levels. The density of shallow traps is greater than density of deeper traps. The origin of these traps can be understood as follows.

Ferroocene is markedly aromatic in character, therefore, allows nuclear substitutional reaction which is due to active Π-bond. Its metal atom of iron is being bound to each ring by four covalent bonds. Its electronic configuration accounts for diamagnetic behavior. Such structures have shallow traps with large density of deeper traps. The more electro-negative substituents provide a more stable charge storage sites for negatively charged electrets.

Therefore, second current maximum is exhibited by releasing charges from shallow traps. The activation corresponding to it is
lower i.e., of the order of 0.35 eV. It means the charges from
detrapping of first relaxation are also contributing to this peak.
The maxima with an activation energy 1.67 eV contributed by
clearance of deeper traps at softening point, has occurred around
150°C. This is a peak and markedly affected by polarization
temperature. The charging corresponding to this peak is due to
ohmic conduction of thermally activated carriers present due to
impurities and SCL drift and diffusion of carriers either injected
or/and due to ionic deposition from corona-discharge.

6.8.3  Mixture  -  The TSD current is measured as a function of
field, temperature, rate of heating and rate
of cooling. The results are summarized as follows.

6.8.3(1)  Comparison  -  A comparative study of naphthalene,
ferrocene and their mixture in identical
conditions revealed new trapping sites in mixture. These three
materials are polarized at 72°C with 9 kV/cm field strength and
cooled with medium rate of cooling ( γ ). Such thermograms are shown
in Fig. 6.5 and their log I Vs. \( \frac{1000}{\tau} \) plots are shown in Fig. 6.6.
The calculated relaxation parameters are shown in Table 6.3. TSC
spectra of naphthalene exhibit only one peak at 55°C while that of
ferrocene at 123°C. In the case of mixture two current maxima at
55°C and 81°C are observed.

The charging and discharging processes in case of naphthalene
and ferrocene have already been discussed. The carriers due to injection
FIG. 6.5 TSC SPECTRA OF ELECTRETS
POLED AT 72°C

FIELD = 9 kV/cm

CURRENT AMPS

TEMPERATURE °C

NAPHTHALENE $\times 10^{-8}$

MIXTURE $\times 10^{-11}$

FERROCENE $\times 10^{-12}$
FIG. 6.6 INITIAL RISE PLOTS

- Current Amps
- \(10^{-10}\) to \(10^{-12}\)

- \(1000/T (K^{-1})\) from 2.55 to 3.25

- Lines labeled:
  - Mixture (I Peak)
  - Mixture (II Peak)
  - Naphthalene
  - Ferrocene
### TABLE 5.3 for (Fig. 6.5) Data for TSC thermograms for comparative study.

<table>
<thead>
<tr>
<th>Curve No.</th>
<th>Pol. Field (kV/cm)</th>
<th>Pol. Temp. (°C)</th>
<th>Rate of stimulation (°K/m)</th>
<th>Peak Temp. (°C)</th>
<th>Peak current in Amp.</th>
<th>Activation energy in eV</th>
<th>( \tau_0 ) in sec. at infinite time</th>
<th>( \tau_{300} ) in sec. at 300°K</th>
<th>( \tau_m ) in sec. at peak temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>9</td>
<td>72</td>
<td>8</td>
<td>55.00</td>
<td>1.8\times 10^{-8}</td>
<td>0.47</td>
<td>1.54\times 10^{-5}</td>
<td>1191.00</td>
<td>151.00</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>9</td>
<td>72</td>
<td>8</td>
<td>123.00</td>
<td>0.25\times 10^{-10}</td>
<td>0.35</td>
<td>1.10\times 10^{-2}</td>
<td>8052.00</td>
<td>297.00</td>
</tr>
<tr>
<td>Mixture-I</td>
<td>9</td>
<td>72</td>
<td>9</td>
<td>55.00</td>
<td>2.5\times 10^{-10}</td>
<td>0.57</td>
<td>2.57\times 10^{-7}</td>
<td>923.00</td>
<td>125.00</td>
</tr>
<tr>
<td>Mixture-II</td>
<td>9</td>
<td>72</td>
<td>8</td>
<td>91.00</td>
<td>2.5\times 10^{-10}</td>
<td>0.60</td>
<td>4.25\times 10^{-7}</td>
<td>4150.00</td>
<td>139.00</td>
</tr>
</tbody>
</table>

### TABLE 5.4 for (Fig. 5.10) Data for TSC thermograms of Mixture. Effect of Rate of Cooling (Crystallinity)

<table>
<thead>
<tr>
<th>Curve</th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
<th>(4)</th>
<th>(5)</th>
<th>(5)</th>
<th>(7)</th>
<th>(9)</th>
<th>(9)</th>
<th>(10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curve-1</td>
<td>12</td>
<td>72</td>
<td>7</td>
<td>97.00</td>
<td>0.12\times 10^{-9}</td>
<td>0.10</td>
<td>47.72</td>
<td>1931.00</td>
<td>1059.00</td>
<td></td>
</tr>
<tr>
<td>Curve-2-I</td>
<td>12</td>
<td>72</td>
<td>7</td>
<td>59.00</td>
<td>0.18\times 10^{-9}</td>
<td>0.40</td>
<td>1.60\times 10^{-4}</td>
<td>859.00</td>
<td>214.30</td>
<td></td>
</tr>
<tr>
<td>Curve-2-II</td>
<td>12</td>
<td>72</td>
<td>7</td>
<td>82.00</td>
<td>0.20\times 10^{-9}</td>
<td>1.06</td>
<td>1.60\times 10^{-13}</td>
<td>101\times 10^{3}</td>
<td>92.68</td>
<td></td>
</tr>
<tr>
<td>Curve-3-I</td>
<td>12</td>
<td>72</td>
<td>7</td>
<td>24.00</td>
<td>0.55\times 10^{-8}</td>
<td>1.79</td>
<td>4.17\times 10^{-29}</td>
<td>14.22</td>
<td>3.87</td>
<td></td>
</tr>
<tr>
<td>Curve-3-II</td>
<td>12</td>
<td>72</td>
<td>7</td>
<td>59.00</td>
<td>0.48\times 10^{-7}</td>
<td>0.40</td>
<td>1.60\times 10^{-4}</td>
<td>1931.00</td>
<td>1059.00</td>
<td></td>
</tr>
<tr>
<td>Curve-3-III</td>
<td>12</td>
<td>72</td>
<td>7</td>
<td>77.00</td>
<td>0.22\times 10^{-9}</td>
<td>0.35</td>
<td>2.24\times 10^{-3}</td>
<td>1811.00</td>
<td>271.00</td>
<td></td>
</tr>
</tbody>
</table>
ionization of impurities, ion-deposition from corona-charge are
trapped. Such carriers when detrapped contribute to SCL and the
corresponding current maxima is observed. The peak due to
detrapping from surface states might have occurred below room
temperature, it is not observed in case of naphthalene as the
cooling rate is medium one.

The formation of temperature in case of ferrocene is very
lower than its softening temperature, therefore, the charging
corresponding to shallow traps level may be expected in it.

In case of mixture electrons of \( \pi \)-bond may be activated
with molecular vibrations at the softening point of mixture and
are frozen at the interior during cooling giving rise to internal
polarization. The charging may be due to filling of shallow and
deeper traps. Depolarization of such charging exhibit two current
maxima.

6.8.3(11) Effect of rate of cooling or crystallinity

cooled slowly to 35\(^{\circ}\)C (say with \(X\) cooling rate) are shown in
Figs. 6.7 and 6.12. The peak current decreases and the curvature
around 55\(^{\circ}\)C increases with increasing field strength. The peak is
shifted to higher temperature side on increasing the forming field
(Fig. 6.7) and rate of heating (Figs. 6.9, 6.9 and 6.10). In
Fig. 6.7 there is a sharp rise in initial current near peak
temperature, the current is nearly constant during the temperature
TSC SPECTRA OF ELECTRET (MIXTURE)
POLED AT 72°C

FIG. 6.7 COOLING RATE X

FIG. 6.8 COOLING RATE Y

FIELD
\( \text{KV-Cm}^{-1} \)
1 4.5
2 6.0
3 12

STIMULATION
\( ^\circ \text{K-m}^{-1} \) RATE
1 9
2 9
3 7

FIELD
\( \text{KV-Cm}^{-1} \)
1 6
2 12
3 12

STIMULATIONS RATE
\( ^\circ \text{K-m}^{-1} \)
1 8
2 9
3 7

CURRENT AMPS

TEMPERATURE \( ^\circ \text{C} \)
range $50^\circ$-$80^\circ$C for curve 3. The current rises beyond the temperature $100^\circ$C without exhibiting any current maxima which is clear from Fig. 6.12. The peak position corresponding to curves 1, 2 and 3 of Fig. 6.7, are $72^\circ$, $90^\circ$ and $87^\circ$C respectively.

The thermoelectrets cooled at faster rate than the previous one (say with $Y$ cooling rate) when depolarized by heating exhibit two current maxima and they are quite sharp in comparison to previous one but are joined together at base. These thermograms are shown in Fig. 6.8. The peak current decreases with increasing forming field but the decrease is less than the previous one. The second peak is very much affected by rate of heating and forming field than the first one. The current maxima corresponding to curves 1, 2, and 3 of Fig. 6.8 are at $57^\circ$, $75^\circ$C; $59^\circ$, $83^\circ$C; $59^\circ$, $82^\circ$C respectively.

The thermograms in Fig. 6.9 are of those thermo-electrets which have been cooled rapidly to $0^\circ$C (say with $Z$ cooling rate). Three current maxima are present in case of curves 2 and 3 whereas only two current maxima are there in case of curve 1. But in all cases they are quite resolved to each other. The first peak does not respond to rate of heating while the remaining two respond for both i.e., rate of heating and forming field. In case of curve 1 first current maxima is absent at low forming field. The peak height and width of peak is more in all the three cases.
FIG. 6-10 TSD SPECTRA OF ELECTRET POLED
AT 72°C, FIELD KV CM⁻¹, RATE OF HEATING
7 KMʰ⁻¹ AND COOLING RATE 1-2, 3-4, 3-2

FIG. 6-9 TSD SPECTRA OF ELECTRET
POLED AT 72°C, COOLED WITH
RATE Z
1. EP 4.5 KV CM⁻¹, RP 15 KMʰ⁻¹
2. EP 11 KV CM⁻¹, RP 10 KMʰ⁻¹
3. EP 13 KV CM⁻¹, RP 7 KMʰ⁻¹
FIG. 6.11 INITIAL RISE PLOTS FOR CURVES OF FIG. 6.10
FIG 6.12  TSC SPECTRA OF MIXTURE
COOLING RATE X

WITH POLING PARAMETERS

<table>
<thead>
<tr>
<th></th>
<th>$E_p$ (kV/cm)</th>
<th>$T_p$ (°C)</th>
<th>$R_p$ (°C/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.3</td>
<td>50</td>
<td>9</td>
</tr>
<tr>
<td>2</td>
<td>8.3</td>
<td>50</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>13</td>
<td>50</td>
<td>9</td>
</tr>
<tr>
<td>4</td>
<td>8.3</td>
<td>72</td>
<td>9</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>55</td>
<td>9</td>
</tr>
</tbody>
</table>

CURRENT (A)

TEMPERATURE °C
To observe the effect of rate of cooling on TSD thermograms of thermo-electrets prepared under identical conditions but cooled with three different rate of cooling are shown in Fig. 6.10. Semi-log plots of current Vs. reciprocal of temperature are shown in Fig. 6.11. The activation energies were calculated by initial rise method of Garlick and Gibson. 62 The different relaxation times were calculated according to Bucci et al. 3 theory and Cowell and Woods technique. 75 These relaxation parameters are shown in Table 6.4.

The activation energy corresponding to curve 1 of Fig. 6.10 is found to decrease due to the fact that there is an increase in crystallinity 47 (when cooled with slow rate). The peak position is shifted to higher temperature side with increasing crystallinity. These two facts are observed in these measurements. There is a knee in the temperature range 55°C-60°C therefore a peak which is not separated is expected. Rise in TSD current is suspected due to space-charge limited current. It is also possible that during slow cooling, the carriers detrapped from deep levels due to molecular vibrations are trapped at shallow trapping sites. During discharge process interaction of charge carriers with molecular motions and with carrier itself, may control release of charge carriers and hence the TSD current. This explains the broadening of TSD thermogram with high crystallinity and distribution of activation energies. In case of curve 2 of Fig. 5.10, because of faster rate of cooling crystallinity may be less or more disordered.
but at the same time trapped charge carriers are frozen sooner
with slight effect of molecular motions on them and hence two
current maxima are present. Setting of molecular motions affects
the trapping sites and hence the stepping polarization. Therefore,
the peaks are not completely resolved. The response of forming
field and rate of heating is more in case of second peak than the
first one which is clear from Fig. 6.10.

The first current maxima in Fig. 6.9 of curves 2 and 3 are
independent of rate of heating and is absent at low forming field.
It occurs below room temperature. The activation energy
Corresponding to these peaks is maximum 1.78 eV and hence the
relaxation time is minimum. Such peaks are due to discharge of
ions deposited during corona-discharge, displacement of ions due
to rotation of cations around iron anion may also contribute it.
Such charging occurs as if induced dipoles are produced in the
material. It may be possible that one of the component of mixture
is ionized at higher temperature with such field and thus inducing
dipoles then this current maxima will be due to first order
kinetic polarization. 77 The second current maxima may correspond
to filling of shallow traps which are increased relative to
individual components. This peak is large in comparison to first
and third peak. The third current maxima is due to detrapping of
charge carriers from deep traps.

6.8.3(iii) Temperature Effect — The TSD thermogram in
Fig. 5.12 are of electrets
poled with different fields and temperatures but cooled with slower rate X. Such thermogram exhibit only single peak. The area of the peak increases with field and temperature. Temperature effect is much more than field. The peak temperature shifts to higher temperature side with heating rate. The current continuously increases above 100°C without exhibiting current maxima. The charging corresponding to these thermogram is suspected to be trapping of carriers at different levels. The continuous increase of current may be because of change of phase and contact potential of electrode and material.

6.8.3(iv) Effect of rate of Heating — The effect of rate of heating can be studied from thermogram of electrets poled at 34°C with field 12 kV/cm as shown in Fig. 6.13. These electrets are cooled with faster rate of heating Y than thermograms of Fig. 6.12. The observed two peaks shift towards higher temperature side. The charges which contribute to these peaks are released from two different trapping levels. The released charge depends on rate of stimulation which is clear from Fig. 5.14. It increases with rate of heating.

6.83(v) Field Effect — The Fig. 5.15 shows thermograms of electrets poled at room temperature and then cooled with faster rate Y. The first peak is very prominent whereas second peak which only occurs for higher field is small one. It indicates that at room temperature only shallow
FIG 6.14
TSC SPECTRA OF MIXTURE
POLED AT 72°C WITH 12 KV CM⁻¹
RATE OF STIMULATION 9°CM⁻¹
CURVE-1 COOLED WITH FASTER RATE THAN CURVE-2

FIG 6.15
TSC SPECTRA OF MIXTURE
POLED AT 34°C

<table>
<thead>
<tr>
<th>THICKNESS</th>
<th>FIELD VOLTS</th>
<th>RATED STIMULATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>740</td>
<td>14.8</td>
</tr>
<tr>
<td>2</td>
<td>740</td>
<td>16.6</td>
</tr>
<tr>
<td>3</td>
<td>500</td>
<td>13.5</td>
</tr>
<tr>
<td>4</td>
<td>500</td>
<td>16.6</td>
</tr>
</tbody>
</table>

TEMPERATURE °C
FIG. 8.13  TSC SPECTRA OF MIXTURE
POLED AT 34°C WITH FIELD 12 KV/CM⁻¹

COOLING RATE Y

STIMULATING RATES
1 - 6 °Cm⁻¹
2 - 7.5 °Cm⁻¹
3 - 9 °Cm⁻¹

CURRENT (A)

TEMPERATURE °C

30 40 50 60 70
traps are filled. The released charge from these traps exhibits first peak. The deeper traps contribute a little. The homocharge deposition at higher field controls diffusional migration and hence trapping, therefore, area under curves 2 and 4 is less than for curves 1 and 2 at lower field. Rate of heating shifts peak to higher temperature side. The semi-log plots of current vs. inverse of temperature for thermograms of Figs. 5.14 and 5.15 are shown in Fig. 5.16. The relaxation parameters are given in Tables 5.5 and 6.6. The activation energy decreases with increasing field and crystallinity.

6.8.3(vi) Multi-Run TSDC — The behaviour and nature of thermograms of Fig. 6.17 are the same as that of Figs. 5.14 and 5.15. The difference is that the current increases to negative side when depolarization is over. To understand this behaviour, second run TSD current is observed. In Fig. 6.18 the curves for first and second run TSD are represented. In second run TSD the depolarized current is observed but without exhibiting peak. It seems that the current is stabilized during second run TSD due to SCL drift effect. A negative current is again observed. It can be explained as follows.

Ferrocene is dissolved in naphthalene. The latter is having traps with exponential distribution of energy and such traps are electron traps. If non-bonding electrons of ferrocene are shared with the electron-traps then the traps created due to mixing will not be neutral. Such traps could not be filled at room temperature
FIG 6.16 INITIAL RISE PLOT OF CURVES IN

FIG 6.15 AND FIG 6.14

1
3
2
4

$\times 10^{-9}$

$\times 10^{-9}$

CURRENT (A)

$\frac{1000}{T}$ (°K⁻¹)
FIG 6.17
TSC SPECTRA OF MIXTURE
POLED AT TEMPERATURE 34°C

<table>
<thead>
<tr>
<th>THICKNESS FIELD</th>
<th>1 mm</th>
<th>VOLT</th>
<th>KV/CM</th>
<th>RATE °C/µm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.5</td>
<td>270</td>
<td>5.4</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>.5</td>
<td>740</td>
<td>14.8</td>
<td>9</td>
</tr>
<tr>
<td>3</td>
<td>.3</td>
<td>740</td>
<td>24.6</td>
<td>8</td>
</tr>
<tr>
<td>4</td>
<td>.3</td>
<td>500</td>
<td>16.6</td>
<td>8</td>
</tr>
</tbody>
</table>

CURRENT (A)

10⁻³

+VE

1x10⁻¹

-VE

1x10⁻¹

TEMPERATURE (°C)

30  40  50  60  70  80  90  100  110  120  130
FIG 6.18

TSC SPECTRA OF MIXTURE
POLED AT 34°C WITH
FIELD 11 KV CM⁻¹
RATE OF STIMULATION °C m⁻¹

FIRST RUN CURVE - 1 - 5
" - 2 - 8
SECOND RUN CURVE - 3 - 5
" - 4 - 8
### TABLE 6.5 for (Fig. 6.14) Data for TSC thermograms of Mixture.

<table>
<thead>
<tr>
<th>Curve No.</th>
<th>Pol. Field kV/cm</th>
<th>Pol. Temp. °C</th>
<th>Rate of stimulation °K/m</th>
<th>Peak Temp. °C</th>
<th>Peak current in Amp.</th>
<th>Activation energy in eV</th>
<th>( \tau ) in sec. at infinite time</th>
<th>( \tau_{300} ) in sec. at 300 K</th>
<th>( \tau_m ) in sec. at peak temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 - I</td>
<td>12</td>
<td>72</td>
<td>9</td>
<td>59.00</td>
<td>0.12x10^{-7}</td>
<td>0.55</td>
<td>3.01x10^{-7}</td>
<td>8.59x10^{2}</td>
<td>111.94</td>
</tr>
<tr>
<td>1 - II</td>
<td>12</td>
<td>72</td>
<td>9</td>
<td>82.00</td>
<td>0.13x10^{-7}</td>
<td>0.75</td>
<td>1.53x10^{-9}</td>
<td>9.09x10^{3}</td>
<td>95.43</td>
</tr>
<tr>
<td>2 - I</td>
<td>12</td>
<td>72</td>
<td>9</td>
<td>59.00</td>
<td>0.75x10^{-8}</td>
<td>0.38</td>
<td>2.00x10^{-4}</td>
<td>594.74</td>
<td>152.54</td>
</tr>
<tr>
<td>2 - II</td>
<td>12</td>
<td>72</td>
<td>9</td>
<td>82.00</td>
<td>0.82x10^{-8}</td>
<td>1.17</td>
<td>1.24x10^{-15}</td>
<td>7.02x10^{4}</td>
<td>61.55</td>
</tr>
</tbody>
</table>

### TABLE 6.6 for (Fig. 6.15) Data for TSC thermograms of Mixture.

<table>
<thead>
<tr>
<th>Curve</th>
<th>Pol. Temp. °C</th>
<th>Rate of stimulation °K/m</th>
<th>Peak Temp. °C</th>
<th>Peak current in Amp.</th>
<th>Activation energy in eV</th>
<th>( \tau ) in sec. at infinite time</th>
<th>( \tau_{300} ) in sec. at 300 K</th>
<th>( \tau_m ) in sec. at peak temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>14.8</td>
<td>34</td>
<td>8</td>
<td>52.00</td>
<td>0.57x10^{-8}</td>
<td>3.01</td>
<td>3.93x10^{-45}</td>
<td>1.79x10^{5}</td>
</tr>
<tr>
<td>II</td>
<td>15.0</td>
<td>34</td>
<td>12</td>
<td>55.00</td>
<td>0.55x10^{-10}</td>
<td>0.16</td>
<td>1.00</td>
<td>491.19</td>
</tr>
<tr>
<td>III</td>
<td>13.5</td>
<td>34</td>
<td>12</td>
<td>55.00</td>
<td>0.40x10^{-8}</td>
<td>2.13</td>
<td>3.81x10^{-32}</td>
<td>2.49x10^{4}</td>
</tr>
<tr>
<td>IV</td>
<td>15.5</td>
<td>34</td>
<td>8</td>
<td>49.00</td>
<td>0.57x10^{-7}</td>
<td>1.15</td>
<td>3.40x10^{-17}</td>
<td>1.08x10^{3}</td>
</tr>
</tbody>
</table>
even with high field and their number is large. Thus during stimulation the charges are trapped again which contribute to second run TSD current at the same time traps are not neutral therefore a negative current is observed.

6.9 CONCLUSIONS

Thus three level polarization is present in mixture. As due to large aromacity of these materials shallow traps are dominating over deeper traps due to structural defects and/or foreign materials. In the mixture of these two materials the density of deeper traps is also increased but charging at shallow trapping level which form a barrier, restrict filling of deeper traps at room temperature. At higher temperature molecular motions are prominent and therefore deeper traps are also filled due to increased conductivity of mixture.

The ion-deposition in homo charging with filling of shallow and deeper traps contribute to net polarization. Homo charging is related to surface phenomena i.e., charging corresponding to surface states. Such polarization seems to be dipolar polarization due to ion displacement.

The activation energy decreases with increasing crystallinity and field. The decrease of activation energy with field indicates barrier polarization.

It may be said that at higher temperature during mixing, the electrons of ferrocene at non-bonding state are shared at
antibonding states of naphthalene or trapped at its molecular sites.

Such sharing may result in creation of electron-traps in ferrocene, a component of mixture. These traps could not be filled at room temperature and therefore during stimulation at higher temperature, the negative current is observed.
REFERENCES


55 A. Gemant. Direct Current 1, 145 (1933).


