CHAPTER IV
STUDY OF THE THERMOELECTRETS
IV.1 Introduction

Following Uguchi's electrets, workers in this field have studied a number of organic and inorganic substances and polymers as electret forming materials. Various substances such as carnauba wax, perspex, polystyrene, ceramics, sulphur etc. have been used as basic electret forming materials.

In the present work, the electret state was produced in carnauba wax, perspex, melinex, fluorocarbon and mica. The electrets of carnauba wax, fluorocarbon and mica were studied in some detail.

Carnauba wax was chosen, being a basic electret forming material, and exhibiting very clearly nearly all the properties characteristic of an electret. The interest in the wax electrets has been recently reduced because of the success in polymer electrets. Yet, a further investigation on the thermoelectret state in carnauba wax is suggested in view of the fact that carnauba wax can be taken as the standard material for comparative study since some remarkable properties of the carnauba wax electrets are found in other organic materials also.

Carnauba wax is a yellowish brittle material of exceptionally high melting point (83-86°C), extracted from the Brazilian palm corypha cerifera. This wax contains minor amounts of hydrocarbons, wax alcohols, and higher fatty acids in addition to higher wax esters of alcohols
and acids, containing from 26 to 34 carbon atoms.
Chemical structure as quoted by Callianas (69) is shown
in Fig. 4.1 (a).

Chemically, carnauba wax is a mixture of Alkyl esters
(85,8) and uncombined acids alcohols, lactides and hydro-
carbons. Approximately 40% of the wax consists of omega
hydroxy acid esters having the formula
\[ HO - C_nH_{2n} - O(0)OC_mH_{(2m+1)} \]
The second substance chosen for the study was fluorocarbon.
This forms a class of substances like Teflon, tetrafluoro-
ethylene resins and "Kel-F" chlorotrifluoroethylene resins,
which are the two outstanding examples of this class. They
are not new, but recent commercial developments (e.g.
larger production lower price, and new ways of handling)
lend new interest to them. The replacement of one fluorine
atom in \( C_2F_4 \) with chlorine gives a polymer of higher
rigidity, strength, and better molding properties. The
symmetrical structure of polytetra-fluoroethylene, as shown
in Fig. 4.1(b) makes it quite crystalline; the individual
molecules are quite stiff. A first order transition
occurs near 20°C and the crystal melts at 327°C to a very
high viscosity gel.

Recent tests show the viscosity of Teflon to be around
\( 10^{11} \) poise at 380°C. This material being a very highly
resistive polymer is considered to be well suited for
stable electret formation.
FIG 4.1(a) Vectorial representation of Trans Trans Omega hydroxy acid esters.

FIG 4.1(b) Typical linear polymers “Teflon” polytetrafluoroethylene.
The third material mica, is a ceramic having a sheet structure containing silicate tetrahedral units into a plane. On the lower side of the sheet every oxygen is completely satisfied with a full complement of eight available electrons because these atoms of oxygen share pairs of electrons with adjacent silicons. Cleavage of mica is a consequence of such a structural arrangement shown in Fig. 4.1 (c).

Perspex (polymethylmethacrylate) is a thermoplastic (linear) polymer; it actually melts and loses all resemblance of crystallinity at high temperatures. Predominantly covalent bonds of all polymers limit electron conduction. The dielectric properties of polymers are sensitive to the polarization of the structure. The polarization is greatest in polymers, with natural dipoles. Polymethylmethacrylate is a polar substance and therefore is chosen as a promising electret forming substance and its intrinsic and extrinsic polarizations are studied, which are explained in Chapter VI.

Perspex is a glassy, high resistive, optically smooth substance, whose refractive index is very near to that of glass; has a light transmissibility in the visible, which is superior to that of glass.

The melinex foil, which was also chosen as a suitable material for the electret formation, has a high dielectric strength. Its high softening point enables melinex to be
Projected view

Exploded view

FIG-41 (c) STRUCTURE OF MICA
used at temperatures above the operating limit of paper insulation. It has a high volume resistivity \((4 \times 10^{15}\ \text{ohm-cm})\) and a good resistance to weathering. Moreover, it has a glass transition temperature near \(80^\circ\text{C}\). It is amorphous below this temperature and partly crystalline above it.

IV.2 Measurement of polarization

The total charge in an electret was studied mainly by two methods.

(a) Surface charge measurement; as described in Section III.4.

(b) Thermal depolarization method; as explained in Section III.6.

The charge induced on the surface of an electret, is a measure of its volume polarization. The density was measured with a dynamic condenser. The advantage in this method, compared with the thermal method, is that the sample is not destroyed; and the study could be made in ambient conditions.

The second method is a useful tool in looking into the electret's volume polarization. Though the electret is destroyed after the measurement, there is no fear of any part of the polarization being lost due to imperfect shielding, or the natural decay of some of the charges. The electrets were thermally stimulated, immediately after
removing the polarizing field.

IV.3 Effect of temperature

The influence of temperature upon the dielectric absorption has been treated in a general way by Wagner (70). He showed that for heterocharge dielectric, the total amount of absorption is nearly independent of the temperature, while, the rate of absorption increases strongly with increasing temperature. According to Gross (71), if the capacitor is charged for the same time once, at a low temperature and a second time at a high temperature, then, according to the data of isothermic curves, in the second case more electricity is stored up in the system than in the first one. Therefore, the same capacitor, while energized by a constant voltage source, is raised from a state of low absorption to a state of high absorption.

(a) Carnauba wax

In Fig. 4.2, a comparison is shown between the charge decay of two carnauba wax electrets, excited at two different temperatures, keeping the other parameters same. It is observed that the sample polarized at 67°C exhibits charge reversal and attains a higher mean value of homocharge. The electret polarized at 63°C exhibited an initial net homocharge. This shows (in conformity with Gross) that a stable homocharge and more heterocharge is
formed at higher temperature. Large homocharge at high temperature is a result of large heterocharge. Thus, true volume polarization, namely heterocharge, increases with the increasing temperature, up to a certain limiting value. Higher electric fields are required to increase the heterocharge at high temperature.

However, in all the experiments with carnauba wax, electrets were prepared at 63°C keeping in view the practical difficulties such as change in the shape and thickness of electret at higher temperatures.

(b) Fluorocarbon electrets

The effect of temperature was also observed on the fluorocarbon electrets as shown in Fig. 4.3. The substance was polarized at two temperatures: 130°C and 230°C. The electret formed at 230°C shows a larger net heterocharge, which slowly decayed to a more or less constant value of heterocharge.

Thus, the value of the high temperature, below melting point, is an important factor in determining the total charge of an electret.

IV.4 Duration of polarization and rate of cooling

In the present experiments the time of polarization at constant temperature was fixed at two hours. The temperature was brought down to ambient temperature in six to ten hours. Caserta and Serra (60), worked also
with different polarizing times (1, 3, and 18 hours). The results were independent of the choice of polarizing time.

However, Good and Stranathan (44) studied the effect of the state of cooling. The electrets yielded quite a consistent evidence that the time for reversal of charge becomes longer and final density of charge becomes smaller as the time of cooling under the electric field is increased.

Thus, a moderate value of rate of cooling and the time at high temperature were chosen in these experiments to gain the maximum effects.

IV.5 Effect of the electric field strength

(a) Effect on carnauba wax

Fig. 4.4 shows the effect of increasing the field strength on the homocharge decay of carnauba wax electrets. The behaviour shows that the homocharge first increases to a higher value, and then decays exponentially to a slowly decaying homocharge. However, net homocharge increases with the field strength. The maximum homocharge also exhibits an increasing tendency with the increasing field strength.

Initial rise in the homocharge of these electrets is due to the decay of the volume polarisation, the rate of
which is large compared to that of the surface charge. Even though, according to Swann (52) the rate of heterocharge decay $\frac{dp}{dt}$ is so small, that one can assume the polarization $P_m$ present at the point of inflexion to be equal to the initial polarization $P_0$.

The decay of homocharge is partially due to the decay of heterocharges, which keep these surface charges bound, deep into the volume. Thus, heterocharge decay is always accompanied by a homocharge decay. The net effect, observed on the surface is, the combination or net result of the decay of the volume charges as well as the surface charges of an electret. Thus, the point of inflexion gives an idea about the electret polarization.

Increasing the field beyond 12 kV/cm does not help in increasing the stability of electret. The anomaly observed in the nature of decay was, that the rate of decay was observed to be faster for high field electrets.

(b) Effect of the electric field on the fluorocarbon electrets

The role of the polarizing field in fluorocarbon electrets formed at 230°C is shown in the Fig. 4.5. The sample electrified at 8 kV/cm, showed net heterocharge, which slowly attained a steady state in heterocharge region. When the field was increased to 48 kV/cm, the total heterocharge increased. Electret excited at 60 kV/cm exhibited net homocharge, which after 40 days attained a slowly
decreasing value. The homocharge in the electret, polarized at 80 kV/cm first increased to a maximum and then decayed to a constant value. The application of 80 kV/cm hardly reveals any difference in steady state homocharge, than that formed at 60 kV/cm. Thus, more or less a saturation field is attained, suggesting a saturation of the extent, of polarization, contributed by dipole orientation and trapping of charge carriers.

The results are in conformity with the results obtained by Wieder and Kaufman (23). They have obtained similar results with perspex electrets. Johnson and Carr (21) have reported that application of fields in excess of 10⁻¹² kV/cm does not seem to lead to any further increase in the resulting charges in carnauba wax.

This can be concluded from the results of the effects of field on the electret's charge, that there exists a moderate field and temperature in accordance with Latour (72). He studied the conditions of formation and decay of charges on electrets, obtained from polar polymers like PMMA and PVC, and obtained critical values of field and temperature of formation.

The thermal depolarisation current was measured for a set of experiments, in which electrets were prepared at different field strengths, ranging from 1 kV/cm to 7.4 kV/cm. The total charge increased linearly with field strength up to 5 kV/cm but was non linear afterwards.
Figs. 4.6(a), 4.6(b) and 4.6(c) show these effects. The discharge currents for electrets formed below 4 kV/cm were accompanied by two peaks. The second peak always occurred at the same time in all the electrets.

The maximum current varies with the applied field, linearly up to 6 kV/cm. Lilly (73) obtained a linear relation indicating a dipolar nature of polarization in mylar electrets. Hence the present results do not favour uniform polarization.

IV.6 effect of thickness
(a) Charge decay study

The overall behaviour of electret, when the field was kept constant, and the voltage is varied, was studied with electrets of thicknesses ranging from 2 mm to 9 mm. These were polarized at 8 kV/cm at 63°C. Fig. 4.7 compares the decay curves for these, measured over time for 40 days. The nature of decay of each electret up to a constant homocharge is different. The initial charge varied considerably even though the constant homocharge was obtained in these electrets after about 40 days. The charge reversed from hetero to homocharge in 4 mm electret. The maximum homocharge also varied with the thickness. Fig. 4.7 (b) shows variation of the maximum homocharge with the thickness.

Yamanka (36) found that the applied voltages are important in determining the formation of electrets under
certain electric fields. For instance, at the same field strength of 7 kV/cm under the applied voltage 1 kV, he observed that the electret was always charged as hetero which decayed with time, while at applied voltage of 1-3 kV/cm the electrets reversed their sign from hetero to homo. He explained this voltage dependence, as due to the distortion of the inner field of electrets on account of space charges.

Recent investigation on the variation of thickness of the electret made by Khanna (74) shows significant difference between the electrets of different thicknesses. Results of charge decay studied showed that the magnitude and the sign of the charge depended upon the thickness of the electret. The magnitude of the initial heterocharge increased as the thickness decreased.

(b) Thermally stimulated currents and volume polarization

Gross has explained the effect of polarization on thickness as due to the non-uniformity of polarization in electret. With a uniform volume polarization, the value of the released charge is independent of thickness and location. This is shown by a simple consideration (75). The displacement $D$ is expressed as a function of component $\varepsilon_S$ in phase with the field $S$ and a component $P$ out of phase with field. Thus

$$D(t) = \varepsilon_S(x,t) + P(x,t)$$

(4.1)
This formal representation does not imply specific assumption about the nature of the persistent polarization $P$ which might be ionic, electronic, or dipolar. In the absence of space charges, $D$ must be independent of $x$. If the sample of thickness $d$ is shorted, one has

$$\int_0^d E \, dx = 0 \quad (4.2)$$

Integration of equation (4.1) over $x$ between 0 and $d$, then gives

$$D(t) = \frac{1}{d} \int_0^d P(x,t) \, dx \quad (4.3)$$

The discharge current during depolarization is given by $J(t) = -\frac{dD}{dt}$, where $A$ is the electrode area. The total charge released is therefore,

$$Q = \frac{A}{d} \int_0^d P(x,0) \, dx = A \bar{P}(0) \quad (4.4)$$

where $\bar{P}(0)$ is the average 'persistent' polarization of the section before depolarization. Therefore, the released charge need not decrease with decreasing thickness. A uniform volume polarization gives constant charge values.

In view of the study of the uniformity of polarization, the thermal depolarization currents for electrets of different thicknesses were measured. The results are shown in the table 1 and figs. 4.8, 4.9 and 4.10. The observed values of total charge released as determined by numerical
FIGURE 4.8.1.C. FOR THERMO ELECTRET OF CARNAUBA WAX, OF DIFFERENT THICKNESSES
**FIG 4.9** VARIATION OF TOTAL CHARGE WITH THICKNESS

- **Fp = 4 kV/cm, Tp = 63°C**
  - 10 mm: $5.025 \times 10^8$ coul
  - 5 mm: $7.037 \times 10^8$ coul
  - 4 mm: $4.800 \times 10^8$ coul

**FIG 4.10** THERMAL DEPOLARIZATION CURRENTS EFFECT OF THICKNESS

- **Fp = 5 kV/cm, Tp = 68°C**
  - 5 mm: $1.08 \times 10^9$ coul
  - 10 mm: $7.89 \times 10^8$ coul
integration of the current-time curves indicates a definite relationship of thickness of the electret with the amount of polarization. However, no direct evidence was observed as regards any direct relationship between these two quantities. But the results directly favour a non uniform volume polarization in electrets.

A uniform polarization would release equal amounts of charge in electrets of different thicknesses, polarized at the same field and temperature.

Gross (75) determined the internal charge distribution of carnauba wax electret by the sectioning method. The total released charge determined by the numerical integration of the corresponding current-time curve, gives the polarization of each section. The measurements gave constant values of charge released irrespective of the thickness of the sample. This, therefore, proved the existence of a uniform volume polarization of the electret, in his experiments.

The results reported in this thesis, therefore, contradict the possibility of uniform volume polarization reported by Gross. Uniform polarization cannot be certainly expected due to the trapping of charge carriers and migration of ions in macroscopic regions, giving rise to space charges near the electrodes. The field due to dipoles remains the same irrespective of the thickness, but that caused by the space charge formation near the electrodes, would give
<table>
<thead>
<tr>
<th>Material</th>
<th>Ser. No.</th>
<th>Thickness of electret</th>
<th>Forming field Fp.</th>
<th>Total volume charge $\text{coul/cm}^2$</th>
<th>ref.</th>
<th>Fig. No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carnauba wax grade I</td>
<td>1</td>
<td>12.0 mm</td>
<td>5 kV/cm</td>
<td>$1728 \times 10^{-8}$</td>
<td></td>
<td>Fig. 4.8</td>
</tr>
<tr>
<td></td>
<td>8.7 mm</td>
<td>»</td>
<td>»</td>
<td>$81.2 \times 10^{-8}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.0 mm</td>
<td>»</td>
<td>»</td>
<td>$228 \times 10^{-8}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.0 mm</td>
<td>»</td>
<td>»</td>
<td>$576 \times 10^{-8}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.0 mm</td>
<td>»</td>
<td>»</td>
<td>$324 \times 10^{-8}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.0 mm</td>
<td>»</td>
<td>»</td>
<td>$111.6 \times 10^{-8}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carnauba wax grade II</td>
<td>2</td>
<td>10.0 mm</td>
<td>4 kV/cm</td>
<td>$50.2 \times 10^{-8}$</td>
<td></td>
<td>Fig. 4.9</td>
</tr>
<tr>
<td></td>
<td>5.0 mm</td>
<td>»</td>
<td>»</td>
<td>$72.37 \times 10^{-8}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.0 mm</td>
<td>»</td>
<td>»</td>
<td>$45.00 \times 10^{-8}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carnauba wax grade II</td>
<td>10.0 mm</td>
<td>5 kV/cm</td>
<td>»</td>
<td>$78.9 \times 10^{-8}$</td>
<td></td>
<td>Fig. 4.10</td>
</tr>
<tr>
<td></td>
<td>5.0 mm</td>
<td>»</td>
<td>»</td>
<td>$108 \times 10^{-8}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
rise to unequal fields inside the electret.

Gerrant and Antenen (76) determined the charges by means of a potential probe technique, which indicated the presence of a strong field distortion and space charges, which form the main seat of the heterocharge.

Cross and Hart (30) measured the space charge near the electrodes by probe technique in tetradecanol electrets. Gerson and Rohrbaugh (50) obtained a thickness dependent polarisation.

Gutman (18) and Swann have assumed non-uniform volume polarization for formulating the phenomenological theories. Gutman (77) has illustrated the space charge distribution within an electret, as shown in Fig. 4.8. It is apparent from this graph that the areas under the curve below and above the abscissa are unequal indicating that the electret carries a net negative space charge. This has been confirmed by Jaeger (78).

To further investigate the true nature of volume polarization, and the uniformity of polarization, a thermally activated process was used to measure activation energy of carnauba wax electrets under these conditions.

(c) Uniformity of polarization

A non-uniform volume polarization may be produced by space charge build up associated with the migration of ions within the material over macroscopic distance or charge injection from the electrodes. A uniform volume
polarization may be produced by dipole alignment and/or migration of charges over microscopic distances with trapping.

Cross (79) strongly favours a space charge mechanism and consequently non-uniform polarization in all electrets. Mascarenhas (80) has shown using 'ionic thermal currents' that a portion of the polarization in Sr-doped alkali halides is uniform and directly attributed to the alignment of impurity-vacancy dipoles. In ice, space charge is present and dominant (80). Perlman (81) obtained indirect evidence which strongly favours a uniform volume polarization in carnauba wax. He followed the method of Bucci and Fieschi for analysing the thermal depolarization current and the glow peaks.

IV.7 Thermal depolarization and activation energy

Froiman and Fridkin (82) considered the thermo electret discharge (the destruction of its heterocharge) on heating to be the result of the motion of weekly bound ions and action of internal fields and the result of the destruction of a dipole texture. It is known that the motion of weekly bound ions in a thermo electret may be given in terms of an ionic current in crystals, or liquid dielectrics

\[ i = Ke^{\frac{-U_0\varepsilon}{kT}} \]

where \( \varepsilon \) is the field acting on the ions, \( U_0 \), the activation
energy and \( K \) is a constant. The derivation of Debye relation connecting the relaxation time of dipole molecule and the viscosity of the medium, required the assumption that the dipolar molecule is bound so strongly to the surrounding molecules, that large jumps of the dipole direction are very unlikely. A dipolar molecule will make many jumps over the potential barrier separating it from another dipole direction during the time required for an appreciable change in direction by viscous flow. This holds completely for amorphous solids for which the viscosity is so high that the flow is practically negligible.

In such amorphous solids it is assumed that the dominant process for changing the dipole direction is that involving many large jumps. The probability for the jump over the barrier (height \( H \)) will be proportional to \( \exp \left( -\frac{H}{kT} \right) \). However, the arrangement of the nearest neighbours is not exactly the same for all dipoles and hence the heights \( H \) of the potential barrier will also differ.

Dipolar molecules in such a substance may be classified according to the height \( H \) of their respective potential barriers.

If the substance has been polarized, and the external field has been removed the contribution of the dipoles in a small range of energies near \( H \), will decay exponentially with a relaxation time \( \tau \) related to \( H \) by the relation

\[
\tau = \pi/2w_a. A e^{H/kT}
\]
where \( \bar{\tau} \) is the average time required by an excited dipole.

Calculation of activation energies for the electrets can throw some light on the energies of traps if assumed to be present, or the energy barrier between the dipole. The measurement of relaxation time at room temperature gives a quantitative measure of the life of an electret.

When the stored charge is released on reheating, one measures the discharge current as a function of temperature to obtain a so-called "current glow peak". Bucci and Fieschi (83) have developed a complete theory to account for these peaks when they are due to uniform dipole orientation. Those aspects of the Bucci's dipolar theory that are pertinent to these experiments are summarized here. Bucci named these thermally stimulated currents as "ionic thermal currents".

The rate at which the polarization \( P \) decays with time can be expressed in terms of the polarization and a relaxation time \( \tau \) by

\[
\frac{dP}{dt} = -\frac{P}{\tau}
\]

(4.6)

When the dielectric is warmed, \( \tau \) is a function of temperature, which in turn is a function of time, and the solution to (4.6) is

\[
P = P_0 \exp \left( -\int \frac{dt}{\tau} \right)
\]

(4.7)
If the initial polarization \( P_0 \) has been formed by applying an electric field \( E_p \) at temperature \( T_p \), then, for freely rotating dipoles, one has

\[
P_0 = N \mu^2 E_p / 3kT_p \tag{4.8}
\]

where \( N \) is the dipole concentration, \( \mu \) is the dipole moment, and \( k \) is the Boltzmann's constant. This is the familiar Langevin function. The discharge current \( J \) is simply the rate of change of polarization.

\[
J = - (P_0 / \tau) \exp \left( - \int dt / \tau \right) \tag{4.9}
\]

In solids, a reorientation of dipoles often involves the movement of ions from one equilibrium position to another. The jumping ion must overcome a potential barrier of energy \( \mathcal{E} \) and the jumping probability per unit time is proportional to \( \exp (- \mathcal{E} / kT) \). The relaxation time \( \tau \) is usually interpreted as the average time required for the jump or the reciprocal of the probability. We have

\[
\tau = \tau_0 \exp (\mathcal{E} / kT) \tag{4.10}
\]

where \( \tau_0 \) is constant. If the dielectric is warmed at a uniform rate, then

\[
T = \alpha + \beta t \tag{4.11}
\]

where \( T \) is the temperature, \( t \) is the time, and \( \alpha \) and \( \beta \) are constants. Combining equations (4.8) and (4.11) one has an expression for the glow peak, i.e.,
\[ J(T) = \left( \frac{\mu^2 E_p}{3kT_p \tau_0} \right) \cdot \exp \left[ -\frac{E}{kT} - (\beta_0 \tau_0)^{-1} \int_{-\infty}^{T} \left( -\frac{E}{kT} \right) dT \right] \]

(4.12)

The discharge current versus temperature expression for the release of charge carriers from traps has, under certain conditions, the same form as equation (4.12) and differs only in the constant in front of the exponential.

The total charge released is given by

\[ Q = \int_{0}^{\infty} J(t) dt \]

(4.13)

Inspection of Equation (4.12) shows that \( Q \) should be independent of the thickness of the sample provided that the polarizing field \( E_p \) and temperature \( T_p \) are kept constant, and \( Q \) is proportional to the applied field \( E_p \).

On differentiating equation (4.12) to obtain the temperature \( T_m \) at which maximum current occurs (i.e. set \( dJ/dT = 0 \)) one has

\[ \tau_0 = \frac{kT_m^2}{\beta E \exp (\beta/kT_m)} \]

(4.14)

Thus, \( T_m \) is independent of both \( E_p \) and \( T_p \). It can be easily shown that the low temperature tail of equation (4.12) is given by

\[ \log J(t) = C - \frac{E}{kT} \]

(4.15)

where \( C \) is a constant. Thus, the activation energy can be determined from a semilog plot of \( J(t) \) vs \( \frac{1}{T} \) (This is the
initial rise method of Garlick and Gibson (84). Bucci's theory also contains a method which is independent of heating rate utilising the whole ITC curve. Thus

\[ \tau(T) = - \frac{P(T)}{J(T)} = \frac{Q(t)}{J(t)} \] (4.16)

where \( J(t) \) is determined experimentally using equation (4.16).

From equation (4.10) a plot of \( \log \tau \) vs \( 1/T \) should then be a straight line if a uniform process is operative. The slope and intercept of this line also serve to determine \( \varepsilon \) and \( T_o \).

Alternately one may follow a method suggested by Cowell and Wood (85). Equation (4.12) may be written in the form

\[ J = A \exp \left\{ - t + B \int_0^t \exp (-t) t^{-2} dt \right\} \] (4.17)

where \( t = \frac{\varepsilon}{kT} \), \( A = \frac{N_p^2 E_p}{3kT_p T_o} \) and \( B = \frac{\varepsilon}{k\beta T_o} \) (4.18)

Further information about the nature and the structure of the trapping states may be obtained by the analysis of thermally stimulated current of the formed electret. According to Garlick and Gibson in the case monoenergetic traps, \( \varepsilon \) is the real depth of the trap measured from the bottom of the conduction band; for arbitrarily distributed traps
Goberecht and Hofmann (86), showed that $E$ is the average depth of the traps just emptied.

The average activation energies for the traps in the electrets were calculated in the present case according to Bucci's method. A run of experiments was carried out in which similar discs of carnauba wax, 10 mm thick, were polarized at 63°C at different field strengths ranging from 1 to 7.4 kV/cm. The thermal depolarization currents were measured as described earlier. The activation energy in the process for the electrets were calculated using equation (4.16). The depolarization current curves are shown in Fig. 4.6(a), (b). The plots of $\log \tau$ vs $1/T$ for different field strengths are shown in Fig. 4.11. Activation energies were obtained by measuring their slopes. Low temperature tails of the ITG curves were utilised. Obviously the activation energy depends upon the value of the polarizing field. The variation in activation energies with the field strength is listed in Table 2(a). The temperature at which the maximum current was obtained i.e. $T_m$ is also listed in the same table.

Another set of experiments was carried out with a different quality of carnauba wax. Discs of the same area were cut out from the same material and plane parallel slabs of different thicknesses were obtained. The thicknesses varied from 2 mm to 12 mm. The polarizing field was kept constant at 5 kV/cm. These electrets were polarized at
Table 2

<table>
<thead>
<tr>
<th>Field $F_p$ (kV/cm)</th>
<th>Thickness (mm)</th>
<th>Activation energy in ev. $E$</th>
<th>Constant thickness=10 mm</th>
<th>Constant field = 5 kV/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.4</td>
<td>12</td>
<td>0.82 ev.</td>
<td></td>
<td>2.05 ev.</td>
</tr>
<tr>
<td>6</td>
<td>8.7</td>
<td>0.8109 ev.</td>
<td></td>
<td>4.07 ev.</td>
</tr>
<tr>
<td>5</td>
<td>7.7</td>
<td>1.24 ev.</td>
<td></td>
<td>8.90 ev.</td>
</tr>
<tr>
<td>4</td>
<td>6.0</td>
<td>1.19 ev.</td>
<td></td>
<td>1.375</td>
</tr>
<tr>
<td>3</td>
<td>5.0</td>
<td>1.43 ev.</td>
<td></td>
<td>5.611 ev.</td>
</tr>
<tr>
<td>2</td>
<td>4.0</td>
<td>1.54 ev.</td>
<td></td>
<td>1.92 ev.</td>
</tr>
<tr>
<td>1</td>
<td>3.0</td>
<td>1.52 ev.</td>
<td></td>
<td>4.46 ev.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>12 mm</td>
<td>323$^\circ$A</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8.7 mm</td>
<td>320</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.7 mm</td>
<td>326.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6.0 mm</td>
<td>319.5$^\circ$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.0 mm</td>
<td>324.6$^\circ$A</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4.0 mm</td>
<td>316.4$^\circ$A</td>
</tr>
</tbody>
</table>

71°C. The ITC currents were measured using a linear heating rate in the experiment. The rate of heating was 1°C per minute. The activation energies were calculated from the semilog plot of $J(T)$ vs $1/T$ for the low temperature tail of the peak. The slopes of the straight lines gave values of $E$. These values and $T_m$ are recorded in Table 2(b). Corresponding results are shown in Figs. 4.12 and 4.13.

From the study of the above quantities, the following results are summarised.

(a) The results obtained from this study of activation energy at different $F_p$s point out to a process which depends upon the field strength. Although $\log (t)$ is linear with
1/T as shown in Fig. 4.11, the energy obtained depends somewhat on the applied field. This probably indicates either the presence of additional mechanism as consisting of dipoles, trapping due to migration of ions into microscopic distances, and space charge due to drift of charge carriers near the electrodes.

The trapping of free charges in these levels is strongly dependent on the electret polarizing field, since the activation energy decreases as the polarizing field increases. This may be interpreted in terms of lowering of the barrier height of traps because of the field.

(b) The study of energy with the thickness of the electret does not show any variation in a specified direction, but widely differing values are obtained. This kind of variation of the energy with the thickness of the electret is suggestive of a mechanism which is not singular but consists of a combination of processes which are arbitrary in nature. Migration of ions and trapping of energy levels into unspecified traps may be expected. The formation of large number of traps manifest themselves as space charge effect in electrets. The presence of space charge should, therefore, be an unavoidable contribution towards volume charge of an electret.

Variation of T_m, the temperature at which the maximum current is obtained is thickness dependent. The unspecified nature of this quantity also points out to a non-uniform
nature of volume polarization. (The trapping of the charges involves a layer close to the electrode, where they are squashed up, to exhibit a space charge cloud near the electrode).

Caserta and Serra (60) studied the activation energy as a function of field. The second peak of their glow peak curves contributed activation energies which decreased with increasing field strengths.

Lilly et al. (73) also obtained a field dependent energy of mylar electrets. They have predicted either the presence of additional mechanisms or an inadequacy in the theory. They obtained increase in activation energy with the field.

Perlman (81) has observed the energy to be independent of the forming field, which points to a uniform volume polarisation. He has ruled out the possibility of space charge.

IV.3 Isothermal decay currents

Isothermal decay current of an electret is the current flowing through the short circuit at room temperature. The measurement of this current gives some information about the nature of the depolarization of electret at room temperature.

Typical isothermal decay current curves of 3 mm electret is shown in Fig. 4.14. The isothermal current curves obtained
FIG 4.15. LOG LOG PLOT OF ISOTHERMAL CURRENT DECAY FOR C. WAX ELECTRETS.
for the set of experiments with different field strengths, are shown in Fig. 4.15. The current $i$ for all of them is related by a power law relation namely

$$i = At^{-n}$$

where $A$ and $n$ are constants. The constant $n$ varied for different field strengths. The constant $A$ was found to increase with increasing field strength.

The power law relationship is characteristic of both dipole relaxation and release of electrons from traps characteristically described in energy (87).

In another batch of experiments, the isothermal decay curves were measured with electrets of different thicknesses, ranging from 12 mm to 3 mm, polarised at 5 kV/cm. Fig. 4.16 shows a comparison of these. The curves are not overlapping. This shows a thickness dependent polarization consisting of traps.

IV.9 Domains in electret

The irregularities in the charge decay of all the electrets speak about non-uniform polarization within the substance of the electret. A structure similar to domains may be expected to solve the problem. These domains having different relaxation times would give rise to pulses in the charge decay.

Bauman and Wiseman (88) observed noise pulses at
FIG-416: Isothermal discharge currents of the thermo electrets of carn wax of different thickness. $F_p=5 \text{ kV/cm}$, $T_p=71^\circ \text{C}$

- $1.2 \text{ cm}$
- $0.87 \text{ cm}$
- $0.77 \text{ cm}$
- $0.60 \text{ cm}$
- $0.50 \text{ cm}$
- $0.40 \text{ cm}$
- $0.30 \text{ cm}$
elevated temperatures in polarized dielectrics (electrets), made of carnauba wax and vinyl acetate polymers. Their experiments indicated that the pulses were associated with the decay of volume polarization rather than with real surface charge. These pulses may be attributed to the domain groups in the electret.

Binder (24) observed an extremely non-uniform pattern with positively and negatively charged patches suggesting domainlike behaviour.

Gemant (89) explained the stability of dipole orientation in dielectrics in terms of domain-like groups.

It was found from the charge decay of carnauba wax and fluorocarbon electrets formed at higher temperatures that the small variations in the charge are less for the net heterocharge electret. Natarajan (90) has also found similar results in Polymethyl methacrylate electrets.

IV.10 Mode of charge decay of electrets

Study of charge decay revealed that the decay is accompanied by more than one exponential. The exponentials depend upon the state of polarization in the electret.

Semilog plot of the relative charge \( \frac{Q_t}{Q_o} \) revealed that the equation governing their decay may be expressed as

\[
\frac{Q_t}{Q_o} = A_1 e^{-a_1 t} \theta(x_1 - t) \theta(t - x_0) + A_2 e^{-a_2 t} \theta(x_2 - t) \theta(t - x_1) \\
+ A_3 e^{-a_3 t} \theta(x_3 - t) \theta(t - x_2) + \ldots \tag{4.19}
\]
where $A_1$, $A_2$, $A_3$, $a_1$, $a_2$ and $a_3$ are constants, $x_1$, $x_2$, $x_3$...$x_i$ represent the time at which the rate of decay is changed, or rather the next relaxation time starts playing its part. $q_o$ is the maximum homocharge of the electret, (immediately after removing the field). $q_t$ represents the charge at an arbitrary time $t$. The function $\Theta(x)$ is defined by $\Theta(x) = 0$ when $x < 0$

$$\Theta(x) = \begin{cases} 1 & \text{when } x > 0 \\ 0 & \text{when } x = 0 \end{cases}$$

$\Theta(x)$ is not defined at $x = 0$. But at the points of intersections where $\Theta(x) = 0$ the equation can be written as

$$\frac{q_t}{q_o} = A_i e^{-a_i t} \quad (4.20)$$

where $i$ represents the order of intersection.

Electrets of carnauba wax of 2, 3 and 5 mm. thicknesses, which were polarised at 60°C at 7 kv/cm were analysed. The plots of $\log (q_t/q_o)$ versus time are shown in Figs. 4.17(a), (b) and (c). The equations governing the charge decay in these electrets were as follows.

1. Thickness of electret = 2 mm.

$$\frac{q_t}{q_o} = 1.216 e^{-0.117 t} \Theta(t-2) \Theta(t-0) + 0.716 e^{-0.05 t} \Theta(t) + 0.469 e^{-0.007 t} \Theta(30-t) \Theta(t-12)$$

where $t$ varies from 2 days upto 30 days.
2. Thickness of electret = 3 mm.

\[
\frac{q_t}{q_0} = 0.166e^{-0.27t} \theta(4-t) \theta(t-0) + 0.8318e^{-0.096t} \theta(8-t) \theta(t-4) \\
+ 0.56e^{-0.0085t} \theta(14-t) \theta(t-8) \\
+ 0.3467e^{-0.00368t} \theta(30-t) \theta(t-14)
\]

where \( t \) varies from 2 days up to 30 days.

3. \( \frac{q_t}{q_0} = e^{-0.074t} \theta(4-t) \theta(t-0) + 1.182e^{-0.0195t} \theta(8-t) \theta(t-4) \\
+ 0.8511e^{-0.086t} \theta(12-t) \theta(t-8) \\
+ 0.537e^{-0.0457t} \theta(20-t) \theta(t-12)
\]

where \( t \) varies from \( t = 0 \) to \( t = 30 \) days.

The deviations in the values of the constants for the electrets of different thicknesses, again prove that the polarization is also a function of thickness.

Similar modes for surface charge decay of electrets were theoretically predicted by Perlman and Meunier (54), in which the net surface charge density is expressed by

\[
\frac{\sigma_f(t) - P(t)}{\sigma_f(0) - P(0)} = \sum_{i=1}^{3} C_i e^{-t/T_i}
\]

IV.11 Charge decay of fluorocarbon

Thin FEP fluorocarbon sheets of thickness .025 cm were polarized at two temperatures. It was found that the electrets
formed at $130^\circ C$ as well as $230^\circ C$ resulted in a net hetero-
charge at $48 \text{kV/cm}$ as shown in Fig. 4.3. The substance
melts to a high viscous gel at about $370^\circ C$. Stable
electretes were obtained in this substance. The order of
charge density was $4 \times 10^{-9} \text{ coul/cm}^2$.

Fig. 4.5 in Section IV.5 (b) shows the effect of polarizing
voltage on the surface charge density and the rate of
decay. Thus, it can be inferred that a good electret for
any application may be obtained by polarizing this sample at
$230^\circ C$ at $100 \text{kV/cm}$ or more than that. The most interesting
result in the fluorocarbon electret was that the homocharge
as well as heterocharge in this substance attains a constant
value for a very long time.

This suggests presence of deep traps inside the material. Teflon has got very little conductivity at room
temperature. Therefore it reduces the possibility of homo-
charge decay as explained by Perlman (54) and Gross (48).
The homocharge decay in a shorted electret is mainly
explained by the ohmic conduction as they cannot surmount
the potential barrier, present at the insulator air boundary.
Thus FEP fluorocarbon can be used in the applications as in
electret microphones, and other pressure transducers (see
Chapter VII of this thesis).

Mode of charge decay

The charge decay of fluorocarbon electret, electrified
at 230°C at 60 kV/cm, was seen to follow a similar equation as mentioned in Section IV.10. A semi-log plot is shown in Fig. 118. The equation governing this charge decay was found to be

\[
\frac{q_t}{q_0} = e^{-0.039t} \cdot e(3.5-t) \cdot e(t-0)
+ 9.05 \cdot e^{-0.015t} \cdot (5.2-t) \cdot e(t-3.6)
+ 8.93 \cdot e^{-0.0105t} \cdot (11.6-t) \cdot e(t-5.2)
\]

the \(\Theta\) function remaining the same.

**IV.12 Polarization in mica**

The effect of persistent polarization was studied in natural mica. This is a crystalline substance with a complex chain structure in the group of ceramics. No dipole orientation can generally be expected in it at considerably low temperature. The second and fourth type of polarization namely electronic and interfacial polarizations could be expected to play some role. Mica being a long chain structured polymer having cleavage surfaces, gives rise to space charge polarization between its layers.

So far much emphasis has not been given to this substance. Persistent polarization was observed in the 0.01 cm thick mica treated with high electric field of the order of 100 kV/cm at 180°-200°C. Higher temperatures failed to produce this effect. The process of heating the polarized
FIG. 418: TYPICAL CHARGE DECAY OF FLUOROCARBON THERMO ELECTRET

$F_p = 60 \text{ kv/cm}$
$T_p = 230 \text{ c}$

FIG. 419: Typical charge decay of thermo electret of mica $F_p = 200 \text{ kv/cm}$
mica at 100°C for two hours did not destroy the polarization. Table 3 gives the values of $V_B$ corresponding to the charge over the surface while the electret was being heated.

Table 3

<table>
<thead>
<tr>
<th>Days</th>
<th>$V_B$ (Volts)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>600</td>
<td>Kept shorted</td>
</tr>
<tr>
<td>1</td>
<td>630</td>
<td>Kept shorted</td>
</tr>
<tr>
<td>1.5</td>
<td>630</td>
<td>Kept shorted</td>
</tr>
<tr>
<td>2</td>
<td>650</td>
<td>Heating under short circuit upto 135°C for two hrs.</td>
</tr>
<tr>
<td>3</td>
<td>750</td>
<td>Kept short circuited</td>
</tr>
<tr>
<td>4</td>
<td>700</td>
<td>Heated at 100°C for one hour</td>
</tr>
<tr>
<td>5</td>
<td>730</td>
<td>Kept shorted</td>
</tr>
<tr>
<td>8</td>
<td>550</td>
<td>Kept shorted</td>
</tr>
<tr>
<td>18</td>
<td>260</td>
<td>Kept shorted</td>
</tr>
</tbody>
</table>

This study proves that a persistent polarization can be induced into this ceramic substance, by a thermal and electrical treatment.

The most interesting property of the mica electret is its high charge density over the surface of the order of $4 \times 10^{-7}$ coul/cm$^2$. Polarization of this ceramic certainly indicates space charge polarization on the surfaces.
Charge decay of mica

Fig. 4.19 shows the typical nature of charge decay of a thermoelectret of mica. This new substance was also observed to be governed by more than one exponential during decay process. Charge decay curve was analysed in the usual way to obtain its equation. The equation of charge decay for this electret was

\[
\frac{q_t}{q_0} = e^{-0.483t} \theta(1.5-t) \theta(t) + 0.575 e^{-0.108t} \theta(11-t) \theta(t-1.5) + 0.407 e^{-0.057t} \theta(25-t) \theta(t-11)
\]

IV.13 Discussion of results

A comparative study can be made as regards the degree of polarization in different electret forming materials. Fig. 4.20 gives a comparison of the surface charge decay for carnauba wax, perspex, teflon, and bakelite. Electrets are electrified at 8 kV/cm at their respective softening temperatures. Bakelite is the poorest material for absorption. Carnauba wax is the best of these materials, and it has comparatively large amount of polarization density. Perspex is a little inferior. Teflon is very near to carnauba wax in its quality of electret formation.

This was a comparison of thick electrets, thickness being more than 1 mm. in every case. Fig. 4.21 shows the behaviour of thin electrets. Thin electrets are useful in
Fig. 4.20 Thermo Electret State in Different Materials

- Perspex
- Camauba wax
- Teflon

Fig. 4.21 Charge Decay of Foil Thermo Electrets

- Mica, 180°C 100 kV.
- Metinex, 130°C 100 kV
- Fluorocarbon, 230°C 80 kV
many applications; they are easy to make, require less amount of voltage giving large field strengths; have large amount of charges, and are useful as pressure transducers. From the figure it is observed that the highest charge density is observed in mica electrets, though it is accompanied by a very fast decay rate and has a short life. Slightly inferior is the melinex electret, which has a large surface charge. The rate of decay is fast during the initial period but attains a slowly decaying polarization in due course. Fluorocarbon has a small surface charge, but is a very long lived electret. Little decay was observed in six months.

The effects of various parameters as the field, temperature, thickness and forming time etc. show that there exists a moderate condition in which stable and long lived electrets may be produced. Moderate field and temperature can always be chosen which can yield strong polarization.

Thickness dependence of polarization may be expected to throw some light on the nature of polarization. As expected by Gross, the total polarization of electret is not uniform inside the volume. The hypothesis of Gross, accepted by Wiseman and Feaster, Perlman and Hennier (75, 55, 53), that the polarization is uniform inside the bulk of the material seems to be incorrect so far as the effect of thickness is considered. Swann has assumed the polarization to be a function of the distance \( x \) from the surface of
the electrode. The assumption of uniformity of polarization is not necessary. All the formulae he derived were valid for the more general case by replacing $P_0 L$ by $\int_0^L P_0 dx$ (52).

Now a true dipole mechanism has already been ruled out by Gross, as even complete alignment of the dipoles would be insufficient to produce the observed charges, and because heterocharges have been observed in non dipolar substances also. An ionic mechanism of the type envisaged by Gerson and Rohrbaugh might be considered, i.e. the migration of ions over limited distances and their trapping due to vacancies and defects. This is a long range effect, a short range mechanism is assumed by Fusch Von Hipple (91). Range effect, that would also produce a persistent polarization, has recently been discussed by these workers, in connection with the analysis of dielectric relaxation spectra. It is the theory of the disorder double well. It refers to the reversible transfer of ions or electrons between equilibrium states. The displacement of such charge carriers corresponds to a reversal of the dipole moments.

Thus, in addition to a dipole mechanism, a space charge polarisation is expected. High fields produce dipoles inside the dielectric. Those present already try to orient along the direction of the field. Still higher fields will try to exert a force resulting into breakdown of the dipoles into free charges.

Amorphous substances always contain ample amount of free,
vacant and defect sites and discrete energy levels, called the localized trap sites. The free carriers have a large probability of being captured into the sites. This leads to colour centres in alkali halides. The space charge may also result from the imperfect contact between dielectric and the electrodes or macroscopic migration of ions into different energy levels. A space charge effect in electrets was considered by Gutman (77). Freeman, Kallmann and Silver (92) found the space charge in anthracene photoelectrets and the polarization was observed to be inhomogeneous.

According to Gutmann a uniform trap distribution will be difficult to realize physically. The space charge density \( q \) is a function of the distance \( x \) from the injecting electrode. A nonuniform field distribution in anthracene single crystals has been observed by Hasegawa (93). The electret thus consists of space charges in addition to the shallow and deep traps inside the bulk and dipoles.

Experimental calculations for energies of activation yielded a non uniform structure of these which depend upon the polarizing field. Similar, theoretical calculations, for the case of energy of the traps were made by Caserta and Serra (59). The energy range in which the traps are uniformly distributed was also calculated for carnauba wax by method of Rose (94) and was found to be equal to about
They found that near the electrodes the number of traps per unit volume was larger and distribution was more uniform than in the middle of the sample. In other words, the band of traps which is present in the bulk gets squashed towards the electrodes.

The decays of the surface charge of the electrets were analysed. The charge decay of an electret cannot be explained by a single exponential, but was found to consist of multi-exponentials, similar to the results obtained by Perlman and Muinier. Gubkin and Swann both allowed a non uniform volume polarization of the electret and assumed that the polarization responds to a single time constant. Their theories agree qualitatively with experiments.

In view of the mechanism of trapping effect, further experiments were aimed at forming electrets with the help of penetrating radiation and, comparing their properties and behaviour, with those of thermoelectrets. The next chapter deals with the results on the radioelectrets. The chief source of radiation was a strong $^{60}\text{Co}$ source (1KC) for gamma rays, but a few experiments were carried with ultraviolet radiations and x-rays also.