CHAPTER IV

THERMOELECTRET

4.1 INTRODUCTION:

Robbilard \(^{299}\) defined electret as "a dielectric which can give rise to a sensibly permanent external electric field". According to Froisman and Fridkin \(^{31}\) bodies which retain volume polarization over a very long period (several months or years) are called electrets. Von Hippel \(^{300}\) describes an electret in terms of "The dielectric—after effect" which in general, is the sign of space charge build up in the dielectric material. This space charge polarization plays a most important and frequently not clearly recognized role in electric polarization phenomena and is for example, the working principle of most electrets.

The first electrets were made by Eguchi with well known carnauba wax and rosin mixture. The mixture, frozen in a strong electric field, exhibited internal electric polarization. Adams \(^{52}\) and Gemant \(^{26}\) found that electrets, when stored between short circuited electrodes, maintained their charge for many years.

Although number of phenomological theories are suggested by Adams \(^{52}\), Swann \(^{65}\), 301-303 Gross \(^{79}\) and Gubkin et al \(^{88}\), yet none of them is found completely satisfactory. All theories or explanation are an attempt to explain:
(a) Formation of hetero and homo-charges.
(b) Longer life of the charges.
(c) Phenomena of charge reversal.

Piech and Handerek\textsuperscript{304-307} gave a theory which speaks against the hitherto considered theories of simultaneous build-up of a real hetero - and homo - charges during the polarization process. According to this theory homo charges in a thermoelectret do not develop during the polarization. Heterocharges are produced during the polarization, they contain the ionic and dipole components. This theory is supported by the Antennen\textsuperscript{308}. The charge reversal from hetero to homo in thermoelectret made of nonpolar dielectric\textsuperscript{35} can be explained by this theory.

Recently Bhatnagar and Srivastava\textsuperscript{228} gave the heterocharge mechanism in Sugar cane wax electrets from dielectric studies and established that permanent dipoles play some role in the production of heterocharge and therefore, the internal field. Singh and Srivastava\textsuperscript{184} reported that by the study of X-ray diffraction in naphthalene thermo electrets the induced dipoles are helpful for increasing internal polarization giving rise to more heterocharge in electrets. Nath and Bhawalkar\textsuperscript{309} gave no change in X-ray diffraction patterns of sealing wax after electret formation.
Electrets of polymer substances were first prepared by Fillipova\textsuperscript{310}. Wiseman and Feaster\textsuperscript{63} have studied the characteristics of plastic electrets in detail. A recent publication by Perlman and Reedyk gives the details of corona charged polymer electrets. They proposed a new polarization method in which the dielectric is inserted between electrodes and charged by corona discharge.

Draughn and Catlin\textsuperscript{311} studied the effect of atmospheric pressure on charge densities at electret surface and concluded that charge decay is not due to local discharges into the air but due to ion desorption from the surface. Electret stability was chiefly determined by homocharge stability. Their results were in agreement with those of others.

4.2 GENERAL METHOD OF THERMOELECTRET PREPARATION

The thermoelectrets are generally formed when the dielectric is subjected to polarizing field at an elevated temperature. The polarizing temperature and polarizing field along with other physical conditions have determining influence on the properties of thermoelectrets.

Although the electret formation has been obtained without heating the dielectrics\textsuperscript{32,53,3,95}, the best thermoelectrets have been obtained by subjecting the dielectric to an electric field when it is in fluid state. Any further increase of temperature above the melting
point does not produce a significant charge\textsuperscript{33,312}. Thermoelectrets of comparatively lower field strength are also reported, to have been prepared at temperature slightly below the melting point of the dielectric\textsuperscript{32,53}.

Rate of cooling of the dielectric under electrical stress has a determining influence on the characteristics of thermoelectrets\textsuperscript{72}. The charge density is found to decrease if the polarizing field is either removed before complete solidification or is kept for too long a time after solidification\textsuperscript{313}.

The thermoelectrets of organic and inorganic materials\textsuperscript{72,81,42,14,314} have been successfully prepared. It was found that the condition for the best results, differs slightly from material to material.

\section*{4.3 PRESENT METHOD OF PREPARATION OF THERMOELECTRET}

(A) Assembly for the preparation of sample and thermoelectret :-

The assembly used for the preparation of sample in mica sheet was prepared locally in the workshop. It consists of the following parts -

(1) Lower Copper electrode(A) -

It is a simple copper plate of dimensions (6 cm. X 4 cm. X .2 cm.). It is planed and made smooth. Four holes are drilled near the edge and at the centre of the four sides of this copper plate.
(2) Upper Copper Electrode (H) -

Upper electrode is also a copper circular plate of dimension (radius 0.9 cm and 0.2 cm. thick).

(3) Spacer Mica (C) -

Smooth and plane mica sheet with a circular hole of size 1 sq.cm. around the centre is selected for spacer mica. Thickness of this mica spacer can be varied depending upon the thickness of the sample desired.

(4) Bridge made from brass sheet to hold fly screw (E) -

A strip of brass (14 cm. x 2 cm. x 0.3 cm.) was bent at four points and turned into the shape as shown in figure 4.1. A threaded hole was made at the centre of the bridge to use a fly screw for providing the pressure on the upper electrode for a better contact with the sample surface.

(5) Mica frame to press the sample holder to the lower electrode (D) -

Area of the mica frame was just similar to the lower copper electrode. Four holes are drilled in the same position as in the lower electrode. A portion of area slightly greater than the area of upper electrode is removed from the centre of mica frame.

(6) Fly Screw (F) -

It is simply a steel screw 6 cm. in length. It is screwed through the bridge hole, to apply a pressure
Fig. 4.1 Components of the Assembly used for preparation of samples
at the centre of the upper electrode.

(7) Non conducting washers(Г) –

These are made of non-conducting material, and used to electrically insulate the upper and the lower electrodes. In the present case the ebonite was used.

(B) Method of Preparation of Samples:

Tin foil used as the electrode material is thoroughly planned and cleaned with benzene. For use as the lower electrode tin foil is placed breadthwise on the polished surface of lower electrode. While the upper metal electrode is covered with the tin foil to serve as the upper electrode. The spacer mica at the centre of lower electrode is kept pressed to it by screwing the mica frame and the bridge to the lower electrode.

This gadget thus assembled is heated in the thermostat set at 100°C for 30 minutes. Small quantity of powdered acenaphthene is taken in clean test tube and is carefully poured in the cavity of the sample holder. The upper electrode covered with the metal foil is then gently placed on solidified substance and is uniformly pressed with the help of the fly screw. The assembly is placed in the thermostat and is allowed to cool to the room temperature. After it has acquired the room temperature, the sample is taken out from the assembly and is examined under microscope to check for cracks, good
surface finish and uniformity. A good number of such samples of thickness 0.5 mm, were prepared in this way for thermoelectret formation.

For controlling of temperature the thermostat and for voltage source the Everedy Batteries are used which have been discussed in 2nd chapter.

(C) Preparation of Thermoelectret :-

The sample found suitable under microscope examination are used for electret preparation. These are clamped in the electret assembly with fresh prepared tin metal foil electrodes. This assembly is then kept in thermostat set at the required temperature.

After the first half an hour the field is switched on and the specimen in the assembly is kept heated for another four hours, and is then cooled to the room temperature by switching off the thermostat at a uniformly controlled rate for 6 hours. After the completion of ten hours the field is switched off and the assembly is taken out of the thermostat. The metal foils are then quickly but gently separated from the sample and the thermoelectret thus prepared is immediately taken to the charge measuring assembly for initial charge measurement.
(B) Preservation of thermoelectret :-

The important parameters affecting the lifetime of thermoelectrets are short-circuiting and humidity. For preservation against humidity they are kept in a desiccator with dry calcium chloride and freshly greased sides. The two faces of the thermoelectrets are shorted in a tin foil to avoid decay of thermoelectret from self depolarization\textsuperscript{102,86}.

(B) Charge Measurement :-

The charge of thermoelectret is generally measured by two methods. The electrostatic method based on induction is called the 'lifted electrode method' and measures the surface charge directly as the induced charge. While in the second method the charge is evaluated by the measurement of Thermally Stimulated Depolarization Current during the thermoelectret depolarization by heating. In the present investigation for the surface charge measurement the lifted electrode method is used. The second method is based for the studies reported in the next chapter and is accordingly discussed there.

4.4 Present Technique

The lifted electrode method using a Lindemann electrometer\textsuperscript{315} has been used in the present investigations. The basic principle of the charge measuring assembly used in the present studies is the same as that of Gemant\textsuperscript{26} and Gross\textsuperscript{79}. The complete electrode assembly is shown in fig.6.1
The thermoelectret for the charge measurement is placed over the lower fixed electrode, which is always earthed. The thermoelectret is placed in such a manner that the face whose charge per square cm. is required faces towards the upper movable electrode figure 4.2. The upper electrode is pressed down and is arrested by the brass screw. The lower weaker spring expands and presses the electrode down to the electret surface. At this position the upper electrode is earthed immediately and is kept as such for one minute, which amounts to short circuiting the electret. The short is broken just at the moment of releasing the upper electrode from the brass screw. The stronger upper spring pushes the electrode system upwards till its upward moment is stopped by the compression of the lower weaker spring, thus ensuring the same amount of lifting every time. Simultaneously the electrode terminal is connected to the electrometer needle terminal. Thus the charge is transferred from the upper electrode to the electrometer needle which then receives a kick and is deflected.

4.5 ELECTROMETER

Lindeman electrometer is used for measuring the surface charges. This electrometer was manufactured and supplied by Cambridge instrument Co. Ltd. London.

The theory of operation of instrument has been fully described by its designer. The following
accessories are provided with electrometer:-

(1) Pneumatically operated earthing switch.
(2) Portable Projector for Lindemann electrometer.
(3) Lindemann electrometer power supply.

(1) Adjustment of the Electrometer

The Lindemann electrometer is worked by a stabilized power supply capable of giving 80 volts. The connecting leads on the projector is connected to the terminal marked 'Lamp Supply' of the power supply. To focus the needle on the projector screen, the focusing knob is pulled slowly in and out in conjunction with turning the adjusting screw AA until the needle of the electrometer is located on the screw. It is brought into focus by turning the focusing knob.

To achieve the coincidence of the mechanical and electrical zeroes, check zero switch is placed in the 'on' position and the mechanical zero is adjusted till the pointer reads zero on the scale provided on the projector screen. The check zero switch is then moved to the 'off' position and the electrical zero control is now adjusted till the pointer again reads zero. The check zero switch can be used at any time during the course of measurement to check that the zeroes are remaining coincident. The switch is used when no voltage is applied to the needle.
(ii) Calibration of Electrometer

The calibration of the electrometer is carried out with the help of a condenser of 50 \( \mu \)F capacity. Known charges are fed to electrometer needle through condenser of 50 \( \mu \)F value and corresponding deflections are recorded. A curve between the deflection and voltage under which the condenser is charged is drawn. As the area of the upper electrode of charge measuring assembly is 0.5 sq.cm., the charge density, i.e. charge on electret surface per cm\(^2\) is given by

\[ \sigma = \frac{C \times V}{S} \]

where \( C = 50 \times 10^{-12} \) F., \( S = 0.5 \) cm\(^2\),

\[ \sigma = V \times 100 \times 10^{-12} \]

\[ \sigma = V \times 10^{-10} \text{ coul./cm}^2 \]

Lindemann electrometer was calibrated for the sensitivity of 10, 20 & 30 volts at which the charge of electret was measured. Electrical circuit used in the calibration is shown in figure 4.2.

(iii) Charge Measuring Procedure

First of all the connections of the electrometer, power supply and the auxiliary circuit alongwith the charge assembly is made using shielded wires as shown in fig.4.2. The proper adjustment of the electrometer is a prerequisite for surface charge measurement. The upper electrode of the charge measuring assembly is lowered on the lower electrodes...
Fig. 4.2 Charge measuring assembly
and is earthed. Key \( k' \) is made of paraffin block by filling mercury into four holes drilled in it. The lead in wires to this key are also fused inside through holes drilled along the side of the key and sealed by pouring melted paraffin wax. The key \( k' \) enables the electrometer needle to be connected to either of the remaining three terminals, respectively connected to the auxiliary circuit, the earth and charge measuring assembly.

The sample to be studied is placed on the lower fixed electrode of the charge measuring assembly. The upper electrode is lowered and is made to touch the upper surface of the sample. The two electrodes are earthed in this position and thus the electret remains short circuited. It is kept in this state for 1 min. which is sufficient for the initial charge to be restored on the surface. Now the connections between upper electrode and earth and that between upper electrode and needle, needle is established simultaneously with the release of the upper electrode. The charge thus induced on the upper electrode is transferred to the electrometer needle and by noting the throw on the scale can be read from the calibration graph.

4.6 RESULTS

In the present investigation the thickness of theacenaphthene specimen (0.5 mm) polarizing time (10 hrs.) and electrode material (Tin) were kept constant. Ten series of thermoelectrets at different
temperature each containing 5 thermoelectrets were prepared. The charge density on the cathode surface of each thermoelectret was measured immediately after the preparation, then once after 12 hours, then after every 24 hours for 30 days and subsequently after every month for 12 months. The variation of surface charge density of thermoelectrets with time is plotted in graphs (figure 4.23 to 4.22).

The conclusions obtained from the study of graphs are given in the following steps:

(1) Initially homo-charge is obtained in each case.

(2) Time of transition from homo- to hetero-charge in all thermoelectrets is nearly two days.

(3) Initial charge in the range of polarizing temperature 65°C to 75°C is greater than that of lower room temperature 35°C and higher temperature 90°C for all the polarizing field from 5.4 kV/cm. to 27 kV/cm.

(4) The charge decays in the beginning irregularly.

(5) After about 15 days the charge decays very slowly and uniformly.

(6) Charge after one month has no symmetry with temperature or field variation.

(7) Final charge after one year in the range of temperatures 60°C to 70°C is found to be less than the
Fig. 4 Decay mode ofacenaphthene thermoelectret prepared at 11.2 kV/cm at different polarizing temperatures
Fig. 4.5 Decay mode ofacenaphthene thermoelectret prepared at 16.2 kV/cm at different polarizing temperatures.
Fig. 4-6 Decay mode of acenaphthene thermoelectric prepared at 21.6 kV/cm. at different polarizing temperatures.
Fig. 4.7 Decay mode of acenaphthene thermoelectret prepared at 27 kV/cm at different polarizing temperatures.
Fig. 4.8 Decay mode ofacenaphthene thermoelectret prepared at 35°C at different polarizing field.
Fig. 4.9 Decay mode ofacenaphthene thermoelectret prepared at 40°C at different polarizing field.
Fig. 4.10 Decay mode of acenaphthene thermoelectret prepared at 50°C at different polarizing field.
Fig. 4.11 Decay mode of acenaphthene thermoelectric at different polarizing field.

Polarizing Temp. 60°C

Charge Density 10^12 Coul/cm^2

0 27 kV/cm
280 kV/cm
210 kV/cm
140 kV/cm
110 kV/cm
54 kV/cm
18 kV/cm
0 27 kV/cm

Days
Decay Time

0 2 4 6 8 10 12 14 20 22 24 30 36 5 9 12

Months
Fig. 4.12 Decay mode ofacenaphthene thermoelectric prepared at 65°C at different polarizing field.
Fig. 4.13 Decay mode ofacenaphthene thermoelectret prepared at 70°C at different polarizing field.
Fig. 4. Decay mode of acenaphthene thermoelectret prepared at 73°C at different polarizing field.
Fig. 4.15 Decay mode ofacenaphthene thermoelectric prepared at 80°C at different polarizing field.
Fig. 4.18 Decay mode ofacenaphthene thermoelectret prepared at 85°C at different polarizing field.
Fig. 4.17 Decay mode ofacenaphthene thermoelectret prepared at 90°C at different polarising field.
Figure 48: Variation of initial-charge density of adsorbed layers with initial poling temperature at different poling fields.

Lines represent the variation of temperature (°C) and field strength (kV/cm) at 75°C, 85°C, 95°C, and 105°C, respectively.

- 11.2 kV/cm
- 16.2 kV/cm
- 21.6 kV/cm
- 27 kV/cm

Initial charge density at cons. field.
Figure 19 Variation of initial charge density of azomethane thermoelectrets with polarizing field at different polarizing field.
Fig. 4.20 Variation of final charge density of acenaphthene thermoelectrets with polarizing field at different polarizing temperatures.
Fig. 5.21 Variation of final charge density of acenaphthene thermoelectrets with polarizing field at different polarizing temperatures.
Fig. 4.22 Variation of final charge density of acenaphthene thermoelectrets with polarizing temperature at different polarising field.
charge at the room temperature and 90°C for all polarizing fields.

(8) The final heterocharge after one year is found to have increased 4 times to the charge found after one month.

(9) The initial homocharge and final heterocharge increase with the increase in polarization field for all temperatures.

(10) The maximum value of final heterocharge is found in the thermoelectrets, prepared at the room temperature (35°C) under all the fields.

(11) It is observed from the graphs that when the value of initial homocharge is smaller then the value of final heterocharge is higher and when the initial value of homocharge is higher then the value of final heterocharge is smaller.

(12) The mode of decay in each case is more or less of the same nature.

(13) It appears from the graphs that the magnitude of surface charge is having a tendency to increase even after one year.

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