CHAPTER V

X-RAY INVESTIGATION OF SHELLAC WAX
SOLIDIFIED UNDER AN ELECTRIC FIELD

Introduction

In addition to investigating the behaviour of the charge on the electret, an X-ray study of the same sample was undertaken. For this purpose a small suitable portion from each electret was removed, and examined for its structure by X-ray diffraction methods. It has been observed that the dielectric polarisation due to an electric field gives rise to the orientation of the crystallites inside. This dipole orientation gives rise to a fiber structure in the wax as has been investigated by various workers by X-ray diffraction methods (1 to 7). Nakata (8) has confirmed the existence of crystalline structure inside the electrets from his Microscopic studies. He used very thin electrets for his investigations. That the electrified wax is in a more ordered state than the unelectrified wax is further shown also by the enhanced thermal conductivity of electrets (9).

The theory of dipole orientation can explain the preferred orientation as shown by diffraction patterns of electret forming waxes, but it cannot give a satisfactory explanation of the similar preferred orientation patterns as obtained by Bennett (3) with paraffin wax, which is non-polar. Good and Stranathan (5) from their X-ray diffraction studies have shown that every electret forming wax containing
dipoles exhibits preferred orientation only in some cases, depending on the method of preparation. Molecular orientation perpendicular to the glass surface with solidified esters on glass surface, has been observed by Trillat and Barbezat (10) by X-ray methods. Yoshioka and Yamamoto (11) studied structures of paraffin films on metal surfaces. The assumption of a crystallite structure in the interior of the electret is also supported by Adams' experiments (4) on piezo- and pyroelectric properties of the electret, though these piezo and pyro-electric properties have not been further confirmed.

The crystalline form of substances of long chain aliphatic series has been discussed by Gascard in 1921. Piper, Chibnall and Williams (12) have discussed the crystalline form and long crystals spacings of higher primary alcohols and n-fatty acids. Similarly, the purity of wheat wax has been established by Pollard and Others (13). Recently Hoppe (14) determined the orientation of organic molecules by means of diffuse X-ray scattering. He concluded that orientation can be deduced even when the crystals do not possess either a layer or chain structure.

From the work of surface energy studies of Hardy, Harkins, Langmuir, N.K. Adams and others, the theory of orientation of molecules at surfaces and interfaces is long well known. In general, the X-ray study of the structure of thin films and surfaces and interfacial layers has fully substantiated the conception of molecular orientations (22). Ida (15) also studied with the help of X-rays, the presence or absence
of orientation in long chain compounds solidified under an A.C. field.

From the results of X-ray analysis the molecular structure of solid bodies can be determined and information about the atomic spacings and orientations can be deduced. Bragg (16) determined the structures of a number of organic compounds e.g. durene, naphthalene, vitreous, silica and bakelite. From the knowledge of the structure the effect of the presence of dipoles can be inferred. The existing knowledge about the preferred orientation during electret formation, is, however, insufficient to deduce definite conclusions and to correlate the properties of electrets.

In the case of Shellac wax the effect of high temperatures at which the field is applied during solidification of the electret, has not been studied systematically. Surface charge studies in this laboratory and elsewhere have shown that the temperature has a definite influence on the nature and magnitude of the charge. Recently Sano and Kakiuchi (17) have investigated the effect of temperature on long chain compounds. Müller (18) has also investigated the effect of temperature on the spacings in normal paraffins.

From the above consideration it seems quite likely that some structural differences may be present in the electrets prepared at different temperatures. In order to investigate the structural variations with the temperature at which the dielectric is polarised, X-ray diffraction studies were undertaken. The temperature was varied from the room temperature to the melting point of wax and further up to 90°C.
From the observations made by Gutman (2) one can assume a transition point in the structure of charged and uncharged dielectrics. Nakata's (8) microscopic studies and Goods and Stratathan's (5) X-ray studies supported the above assumption. In the case of a dielectric, before the application of electric field, the dipoles are arranged at random so that the total electric moment will be zero. But the microcrystals or the dipoles orient themselves under the influence of the electric field. Finally electric moment and surface charges are evolved. Therefore, since the polarization depends on the electric field, one can expect a transition point. Hence it was thought necessary to study the behaviour of dipoles in the wax solidified in an electric field, in addition to the behaviour of dipoles in the wax solidified without field which is already discussed earlier.

2. **Apparatus and Method**

X-ray diffraction photographs were taken with the help of Philips X-ray Diffraction Unit No PW 1010 as shown in the Fig.(Ch.II). Photographs were taken with filtered (Nickel filter) Cu K radiation of wavelength 1.54Å. The flat plate transmission technique was employed. For this purpose a standard Philips flat plate camera with a paper film casket of dimensions 8 x 8 cm and a Collimator of 0.5 mm diameter were used. The tube voltage was kept constant at 30 KV and the tube current at 10 mA. The dimensions of the specimen 7 x 5 x 1 mm were kept constant throughout the experiment for the X-ray beam passing parallel to the field, whereas for
X-ray beam passing perpendicular to the field the specimen had to be cut suitably with a sharp blade to the dimensions $7 \times 1 \times 1$ mm.

The distance between the specimen and film was 5 cm for orientation studies while for (hkl) values it was kept at 2.25 cm. Photographs were taken on Ilford double coated films and the exposure time varied from 3 minutes to 4 hours. The two most intense short spacing reflections (110) and (200) could be obtained with an exposure of 5 minutes. But for the study of outer rings, 4 hours exposure was necessary. The central beam was intercepted at the centre of the film by a lead button of 2 mm diameter and 1.5 mm thickness. All photographs were taken at the laboratory temperature of $28^\circ \pm 2^\circ$C. The usual time temperature development (ID$_{19}$) was used in all cases. The diameter of the rings were measured with a Vernier microscope (already described in chapter II) manufactured by Precision Tools Manufacturing Co., Ltd.

Readings were taken with the cross wires set at the central portion of the rings where the intensity was maximum. A number of readings were taken and the mean of all these readings calculated. Bragg angles were calculated using the relation $\tan 2 \theta = R/D$ where $R = \text{radius of the ring}$ and $D = \text{specimen film distance}$. From $2 \, d \, \sin \theta = n \lambda$, $d$-values corresponding to $\theta$ observed were calculated and verified further from standard charts (19).

Photographic densities along the rings were measured with the help of a Microdensitometer (already described
in chapter II). This apparatus is suited for the measurement of densities at various points along a ring in X-ray diffraction photographs (Sisson and Clark (21)) for comparison of crystallite orientation in cellulose fibres. Rings of any diameter up to 5.0 cm can be accurately measured with this type of arrangement. The density of the line is measured by comparing the known density of a linear neutral absorbing wedge.

3. Electret Preparation

The procedure, method of preparation and the apparatus used was similar to that already described in details in previous chapters. The specimen were in the form of a parallelepiped of suitable size. It may, however, be mentioned that cutting of the bigger specimen to suitable size for X-ray investigations does not influence the orientation appreciably. so far as brittle waxes like Shellac wax is concerned. If softer waxes like bees wax, are cut with a blade, there is a possibility of preferred orientation of surface molecules, as reported in literature. However, to verify this aspect, X-ray photographs were taken with specimens both with and without cutting the Shellac wax with a blade. The results proved that cutting the sides with blades does not produce any effect like surface orientation of molecules.

In order to study the influence of field, photographs were taken when the wax was solidified. Electrets were also prepared at different temperatures varying from room temperature to 90°C (i.e. 12.5°C above the melting point of wax). Details are given in Table I.
TABLE I

Table showing the details of electrets prepared from Shellac wax at different temperatures with the application of electric field:

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Electret No.</th>
<th>Temperature °C</th>
<th>Polarising Time (hours)</th>
<th>Thickness (mm)</th>
<th>Voltage K.V.</th>
<th>Field KV/cm</th>
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<tr>
<td>1</td>
<td>EP10</td>
<td>90</td>
<td>6</td>
<td>1</td>
<td>1</td>
<td>10</td>
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<tr>
<td>2</td>
<td>EP8</td>
<td>80</td>
<td>6</td>
<td>1</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>EP9</td>
<td>77.5</td>
<td>6</td>
<td>1</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>EP4</td>
<td>75</td>
<td>6</td>
<td>1</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
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<td>6</td>
<td>1</td>
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<td>10</td>
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<td>6</td>
<td>EP1</td>
<td>70</td>
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<td>1</td>
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<td>10</td>
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<td>7</td>
<td>EP20</td>
<td>67</td>
<td>6</td>
<td>1</td>
<td>1</td>
<td>10</td>
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<td>8</td>
<td>EP6</td>
<td>64</td>
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<td>1</td>
<td>1</td>
<td>10</td>
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<td>9</td>
<td>EP7</td>
<td>62</td>
<td>6</td>
<td>1</td>
<td>1</td>
<td>10</td>
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<td>10</td>
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<td>6</td>
<td>1</td>
<td>1</td>
<td>10</td>
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<td>11</td>
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<td>1</td>
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<td>10</td>
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<td>12</td>
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<td>1</td>
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<td>1</td>
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<td>10</td>
</tr>
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<td>40</td>
<td>6</td>
<td>1</td>
<td>1</td>
<td>10</td>
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4. **Results and Discussion**

Some typical X-ray diffraction photographs are reproduced in Plates No. I to XIX. The intensity measurements were made along the rings of all the photographs with the help of Microdensitometer, shown in plates 19 to 24. The observed Bragg angles, spacings corresponding to different rings, and the Miller indices are given in Table II.

Shellac wax gives a strong pattern when X-rays are passed either in a direction perpendicular or parallel to the field. Nine distinct rings could be measured and spacings calculated. The complete pattern is given in plate No. 1 while their spacings and corresponding Bragg angles are given in Table II.

In the long spacing region i.e. near the central spot—a halo is observed corresponding to a spacing roughly $7.18\,\AA$. The Bragg angle measurement corresponding to this halo is $6.17^\circ$.

The next two most intense rings correspond to spacings of $4.26\,\AA$ and $3.78\,\AA$ and indices $(110)$ and $(200)$ respectively. The next ring No. 3/medium intensity and about $3.38\,\AA$ spacing. The next two rings No. 4 and No. 5, are strong and their spacings are $3.03\,\AA$ (210) and $2.53\,\AA$ (300) respectively. Similarly the value of spacings of outer rings are tabulated in Table No. II.

The innermost halo as observed in practically all the photographs can be explained in various ways. It may be due to the general radiation present in small proportions, even though filtered Cu K$_\alpha$ radiation of $1.542\,\AA$ was used for the present work. This small proportion of general radiation
TABLE II

Table showing the values of $\Theta$, $d$ and (hkl) for Shellac wax electrets.

Tin foils were used and samples 1 mm were cut and X-ray beam passed:-

(i) in a direction perpendicular to the thickness of original specimen.

(ii) the beam penetrating parallel to it.

Exposures varying for 3 minutes to 4 hours and tube voltage was kept 30 kV and tube current 10 mA. The specimen film distance for orientation studies was kept 5.0 cm, whereas to calculate the $d$-values of full pattern consisting of about 12 rings the distance was kept 2.25 cm. As many as 9 rings could be correctly evaluated.

Classification of the rings were done as follows:-

VVS = very very strong, VS = very strong, S = strong, ms = medium strong, m = medium, mf = medium faint, f = faint, Vf = very faint.

(hko) spacings of normal paraffin hydrocarbon crystallising in the Orthorhombic modification with $a = 7.45^\circ A$ and $b = 4.97^\circ A$ (Müller) (20) compared with the observed spacings in pattern Shellac wax electrets.

The formula used for Orthorhomic system is:

$$\sin \Theta_{hkl} = \frac{\lambda^2}{4} \left[ \frac{k^2}{\alpha^2} + \frac{l^2}{\beta^2} + \frac{t^2}{\gamma^2} \right],$$

where $\lambda = 1.54^\circ A$ for CuK$_\alpha$ radiation

or$$A k^2 + B l^2 + C l^2.$$

Values of $A = 0.01068$

$B = 0.02400$

(Contd. next page)
<table>
<thead>
<tr>
<th>S.No.</th>
<th>Electrode</th>
<th>Intensity Classification</th>
<th>Ring No.</th>
<th>Observed $\theta$</th>
<th>Observed $d_\AA$</th>
<th>Miller Indices (hkl)</th>
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<tr>
<td>1</td>
<td>Tin</td>
<td>Halo</td>
<td>-</td>
<td>6.1667</td>
<td>7.180</td>
<td>-</td>
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<td>2</td>
<td>&quot;</td>
<td>VVS</td>
<td>1</td>
<td>10.4000</td>
<td>4.260</td>
<td>(110)</td>
</tr>
<tr>
<td>3</td>
<td>&quot;</td>
<td>VS</td>
<td>2</td>
<td>11.7500</td>
<td>3.780</td>
<td>(200)</td>
</tr>
<tr>
<td>4</td>
<td>&quot;</td>
<td>mf</td>
<td>3</td>
<td>13.1667</td>
<td>3.385</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>&quot;</td>
<td>S</td>
<td>4</td>
<td>14.7167</td>
<td>3.030</td>
<td>(210)</td>
</tr>
<tr>
<td>6</td>
<td>&quot;</td>
<td>S</td>
<td>5</td>
<td>17.6917</td>
<td>2.530</td>
<td>(300)</td>
</tr>
<tr>
<td>7</td>
<td>&quot;</td>
<td>S</td>
<td>6</td>
<td>19.7833</td>
<td>2.278</td>
<td>(310)</td>
</tr>
<tr>
<td>8</td>
<td>&quot;</td>
<td>mS</td>
<td>7</td>
<td>21.3667</td>
<td>2.116</td>
<td>(220)</td>
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<tr>
<td>9</td>
<td>&quot;</td>
<td>mf</td>
<td>8</td>
<td>24.4167</td>
<td>1.865</td>
<td>(400)</td>
</tr>
<tr>
<td>10</td>
<td>&quot;</td>
<td>f</td>
<td>9</td>
<td>26.0917</td>
<td>1.758</td>
<td>(320)</td>
</tr>
</tbody>
</table>
can cause interference from the important planes of spacings 4.26Å and 3.78Å and this may give rise to such a halo. The halo may have some contribution also from the structure of material used for the preparation of electret.

Shellac wax contains a number of long chain compounds having different chain lengths, melting points and structure (24). The interpretation is rather complicated due to lack of definite information about the nature of the crystallites present in the wax. In the case of X-ray diffraction in liquids (25) specimens of considerable thickness give rise to such effects. In pure compounds the halo may have a contribution also from the diffuseness and overlapping of the high order long spacing reflections.

Kreger (26) has considered two possibilities. In the first case, the crystallite may consist of a mixture of chains of different lengths. In such a mixture, equidistant diffracting planes are not possible and no long spacing reflections can occur. On the other hand, if one chain length predominates over all others, it may give a certain amount of periodicity resulting in a long spacing reflections.

Secondly, each crystallite may consist of molecules of only one chain length. A complicated mixture of chain molecules of different lengths will therefore contain crystallite groups of different chain lengths. Each of this group will give its own contribution to the long-spacing reflections, which will therefore overlap to form a diffuse halo, due to low resolution at the low angle region. The presence of halo in shellac wax diffraction photographs may be due to the many component nature of these waxes. Good and Stranathan
(5) have shown, in the case of electrets prepared out of carnauba wax resin mixture, that halo observed in the photographs has a contribution both from wax as well as from resin.

The third possibility is that halo may have a contribution from the amorphous materials present in the wax, though the intensity due to this will be very weak.

X-ray diffraction photographs of electrets prepared at different temperatures are given in plate Nos. I to XIX. All the necessary details are given along with every photograph for convenience. Practically in all the photographs the intensity along the rings (110) and (200) is not uniform, but is enhanced in the direction of the field as indicated by arrows, while it is reduced in the direction perpendicular to the field. This variation in intensity indicates a preferred orientation of crystallites inside the electret as observed by others and also indicated by charge measurement results in the present investigations. This variation of intensity is maximum in the case of diffraction photographs of electrets prepared at 80°C and 77.5°C.

This leads to the conclusion that at higher temperatures only i.e. near the melting point of the wax, the orientation of dipoles take place in a polarising field. It was therefore thought instructive to study these orientation effects and hence the intensity along the rings was measured with the help of a microdensitometer and curves drawn. The intensity curves along the rings are reproduced in the plate Nos. 19 to 34. The intensity measurements of the rings indicate some interesting features of the orientation as shown in graphs at different temperatures.
Plates for Chapter V

X-ray diffraction patterns of Shellac wax solidified under an electric field of 10 KV/cm between tin foils for six hours at different temperatures, keeping the thickness of the sample constant in all cases.
Key to the Plates of Chapter V

All the points are nearly same size reproductions on Hard printing paper.

Unless otherwise stated, the general conditions are as follows:-

Material: Shellac wax
Specimen: 5 cm
Film distance:
Radiation: Cu Kα radiation filtered (Nickel filter) tube voltage 30 KV tube current 10 mA.
Exposure: 5 minutes to 4 hours.
Laboratory: 28 ± 2°C varying with season
Temperature:

For reasons of brevity, the following abbreviations and symbols are used in describing the photographs:

Sn - \( \perp \) Electret specimen prepared using tin electrodes and a field of 10 KV/cm X-rays perpendicular to the field direction which is indicated by arrow on photographs or placed by the side of it.

Sn - \( \parallel \) Electret specimen prepared using tin electrode and a field of 10 KV/cm X-rays parallel to the field direction.
Plate I

No. 1 $E_{12}$

Shellac wax electret
(Full pattern)

Sn - $\frac{1}{2}$
2 hours
2.25 cm
Plate II

Elecret prepared at 90°C

No. 1  $10^5 E_{as}$
Sn - $\frac{1}{4}$
30 min.

No. 2  $10^5 E_{as}$
Sn - $\frac{1}{4}$
30 min.
Plate III
Electret prepared at 80°C

No. 1 $^9E_{49}$
Sn - 1h
30 min.

No. 2 $^8E_{50}$
Sn - 1h
30 min.
Plate IV
Electret prepared at 77.5°C

No. 1 \( q_{E_{99}} \)
Sn - 1
30 min.

No. 2 \( q_{E_{90}} \)
Sn - \( 1^t \)
30 min.
Plate V
Electret prepared at 75°C

No. 1  $4E_{14}$
Sn - 1°
4 hours

No. 2  $4E_{15}$
Sn - 1°
4 hours
Plate VI

Electret prepared at 73°C

No. 1 "E51
Sn - 1°
30 min.

No. 2 "E62
Sn - //1
30 min.
Plate VII

Electret prepared at 70°C

No. 1 \( ^3E_{18} \)

Sn - \( 1^{h} \)

4 hvs.

No. 2 \( ^3E_{17} \)

Sn - \( / / 1 \)

4 hvs.
Plate VIII
Electret prepared at 67°C

No. 1 $2^0 E_{45}$
Sn = $1^h$
3 hrs.

No. 2 $2^0 E_{46}$
Sn = $1^h$
3 hrs.
Plate IX

Electret prepared at 64°C

No. 1 $^6E_{53}$

Sn - $1^a$
30 min

No. 2 $^6E_{54}$

Sn - $//^1$
30 min.
Plate X
Electret prepared at 62°C

No. 1 $^7_{E_{55}}$
Sn $>$ 1 in.
30 mins.

No. 2 $^7_{E_{59}}$
Sn $>$ 1/4 in.
1 hr.
Plate XI
Electret prepared at 60°C

No. 1 $^{14}E_{5.8}$

Sn = $^{1}$

No. 2 $^{14}E_{5.9}$

Sn = //

1 & 2
Plate XII

Electret prepared at 58°C

No. 1 \( ^{15} \text{E}_6 \)

Sn - \( \frac{1}{1^2} \)

1 \( \text{mV} \)

No. 2 \( ^{15} \text{E}_6 \)

Sn - \( \frac{1}{1^2} \)

1 \( \text{mV} \)
Plate XIII
Electret prepared at 58°C

No. 1 $^{16}_{60}$
Sn - 1 h
15 min

No. 2 $^{16}_{67}$
Sn - 1/2 h
15 min
Plate XIV

Electret prepared at 54°C

No. 1 \[^{17}E_{70}\]
Sn - \[\frac{1}{2}\]n
30 min

No. 2 \[^{17}E_{71}\]
Sn - \[\frac{1}{2}\]f
1 hr.
Plate XV

Electret prepared at 52°C

**No. 1**  \(^{18}E_{82}\)

Sn - \(1^h\)
30 min

**No. 2**  \(^{12}E_{83}\)

Sn - \(1/1^h\)
30 min
Plate XVI

Electret prepared at 50°C

No. 1 \( ^{19}E_{84} \)
Sn - \( ^{1}E \)
30 min.

No. 2 \( ^{19}E_{85} \)
Sn - \( ^{1}E \)
15 min.
Plate XVII

Electret prepared at 40°C

No. 1  E_{RT}, E_{21}
Sn -- l''
30 min

No. 2  E_{RT}, E_{22}
Sn -- l/2
30 min
Plate XVIII

Type - A orientation
Plate XIX

Type - B Orientation
The general nature of the diffraction pattern and the values of spacings indicate rhombic modification of long-chain compounds.

Orientation of microcrystallites inside the electrets was revealed by X-ray diffraction photographs of electrets prepared at 80°C and other temperatures at which homocharge was observed. In the case of electrets prepared at 80°C the photographs showed two types of orientations and this result was further confirmed by photographs of more electrets prepared at the same temperature. These photographs are shown in plate Nos. XVIII, XIX. The intensity of the (110) and (200) rings are shown in graphs given in plate Nos. 35, 36. These two types of orientations have already been reported in literature on electrets and waxes as Type-A and Type-B orientations.

In the case of Type-A orientation, the intensity of the (110) ring is enhanced along the field direction indicated by an arrow and in the case of (200) ring, enhancement of intensity is perpendicular to the field direction. In the case of Type-B orientation, the maximum intensity of both the rings (110) and (200) is in the direction of applied electric field. This is seen clearly from the intensity graphs of Type-A and Type-B photographs. The further interpretation of these two types of orientations can be as follows. Tiku (6) and Kakiuchi (7) have proposed theoretical models to explain Type-A and Type-B orientation. The model is based on rhombic modification of paraffin hydrocarbons which is fully discussed by Müller (80). According to Müller (20) the
Plates for Chapter V

Graphs representing intensity variations around the circumference of the (110) and (200) rings of the X-ray diffraction patterns of Shellac wax electrets prepared at different temperatures under an electric field of 10 kV/cm.

(i) X-rays perpendicular to the field direction.

(ii) X-rays parallel to the field direction.
unit cell has a rectangular base with \( a = 7.45^\circ A \) and \( b = 4.97^\circ A \). The cell is shaped like a parallelepiped and long chain molecules are parallel to the length of parallelepiped (c-axis). The long chains are packed rather closely in this cell.

In the theoretical model to explain the Type-A and Type-B orientations, Kakiuchi considers that the existence of end groups affects the packing of the long chains but little, and that long chain acids, alcohols and waxes have a similar basal structures. Hence in the case of Type-A, the 'b' axis of unit cell is in the direction of the field. (Fig. 2-a) and 'a' axis is perpendicular to field.

The inner ring as shown in (Fig.3-a) corresponds to (110) plane, and the outer ring corresponds to (200) plane. The intensity distribution of these rings is shown in (Fig.35-36) If the orientation of microcrystals is perfect, four spots from (110) planes and two spots from (200) planes should be observed but owing to the distortion in the arrangement they become diffuse arcs in the actual photograph.

The theoretical model of Type-B is shown in (Fig.2b) and the expected pattern in (Fig.3b). The cell can have any orientation around the field direction, with the long chains perpendicular to the field and the diagonal to the basal plane of the cell in the direction of the field. Due to the insufficient resolution the short arcs shown in Fig.3-b smear out to form more extensive arcs.

The similarity of results obtained in the present work by the author to those obtained previously by others lends support to the proposed model.

One more type of orientation with an entirely
Plate No. 36
Type B - Orientation
X-Rays // t. field
Field 10 kV/cm

Plate No. 35
Type A - Orientation
X-Rays // t. field
Field 10 kV/cm
Fig. 1  The Structure of the base of paraffin. C-axis is taken perpendicular to a, b axis.
different kind of apparatus has been observed by Chandy and the model of which is drawn in Fig. 2c and the expected pattern in Fig. 3c. In the case of Type-C orientation, the long chain is perpendicular to the field and the 'a' axis is along the field direction. Comparison of Fig. 2c and Fig. 2a will undoubtedly lead to the conclusion that the previous one is similar to the later diagram rotated through \(90^\circ\) keeping the direction of field constant.

This pattern may indicate four maxima in (110) ring, which may smear out due to distortion and form arcs about a direction perpendicular to that of the field as shown in Fig. 3c. Even though (200) reflection is forbidden due to dispersion of the cells, arcs may be obtained in the direction of the field.

A graphical explanation of Type-A, Type-B and Type-C can also be given as follows:

In Type-A, let the 'b' axis of the cell be in the direction of OF. P is the photographic film which is meant for the recording of the pattern. ON is normal to the (110) planes. W is the 'pole' of the (110) planes. If the cell is rotated around the 'b' axis about the field direction, these poles shall lie on the circle \(\text{WM}^\prime\ \text{SMN}\). on the sphere.

Suppose \(\theta\) is the Bragg angle of reflection for the (110) planes, it can be seen at once, that reflection can occur from (110) planes only if the poles of the (110) planes lie on the circle of reflection the circle of reflection \(\text{WM}^\prime\ \text{QMR}\) on the sphere (angle \(\text{FOR} = \theta\)). So far as the present case is concerned, the circle of reflection will cut out the circle
of poles of (110) planes at two M and M' above and two similar points below as shown in the diagram.

In the case under consideration only four maxima should occur, corresponding to the reflections from (110) planes on the photographic film symmetrically distributed at an angle of $\gamma$ with the field direction. This value of $\gamma$ can be calculated from the knowledge of cell sides, the Bragg angle of reflection, and the angle made by the normal to the particular plane under consideration with the field direction (i.e. angle FON) which is discussed later on in this chapter. The position of any maxima can be worked out by assuming any particular orientation of the cell.

Fig. 3a shows that 4 maxima, symmetrically distributed around the field direction, can be expected on (110) ring, and 2 maxima at right angles to the field direction on the (220) ring. This is what is being observed in Type-A orientation.

To summarise, in all the three types of orientations, the long chains are perpendicular to the field direction. The cells can have any orientation around the field direction subject to the following additional features:

Type-A orientation: - 'b' axis of unit cell in the direction of field.

Type-B orientation: = diagonal to the basal plane of the unit cell in the direction of field.

Type-C orientation: - 'a' axis of the unit cell in the direction of the field.
Estimation of the Amount of Orientation

The ideal pattern is never realised in practice, due to dispersion of unit cells around their ideal positions. This may be brought about by such disturbing influences like random thermal motions, unequal cooling rates and contractions of the same electret in different regions during preparation and local faults. However, by making certain assumptions, a rough estimate of the amount of orientation present can be made.

In general the orientation of all the grains may be randomly distributed in relation to some selected frame of reference or it is just possible that they may tend to cluster, to a lesser or greater degree, about some particular orientation or orientations depending on experimental conditions. Preferred orientation may, therefore, be defined simply as a condition in which the distribution of crystal orientations is non-random. Preferred orientation is rather the rule and not the exception and hence it occurs in many cases. Preferred orientation is only a crystallographic condition and it has got nothing to do with the shape of the grain as disclosed by the microscopic studies. Hence the presence or absence of preferred orientation cannot be disclosed by microscopic studies.

Only X-ray diffraction can give any evidence of preferred orientation. Preferred orientation is best described by means of a pole figure (27), which is based on the treatment of preferred orientation in organic materials as also given by Happey. As mentioned earlier the unit cell of wax crystallites are assumed to be shaped like long para-
lloloped. The basal unit lengths are taken as $a = 7.45^\circ A$, $b = 4.97^\circ A$. The C-axis is the longest and is assumed to be perpendicular to the basal plane. In Fig. 1 the unit cell is shown at the centre O of a sphere, the 'b' axis in the direction of the field OF and C-axis being perpendicular to the plane of figure. XO is shown as the direction of the incident X-ray beam, and O'Y is the photographic film. OP is normal to the (110) plane.

The poles of (110) plane normals will be on the circle PQ'P'QP, if the unit cells have all orientations around the field direction OF. Let us further suppose that $\theta_{110}$ is the Bragg angle corresponding to the (110) planes. Then, it is seen that NL' N'L N is the circle of reflection for these planes. $M_1, M_2$ are two points on the circle of poles which are cut by the circle of reflection, in addition that points $M_3, M_4$ are also cut by the same circle at the lower part of the sphere. These 4 maxima will be found on (110) ring in the shape of arcs as in Fig (2).

These maxima will be symmetrically placed with respect to the field direction, if there is no tilt of the field direction with respect to the X-ray beam. The angular positions of these maxima can be calculated as follows:

Let $\alpha$ be the angle which the (110) plane normals make with the field direction. From Solid Geometry theorem we can write for the spherical triangle $XM_1FX$

$$\cos \gamma_{110} = \frac{\cos \alpha_{110}}{\cos \theta_{110}} \quad (1)$$
where $\gamma_{hkl}$ is the angle at which the maxima on the (110) planes occur with respect to the field direction on the photographic film. The angular positions, with respect to the field, of the maxima on the other diffraction rings can be calculated from relation (1), if suitable values of $\alpha$ and $\theta$ are substituted. $\theta$ the Bragg angle is already known from the measurements on the photographic film. The value of $\alpha$ can be found out as follows:

In the Orthorhombic system, the angle $\alpha$ between any zone axis (uvw) and the normal to any plane (hkl) is given by the relation.

$$\cos \alpha = \frac{(Uu + Vv + Ww) d_{hkl}}{((Uu)^2 + (Vv)^2 + (Ww)^2)^{\frac{1}{2}}}$$

Using this relation, the angle between the 'b' axis and the normals to the different planes can be calculated. Using the value of $\alpha$ and $\theta$ the values of $\gamma_{hkl}$ can be calculated which comes to $30^\circ$ for (110) and $90^\circ$ for (200) planes approximately. For the ideal orientation, the poles of normals to (110) planes will lie on the circle PQ'P'Q Fig. 3.

Let us further suppose that in all other cases there is a dispersion of the poles around the ideal position. Let $\phi$ be the angle of dispersion so that the poles of the (110) planes normals will be between angles ($\alpha - \phi$) and ($\alpha + \phi$) with respect to the field direction of ($\alpha$ is the angle between the field direction and the poles of (110) plane normals to the ideal orientation). The poles of (110) plane normals will therefore lie in a band between $P_2P_2'P_2$ and $P_1P_1'$.
around the field direction.

It is further assumed that the density of the poles of (110) plane normals is maximum along PQ'P'QP and that it decreases towards P₁ and P₂. This can be justified by the fact that even low field strengths are sufficient to produce appreciable orientation. The circle of reflection ML'M'LN cuts the band of poles along four arcs similar to M₁M₂ in Fig. 3. These arcs are symmetrical with respect to the field, if the X-ray beam is perpendicular to the field direction. The maxima on (110) ring will therefore appear as arcs around their ideal positions (Fig. 4, 5). The maximum intensity positions of the arcs correspond to the ideal positions of the maxima. For any maxima, a decrease of intensity on either side of the ideal position can be expected

(i) when \( \alpha - \phi > \theta \) the maxima on either side of field direction will be separated (Fig. 4).

(ii) when \( \alpha - \phi < \theta \) these maxima will overlap producing considerable intensity in the direction of the field (Fig. 5).

The angular extent of the arc (angle E₁₁₀ in Fig. 5) corresponds to the limiting angle \( \alpha + \phi \) of the poles of (110) plane normals, with respect to the field direction. In the case of spherical triangle XM₁FX (Fig. 5) we write

\[
\cos(\alpha_{110} + \phi) = \cos \theta_{110} \cos \left( \frac{E_{110}}{2} \right) \tag{3}
\]

The value of E₁₁₀ can therefore be calculated from the observed value of \( \theta_{110} \) and calculated value of \( \alpha_{110} \).
Assuming that the dispersion of the maxima on (110) ring is produced by a tilt of the 'b' axis with respect to the field (the long dimension of the cell remaining perpendicular to the field) the angle $\phi$ can be calculated from the observed angular extent $E_{200}$ of the arc on (200) ring around its ideal position. Therefore considering the Fig. 6, XSX'S'X is the ideal circle of poles of (200) plane normals. Due to the tilt of the b-axis with respect to the field direction the poles are found in a band about the ideal position in such a way that the angle of dispersion is $\phi$ as shown in Fig.

The (200) ring will occur as arcs, with their maximum intensity regions at 90° with respect to the field direction as shown in Fig. 7. From the Solid Geometry the angle $\phi$ is related to the angular extent $E_{200}$ (as measured in photographs) by the expression:

$$\sin \phi = \cos \Theta_{200} \sin \left( \frac{E_{200}}{2} \right) \quad \text{--- (4).}$$

$\phi$ can be calculated from (4) using the measured values of $\Theta_{200}$ and $E_{200}$. Using this value of $\phi$ and the value of $\alpha_{110}$, $E_{110}$ can be calculated from relation (3). The angles $E_{200}$ and $E_{110}$ were also measured. With the field strength of 10 KV/cm, the observed average value of $E_{200}$ and $E_{110}$ are 60° and 120° respectively; whereas the calculated $E_{110}$ value is about 120.5°.

It can be easily seen from above consideration that observed and calculated values of $E_{110}$ arcs are very nearly
the same. This agreement seems to be better at 10KV/cm. According to the above discussion of Type-A orientation pattern, the maximum intensity positions of the arcs should not vary from the ideal positions of the maxima. It is clear from Fig. 1 that unless the X-ray beam is strictly perpendicular to the field there will be asymmetry in the positions of the maxima with respect to the line on the photograph drawn through the centre of the ring system and perpendicular to the field direction. There are always difficulties in measurements and fair agreement may not be obtained between calculated and observed values. For the foregoing, the validity of the theoretical model used in interpreting the Type-A orientation diagrams is obvious. Further, according to the above discussion, the dispersion $\phi$ as calculated from the extent of the (200) arcs may be taken as an indication of the amount of orientation in the electret specimen. Greater is the orientation the lesser is the value of $\phi$.

From Bennett's curve (3) it is seen that he has taken variation of intensity measured by an ionisation chamber, as an indication of the amount of orientation. In the present work on Shellac wax, the dispersion angle $\phi$ is taken as an indication of the amount of orientation. It has been reported by Chandy and Chilingarian (27) that as the field strength increases, the orientation increases rapidly in carnauba wax. This rapid increase continues upto 0.5 KV/cm. After this the rate is reduced and a maximum orientation is reached around a field strength of 4 KV/cm. For higher field strengths upto about 10 KV/cm the amount of orientation seems
to be more or less constant. This also supports the present investigation on Shellac wax.

The above observations are in agreement with the results obtained by previous workers (2). It is generally known that charge on electret increases with the field strength reaching a maximum value for 10-12KV/cm and homocharges are developed only in electrets prepared with field strengths about 10 KV/cm (2).

**Conclusion**

A systematic study of diffraction photographs and density distribution curves as obtained by the author shows that the patterns obtained in the present work belong to Type-A and B orientation. Both these types have been obtained with the electrets prepared at 80°C and 77.5°C under similar conditions.

Repeated attempts were made to find out the difference in orientations when the preparation conditions like temperature, thickness and field were kept similar for both types which show orientations.

However, an interesting feature was observed in the case of electrets prepared at very high temperature i.e. 90°C as reproduced in the X-ray diffraction photographs in Plate No.II. The probability of orientation of micro-crystals is lessened due to high mobility. It is of course interesting to mention here that at high temperatures i.e. at 90°C in the present study, one can expect a decreasing influence of field in orienting the dipoles. Due to thermal motions the orientation will be further decreased. The abrupt
increase in orientations near the melting point of the wax has been observed by the author as shown in Plate Nos. III to V. This observation is supported by Kakiuchi (7) who also observed increase in orientations near the melting point of wax. The above observation is further supported by the X-ray diffraction studies by Tanaka and Tsuji (23).

Another significant point observed in the present work was non-cracking in electrets. Good and Stranathan observed cracks in electrets due to unequal contraction of wax between the electrodes and outside. As reported by them, the cracking at the periphery inevitably occurred if the field was applied at 90°C (when the wax is completely molten). On the other hand when the field was applied at 75°C, electrets without cracks could be obtained. Electrets prepared by the author in the present work from room temperature to 90°C, showed no cracks due to various precautions, suitable design of the apparatus and technique of preparation. The three types of orientation can be interpreted on the basis of long unit cells of wax crystallites, shaped like paralleloipied, oriented with their lengths perpendicular to the field direction and with particular directions lying along the field.

Type-B orientation pattern can also be interpreted on Kreger's (26) model for examining the orientation pattern obtained from sugarcane wax rods.

Lastly the present work by the author gets further confirmation from the work done by Good and Stranathan (5). These authors found by comparing X-ray diffraction photographs
of freshly prepared electrets with those which had achieved their final homocharge. These authors concluded that the formation of crystallites had no effect on the final strength of electret as found in the present work. These authors also reported that electrets showing strong homocharges may or may not show any orientation effects. In this respect Gross's theory of formation of homocharges is in agreement with the present work on Shellac wax.
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