CHAPTER II - DEPENDENCE OF THE ELECTRICAL CONDUCTIVITY OF POLYETHYLENE AND POLYMETHYL-METHACRYLATE (PERSPEX) ON TEMPERATURE AND ELECTRICAL FIELD.
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1. Introduction. The phenomenon of electret formation has now been well established by different workers, however, the theory of the electret is not universally accepted though various attempts have been made (1 to 5). The reason is partly to be found in the complexity of the phenomenon and its associated effects and partly in the incomplete understanding of the theory of dielectrics. Existing theories of the behaviour of electrets are mostly qualitative and somewhat vague. It seems clear, however, that the more complicated types of behaviour require for their explanation. Microphotographs of the structure of electrets and their X-ray study suggest that units associated with polarisation process may be crystalline needles (6, 7).

Most of the workers in this field have observed only the external electric field of the electret. They could obtain information about the total charge densities, by the study of this field. The total charge densities are made of conduction and polarisation charge densities, \( p_c \) and \( p_p \) respectively. We identify \( p_c \) with a charge density attributed
to an excess of ions or of free electrons or holes and \( \rho \) with a charge density attributed to polarizable and not ionizable molecules. But this requires a definite theoretical interpretation of the observation and becomes uncertain as there is no clear indication of what is happening on a molecular state.

Though the charge on an electret is often mentioned in most of the literature available in this field the term polarisation is seldom mentioned. The original charge which produces an electric moment in the direction of the field is often called heterocharge because on each surface of the electret its sign is opposite to that of the charge on the adjacent electrode; the charge of opposite sign which appears later is called 'homocharge' \((8)\).

Beside the theory of heterocharge on the basis of ionic space charge and dipole orientation as proposed by Gemant \((2, 9)\) of heterocharge, Gerson and Rohrbaugh \((10)\) have proposed another explanation. They assume that there exist in substances capable of forming electrets certain 'traps' for the carrier of charge. Simultaneously with the formation of the heterocharge, the electrons would move into the traps and would then be frozen during the cooling of the wax. There would thus be produced dipoles having little effect on the dielectric constant and since the external field of these dipoles would lead
to annuling of the applied field, there would be produced a weak alignment of the permanent molecular dipoles, as observed experimentally.

The theory of homocharge which is most often accepted is the one due to Gross (11, 12). When the applied field is sufficiently high there occurs a cross-over of the charge at the surface and, the charge is then transferred from the electrode to the surface of the dielectric. Thus the surface is charged with an ionic charge of the same sign as the polarity of the adjacent electrode. When a high electric field is applied, one obtains an ionic space charge in the surface corresponding to the homocharge and heterocharge of the opposite sign. No recombination takes place between the two charges because they are of different nature. When we measure the charge of an electret, we are in fact determining the difference between the two charges. The theory of homocharge has been confirmed by Binder (13).

Baldus (14) demonstrated that the homocharge is caused by charged carriers having either sign which migrate into the dielectric during the polarisation process. The positive charge are then collected in the neighbourhood of the cathodes, so that they are frozen at these places.

From the above mentioned theoretical
analysis of the electret effect it is sufficiently clear that the existence of two different mechanisms is to be assumed, inside the dielectric. It may be worth mentioning at this stage that existence of double structure has got some definite bearing on this effect (15). A satisfactory theory of electret can be worked out by incorporating the idea of double structure with one of the component possessing crystal defects.

Mikola (16) has already given an indication in this direction. He assumes the presence of two types of components in the wax viz. one of comparatively higher conductivity and showing heterocharge and the other of lower conductivity showing homocharge as well. Bhatnagar and Bhawalkar (17, 18) have explained their results on the electrical characteristics of Carnauba wax, Bees wax and paraffin wax on the assumption of a similar double structure. According to them Carnauba wax contains two major components: (A) The first one which crystallizes readily and polarizes under the influence of an electric field and shows lesser conductivity and (B) A component which does not crystallize and has a higher electrical conductivity.

To test various existing theories and mechanisms in connection with electret formation, it is very essential to understand the electrical characteristics of
electret forming substance under these physical conditions to which it is subjected while exhibiting the electret effect. Electrical conductivity is one of the most important parameter which has received considerable attention in bringing some of the most interesting results of electret formation to light. It is worth while to study the electrical conductivity of the samples at different temperatures and fields before preparing electrets from them. Besides providing clues to electret effect such measurements show other interesting properties of the dielectrics also.

2. **Electrical conductivity and its measurement techniques.** The use of conductivity measurements in research work is old and many excellent accounts of measurements are already available (19 to 27). Conductivity is defined in terms of Fig. 1 where the conductivity is given by

\[ \sigma = \frac{I}{V} \cdot \text{A} \]

and is measured in Ohm\(^{-1}\) cm\(^{-1}\). It is implied in the above definition that direct measurement of the current and voltage, together with accurate measurement of dimensions suffice to determine the conductivity to any desired degree of accuracy. This is true only if the number of carriers is sufficiently large so that the thermal variations in the carriers density are negligible. Unless this is so, there will be random fluctuations in the conductivity as a function of time.
**Fig. 1**

Arrangement for resistance measurement by the Ohmmeter method.
and only the time average can be specified accurately. Such problems are important particularly for weakly conducting insulators.

(a) Preparation of samples: Two different methods have been used to prepare samples suitable for the present investigation in the case of polyethylene. The polyethylene samples are obtained from a commercial sheet of 0.018 cm. thickness manufactured by M/S Imperial Chemical Industries Ltd. As the original sheet is rather thin for handling, six sheets are pressed together between two optically plane glass slabs and the temperature is raised suitably till they form one continuous piece. Samples of suitable size could be cut from this new sheet of thickness 0.108 cm. In the other method samples are prepared from solution. Pieces of thin polyethylene are dissolved in hot xylene free from sulphur. This method for preparing the samples is adopted on account of the fact that there is a possibility of inclusion of grease and other impurities in the commercial sheet. The solution prepared in hot xylene is poured in a mica sheet frame of 0.10 cm. thickness and having a hollow square 1 cm. side as shown in Fig. 2(a). The frame is covered with two copper sheets, one below the frame and the other above it as shown separately in Fig. 2(b).
Fig. 2 - Apparatus for preparing samples for conductivity measurements.
The upper copper plate can be well fitted in the hole of another mica frame Fig. 2 (c). After pouring sufficient quantity of solution the polyethylene is allowed to precipitate, while cooling. The upper copper plate fitted in another mica frame is placed over the lower copper sheet on which mica frame carrying the solution is resting. Four screws are tightened and the upper electrode is kept pressed tightly with the help of a spring Fig. 2 (d). The full assembly is shown in Fig. 2 (f). The assembly is kept pressed for one hour so as to allow the specimen to attain the room temperature. Later on screws are loosened and frame is taken out, with the desired sheet of sample in the hole. The thickness of the specimen is carefully measured. Considerable amount of care has to be taken to obtain specimen of uniform thickness. This was achieved after a number of attempts and the procedure standardised.

For preparing the samples of perspex, commercial sheet of 1.5 mm. thickness is used. Suitable pieces of 1 sq. cm. are cut from the sheet very carefully and slowly so as to avoid the generation of heat in cutting it. Preparation of perspex samples from its solution in benzene has been tried to eliminate the impurities. It has been found that perspex, being completely amorphous becomes glassy in the solution and suitable precipitate from the solution could not be obtained on
cooling. The samples prepared thus lacked uniformity of thickness, so they have not been used in the present investigation.

(b) Test cell and electrode assembly. : To minimise the contribution of surface leakage in a conductivity measurement, a guard ring assembly prepared with a special technique is used. Both the collecting electrode and the guard ring are effectively at ground potential, the potential difference being only the potential drop in the grid leak or other resistor used for current measurement. In this method the influence of conducting channels, if there be any, can be minimised provided their thickness is small compared to the width of the guard ring.

The electrode assembly has been prepared keeping in view, the nature of the investigations and limitations of the experimental equipment. Tin foil is used in preparing the electrodes. Two optically plane glass slabs are selected and tin foil of area 1.21 sq. cm. is pasted to one of them. For making electrical contact during measurements, a small portion along one side of the foil is left uncut and is protruded outside the length of the glass slab Fig. 34. On the other slab a guard ring assembly of tin foil is fixed, the area of the guarded electrode being 1.00 sq.cm. The gap between
Fig. 3a - Electrode arrangement and full assembly.
the electrode and the guard ring is 0.05 cm. A small gap of 1 mm. is left in the guard ring to extend the uncut portion of the tin foil of guarded electrode for making contact with the external surface Fig. 3a. This glass slabs assembly carrying the electrodes is kept in a metallic box to ensure proper shielding.

(c) Electrical contact. An extremely important aspect of conductivity measurement is the making of suitable contacts to the specimen. These contacts must be appropriate to the material being studied, the conductivity range, the temperature range, current required and other conditions of measurements. Bad contacts may lead to spurious and unreliable results in the studies of dielectrics. Painted contact is found to be most suitable in the present investigation. Aquadag a suspension of Colloidal graphite has been used for ensuring a good contact between the electrodes and the specimen.

(d) Voltage source. Most measurements of conductivity are made with direct or pulse voltages. The direct voltage sources are not required to produce significant currents but they must be stable. Keeping the question of stability of voltage source in view, twelve 90 volts dry batteries were used. This ensured the variation of voltage
from 0 - 1080 volts in steps of 90 volts.

(e) **Temperature control.** Temperature control is an important factor in all conductivity measurements but particularly so far semiconductors and dielectrics. In some studies, however, direct heating of the sample has been used for rapid determination of conductivity at different temperatures (28). In the present investigation use has been made of an electric oven capable of giving temperature up to 250°C. The temperature is preselected by operation of 3 heat switch and thermostat controls. After stabilization, the thermostat ensures the temperature control better than 1°C.

(f) **Current measuring instrument.** The instrument to be used for measuring current is determined at least partly by the resistance range of the sample and contact system. For applied voltages not in excess of 1000 volts, the current may be as low as $10^{-17}$ amp. Normally the measurements must not require too much time because of the time dependence of resistance. Further, leakage resistance of the measuring instruments are hard to keep above $10^{15}$ Ohms. Hence in practice electronic electrometer methods are employed, with the consequence that currents smaller than $10^{-13}$ to $10^{-14}$ amp. cannot be measured easily with any
degree of accuracy. The limit of resistance readily measured then turns out to be $10^{16} - 10^{17}$ Ohms, this limit can be attained only by minimising leakage currents (29).

Beckman UltraceMeter (30) has been found to be very suitable, keeping in view all the points discussed above. It is a precision instrument for measuring small D.C. currents and voltages over a wide range of values. By the use of inverse feedback to improve the rate of indication response, measurement of direct current leakage resistance and polarisation effects of the capacitors is made usually rapid and simple. High current sensitivity permits these measurements to be performed at low voltages. For convenience in making measurements with small components such as resistors and condensers, a shielded compartment with insulated lead clips is provided as an integral part of the instrument. Three feet leads allow measurements to be made in the shielded compartment on an external components.

The full scale voltage ranges provided are: 20, 50, 100, 200, 500, 1000 and 5000 millivolts. These ranges together with input resistors of $10^6$, $10^8$, $10^{10}$ and $10^{11}$ Ohms, provide current sensitivities of $5 \times 10^{-6}$ to $2 \times 10^{-13}$ amp. full scale. The absolute accuracy of the readings varies with the input resistor used. With $10^6$ Ohms
input resistor, the absolute error of measurements is less than 2%; with $10^{11}$ Ohms. resistor the absolute error is between 3% and 5%. The relative error between two readings made, using the same input resistor and about the same current is within 1%. An internal calibrating circuit is provided by which the high input resistors may be checked against a built in one megohm wirewound precision resistor.

Voltage and currents of either polarity may be measured and the voltage applied for resistance measurements may be reversed for polarisation or dielectric absorption measurements.

Many of the desirable features of the instrument, including high response speed despite large input cable capacities and accurate readings despite relatively low current source circuit insulation resistance are due to degeneration lowering of the input impedance to a small fraction of the value of the input resistor used. This is accomplished in such a way that with proper adjustment, the voltage between conductor and shield in the input cable does not exceed a few millivolts. The input circuit is so connected for current measurements that when positive current flows into it from the external source, tending to increase its potential, the amplifier output to the feedback circuit carries the low end of the input
resistor sufficiently negative to quickly bring the input circuit within a few tenths of hundredths of a millivolt of the equilibrium potential, with respect to the input tube filament. Since the potential across the input capacitance is almost unchanged, very small charging currents are consumed by the dielectric and the circuit quickly reaches a new equilibrium.

(g.) Circuit arrangement and current : The electrical measurements.

for measuring the conductivity of the specimen are shown in Fig. 3b. 'A', the guarded electrode, is connected to the input of Ultrachmther. The high voltage source which is in the form of 90 volts batteries is connected in series with the Ultrachmther. The lower electrode is connected to the ground potential terminal of high voltage source. The guard ring electrode GG is also connected to the ground potential terminal. The box containing the electrode assembly is also kept at ground potential by connecting it to the Ret-Gnd-terminal of the Ultrachmther. When the box containing electrode assembly is transferred to thermostat for measuring the conductivity at elevated temperatures it is found necessary to connect the body of the thermostat to ground terminal. Shielded wires have been used for making all connections. The metallic
Fig. 3b - Circuit arrangement with Beckman's Ultrohmetro for conductivity measurements.
shields of the wires are all connected to ground potential to avoid any leakage current.

The current source is connected between Input and I Ret. Gnd. as shown in the diagram Fig. 3b. The proper signal polarity is selected, and the proper INPUT resistor and voltage range is also selected. Keeping in view the order of the current. If the order of the current is not known, the meter is set to the least sensitive condition and voltage sensitivity and/or the input resistor is adjusted until a suitable reading is obtained. The meter is brought to zero with the input resistor and voltage range to be used; the 'INPUT' switch is turned to 'ON' and the reading of the meter is noted. The meter reading indicates the voltage developed across the input resistor, found by calibration of input resistors and the value of the current is given by,

\[ I = \frac{\text{voltage range} \times \text{meter reading}}{(R_{\text{input}}) \times 100} \]

The value of conductivity can be obtained from the following formula,

\[ = \frac{I \cdot L}{V \cdot A} \]
3. Details of conductivity measurements:

(a) Polyethylene: Separate samples have been used for different measurements. The temperature of the specimen is controlled with the help of a thermostat and is measured by a calibrated thermocouple.

The measurements are divided into the following parts:

(i) With temperature constant, field varying.
(ii) With field constant, temperature varying.

In the first instance of the experimental work, the current is measured at 30°C by varying the fields from 0.9 kV/cm to 9.9 kV/cm in steps of 0.9 kV/cm. The current is also noted while decreasing the value of the field from 9.9 kV/cm to 0.9 kV/cm, in steps of 0.9 kV/cm. These measurements are repeated at the temperatures ranging from 30°C and 70°C to 130°C. Special precautions are taken while performing the measurements at higher temperature in maintaining the uniformity of the temperature throughout the whole body of the specimen. This is done in the following manner: The thermostat knob is placed at the maximum position on its dial. When the desired temperature is exceeded by about 5°C, the thermostat knob is turned backward half a division at a time.
allowing a few seconds before every further adjustment, until the pilot lamp switches off. Immediately this occurs, the knob is turned clockwise to the smallest possible degree. The oven is now allowed to work for sometime till the temperature stabilises, after which further fine adjustment can be made to fix the temperature at the desired level.

In the second part of measurements the field is kept constant and the temperature is varied from $30^\circ C$ to $130^\circ C$ in steps of $10^\circ C$. Every reading is recorded when the deflection became steady and the current did not show any tendency to grow.

The field used is varied from 0.9 kV/cm to 9.9 kV/cm. The readings are also noted while decreasing the temperature of the specimen from $130^\circ C$ to $30^\circ C$. The rate of rise and fall of temperature is also recorded. While decreasing the temperature, it is found convenient to switch off and allow the oven to cool to the desired temperature before turning the control knob backward.

All these measurements have been carried on both types of samples.

(b) Perspex. Similar types of measurements are made on perspex. Conductivity is
measured at a fixed temperature as a function of field by increasing it from 0.6 kV/cm to 6.6 kV/cm in steps of 0.6 kV/cm. The field is decreased from 6.6 kV/cm to 0.6 kV/cm and current readings are noted. The thickness of the specimen used is 1.5 mm. and its area is 1 sq. cm. Temperature of the specimen at which these studies are conducted ranged from 80°C to 120°C.

4. Results.

Part I - Polyethylene.

(a) Conductivity variation with field. : The initial conductivity at room temperature was found to be of the order of \(10^{-17}\). In the first instance the variation of current with field at room temperature is studied. On applying the field the specimen exhibited current drift which continued for about 5 hours. The value of the deflection is noted every half an hour till a steady deflection is reached. The value of the field is raised in steps and is maintained at each step till the deflection becomes steady. After reaching the maximum value of the field, it is reduced in steps and again the deflection are noted.

A fresh specimen is put in the electrode assembly and its temperature is raised to 50°C. It necessitated
waiting for about two hours before the current settled down again. The field is varied from 0.9 kV/cm to 9.9 kV/cm and the steady deflection is noted at every step. The field is reduced in regular steps and deflection is noted again.

A fresh specimen has been used every time for measurements at the following temperatures: - 70°, 80°, 90°, 100°, 110°, 120° and 130°C.

Curves are drawn for the current "i" through the sample and the corresponding voltage applied. The curve for field increasing is different from the curve for field decreasing. The current corresponding to a particular field value on the decreasing side is found to be higher than on increasing side of the field. The appearance of these two curves on the same graph is something like the hysteresis curve. The area of the curve is found to be increasing with temperature up to 90°C but it decreased for 100°C and 110°C and then again started increasing and became maximum at 130°C. No observation above 130°C could be taken by this method as polyethylene starts flowing above this temperature, Fig. 4 & 5.

Simultaneously values of the electrical conductivity $\sigma^-$ of the samples are calculated from the dimension of the sample. Curves between $\log \sigma^-$ and $F$ are plotted
Fig. 4a - Variation of current with field in polyethylene, at specimen temperature = 30°C. and 70°C.

Fig. 4b - Variation of current with field in polyethylene, at specimen temperature = 80°C and 90°C.
Fig. 5a - Variation of current with field in polyethylene, at specimen temperature = 100° and 110°C.

Fig. 5b - Variation of current with field in polyethylene, at specimen temperature = 120° and 130°C.
for every temperature. From the study of these curves it may be seen that the curves for temperature up to 90°C can easily be resolved into two parts: (1) One part showing a complicated type of relationship between $\sigma$ and $F$ and (2) The other part showing a linear relationship. The fields corresponding to the points from where the curves show linearity are found to be different for different temperatures. The curves indicate a linear relationship between $\log \sigma$ and $F$ for temperatures above 90°C. Fig. 6 (a).

The portion showing linear relationship can be represented by the equation,

$$\log \sigma = \text{Const.} - p F$$

Efforts have been made to establish a relationship between field and conductivity for non-linear portion by plotting them on a log-log graph. It is found that it follows a power law relationship.

$$\sigma = a F^n$$

(b) Conductivity variation with temperature: Curves are plotted between conductivity of the specimen and temperature for different fields. The study of these curves indicates that the electrical conductivity does not change appreciably with temperature upto
Fig. 6a - Field dependence of the conductivity of polyethylene at different temperatures.

Fig. 6b - Variation of current with temperature in polyethylene at $F = 0.9, 1.8, 2.7$ and $3.6$ kV/cm.
90° C. Above 90° C the conductivity rises rapidly and the curve shows almost a vertical rise. Curves for higher fields i.e. 6.3 to 9.9 kV/cm. show also another abrupt rise in conductivity above 120° C. The second rise is absent in the curves for lower fields and they show almost a tendency of saturation. The rise at 90° C is also not very sharp Figs. 6 (b), 7 and 8 (a).

The variation of the current with decreasing temperature has been drawn along with variation on increasing side of temperature on the same graph. Both curves appear to be quite distinct. Another important feature of these curves is that conductivity at room temperature does not attain its former value. It remains always higher and the difference goes on increasing with the field.

Curves have also been drawn between log. \( \sigma \) and 1000/\( T \). These plots are composed of two roughly straight portions of different slopes. Conductivity thus, follows distinct exponential relationship with reciprocal of absolute temperature starting from 373° K upto 403° K. Below 373° K the curves show inflection and another straight line is obtained. There is a sharp drop in the value of conductivity at 363° K Fig. 8 (b) and 9.
**Fig. 7a** - Variation of current with temperature in polyethylene at $F = 4.5$ and $5.4$ kV/cm.

**Fig. 7b** - Variation of current with temperature in polyethylene at $F = 7.2$ and $8.1$ kV/cm.
Fig. 8a - Variation of current with temperature in polyethylene at $F = 9.0$ and $9.9$ kV/cm.

Fig. 8b - Temperature dependence of the conductivity of polyethylene at fields $= 0.9$, $1.8$, $2.7$ and $3.6$ kV/cm.
Fig. 9a - Temperature dependence of the conductivity of polyethylene at $F = 4.5, 5.4, 6.3$ and $7.2$ kV/cm.

Fig. 9b - Temperature dependence of the conductivity of polyethylene at $F = 8.1, 9.0$ and $9.9$ kV/cm.
Part II - Perspex

(a) Conductivity variation with field: The electrical conductivity in this case is found to be higher at room temperature and the current flowing through the specimen attained an equilibrium soon after applying the field.

Curves are drawn for the current through the specimen and field applied. The curves are shown in Figs. 10 and 11. The value of the current while decreasing the field is found to be higher than while increasing the field for temperatures up to 140°C. The curve for 140°C can be divided into three distinct regions i.e. region of low fields, medium fields and regions of higher fields. The nature of the curve from 0.6 kV/cm to 3.0 kV/cm is found to be similar to that obtained at low temperatures. From 3.0 kV/cm up to 5 kV/cm the paths taken by the current on increasing and decreasing side of the field concided. The value of the current on increasing side of the field attained higher value than that on decreasing side of the field from 5.0 kV/cm up to 6.6 kV/cm.

For temperatures higher than 140°C the current on decreasing side of the field followed a path lower than the path followed by the current on increasing side of the
Fig. 10a  -  Variation of current with field in Perspex at
          $T = 32^\circ$ and $80^\circ$C.

Fig. 10b  -  Variation of current with field in Perspex at
          $T = 100^\circ$ and $120^\circ$C.
Fig. 11a - Variation of current with field in Perspex at 
$T = 140^\circ$ and $160^\circ$ C.

Fig. 11b - Variation of current with field in Perspex at 
$T = 160^\circ$ and $180^\circ$ C.
field. The deviations in the values of the current continued and consequently the area enclosed by both curves increased and became maximum at 180°C.

The logarithm of conductivity is plotted on the axis of ordinates and the field on abscissa as shown in Fig. 12 (a). These curves show that there exists a linear relationship between log $\sigma$ and the field above 1.8 kV/cm for lower temperatures. At higher temperatures the deviation from linear relationship below 1.8 kV/cm is not very marked.

From the studies of these curves it can be inferred that the conductivity is decreasing with increase in the field for temperatures above 140°C. The log $\sigma$ Vs $F$ curve becomes horizontal at 140°C. The curves below 140°C show clearly that the conductivity is increasing with increase in the field. We can divide the temperature region of this study in two parts i.e. below 140°C and above it. At lower fields the conductivity follows a linear relationship with field as shown in Fig. 12 (a).

(b) Conductivity variation with temperature. In this part of the study the field is kept constant and the temperature is varied from 40°C to 180°C. The specimen is cooled with the field
**Fig. 12a**  - Field dependence of conductivity of Perspex at different temperatures.

**Fig. 12b**  - Variation of current with temperature in Perspex at $F = 3.0, 3.6$ and $4.2 \text{ kV/cm}$. 
Fig. 13a  -  Variation of current with temperature in Perspex at \( F = 4.8, 5.4, 6.0 \) kV/cm.

Fig. 13b  -  Temperature dependence of conductivity of Perspex at \( F = 0.6, 1.2, 1.8 \) and 2.4 kV/cm.
Fig. 14a - Temperature dependence of conductivity of Perspex at $F = 3.0, 3.6, 4.2$ and $4.8$ kV/cm.

Fig. 14b - Temperature dependence of conductivity of Perspex at $F = 5.4, 6.0$ and $6.6$ kV/cm.
on and the value of the current noted down at regular steps. Curves are plotted between the current and absolute temperature. The current does not vary much upto $130^\circ C$ but above this temperature there is a slow rise which becomes very sharp at $170^\circ C$ and $180^\circ C$. The current rises almost vertically at these temperatures. The value of the current recorded at $180^\circ C$ is found to be decreasing for higher fields. The current during cooling of the specimen is always found to be higher than the corresponding value of the current when the specimen is being heated Figs. 12 (b) and 13 (a).

The value of the logarithm of the conductivity is plotted with the reciprocal of the absolute temperature. For lower fields the curves can be divided into two portions. The knee which divides the conductivity curve into two regions occurs at a definite temperature. For higher fields the knee is not so sharply marked but the curves do not follow a single linear path. There definitely exist two distinct regions; one below $140^\circ C$ and the other above it. It has been observed that there is a sharp transition in the conductivity above $140^\circ C$ Figs. 13 (b) and 14.

5. Discussion: Recently it has been found that the electrical conduction in dielectrics and ionic crystals shows marked deviation from
Ohm's law in a strong electric field (31). Deviation from Ohm's law in case of dielectrics are due to two defects: (1) The relative diminution of the e.m.f. of polarisation at high as compared to low voltages and (ii) An increase in the true electrical conductivity of the dielectric. The later phenomenon may, in the case of ionic dielectrics, be due to two causes (i) The emergence of the electronic current component and (ii) An increase of the ionic component of the conductivity (32). Skanavi (33) introduced the concept of dielectrics comprising of ions which may exist in the crystal lattice in two equilibrium positions near to each other.

Quittner (34) and Schiller (35) have shown that the dependence of the resistivity of various types of glasses on the field strength $F$ for a given temperature is given by a formula of the type $\sigma = \sigma_0 e^{-\lambda F}$ in which $\lambda$ is a constant and $|F|$ is the absolute value of field. The relation mentioned above is often known as the Poole relation since the later was the first to use it in the case of mica (36). Venderovitch and Chernykh (37) also describe their resistivity measurements on glass for microscope covering slides with the aid of the Poole's formula. Maurer (38) confirms the formula for a commercial soda lime glass and pyrex glass. Vermeer (39) examines the resistivity
of four different types of glass as a function of the field strength between 0 and 1.5 MV/cm and verifies the Poole's formula.

Munick (40) also reports in the case of Plexiglas conductivity following an exponential relationship with the applied field in the region of 2.6 to 29 MV/cm. Presnov and Gaman (41) report that the increase of electrical conductivity in strong electric fields obeys an exponential law. Tantalum oxide also exhibits an ionic conduction at higher fields i.e., \( \sigma^+ = \sigma_0 e^{-\sqrt{E/kT}} \) (42).

Khanna and Bhawalkar report that the current flowing through Delaron laminated plastic follows an exponential relationship for voltage greater than 400 volts (43).

In the course of study of the induced conductivity in polyethylene it has been indicated that contribution of an ionic conductivity should be larger in this plastic on account of higher mobility of hydrogen ions (44). Polyethylene is a nonpolar high polymer. In general, solids containing more than one type of atoms but no permanent dipoles exhibit electronic as well as atomic polarisation. Apart from electronic displacements in the ions relative to the nuclei, the positive ion lattice will tend to move as a whole relative to the negative ion lattice, on the application of an electric field. In this case the current density will be directly
proportional to field so long as $a e E \ll k T$ ($1/2a^2$ is the number of positive ions sites) and Ohms law will be valid. For high electric fields where $a e E$ is not small compared to $kT$, the current increases exponentially with the field strength (48).

It may be noted from current-field curves that the curve changes its nature above 90°C. In low temperature region the specimen shows no true volume conductivity for low fields as shown by the curves between $\log \sigma$ and $F$ up to 90°C, on account of space charge effect. For higher fields even in low temperature region $\log \sigma$ vs $F$ graphs yield a straight line which agrees quite well with ionic conduction mechanism. The ionic conduction range widens at higher temperature. It can easily be concluded that conductivity follows an exponential law for fields $F > 3.8 \text{kV/cm}$ and Poole's relation is completely satisfied.

In the light of the above discussion the linear relationship between $\log \sigma$ and $F$ at higher fields is not very surprising. At lower fields for low temperature region the correct volume conduction is masked by space charge effects and therefore no conclusion can be drawn regarding the nature of conduction at lower fields. The straight portion of $\log \sigma$ and $F$ curve increases for higher
temperature and it appears that even at lower fields the conduction may be of ionic nature. It can be easily concluded that conduction in polyethylene may be ionic for fields greater than 3.6 kV/cm at temperature above 70°C.

It is very difficult to say anything at this stage regarding the hysteresis type of loop obtained for two values of current i.e. during increasing and decreasing of the field.

The sudden rise of current for higher fields above 90°C may be due to the fact that polyethylene starts softening at 95°C. The flowing point of the sample is beyond 120°C which is marked by another steep rise in the value of the current at 130°C. These sharp changes in the values of the currents are absent at lower fields. This appears to be quite in agreement with the observations referred to in the above discussion i.e. the conduction mechanism at low fields is not well defined and space charges play dominant role at lower fields. These large fluctuations in the values of the current may be on account of the ionic contribution of the current at higher fields.

It is observed that current rises with time at high fields and sufficiently high temperatures. The rise in current gives rise to higher values of conductivity
during cooling the specimen as compared to those obtained while the specimen is heated, which results in the typical hysteresis loop. This condition can be explained in terms of intense reabsorption of high voltage polarisation or by a change in the number of current carriers. Intense reabsorption of high voltage polarisation is the first cause of the increase of the current with time at high temperatures in strong fields which can not be excluded on account of the ionic constitution of the current, the presence of which is fully proved by log $\sigma$ and $1/T$ curves at higher temperatures.

These curves can be divided in two parts. Log $\sigma$ follows a linear relationship with $1/T$ above $90^\circ C$. At $90^\circ C$ the conductivity suddenly drops down. The bend which is a limit of two different laws in the temperature dependence of conductivity is distinctly seen in every curve. The shape of the curve below $90^\circ C$ can not be taken as a straight line but it is more or less curvilinear. The high temperature conductivity above the bend is structure sensitive and depends which specimen of the substance we examine.

From the study of these curves two facts stand out plainly. The first is the existence of two main regions in the conductivity curves, the second is that in both these regions the logarithm of conductivity is roughly a linear
function of \( T^{-1} \). The high temperature section of the curve, above the transition region or 'knee' in general, is an intrinsic property of the substance and measurements in this region are quite reproducible. On the other hand, the low temperature conductivity not only displays a smaller slope but depends in magnitude on the particular specimen employed and to some extent on its thermal history.

The conductivity measurements of perspex yield some interesting results. Apart from the fact that conduction is mainly ionic, the dependence of electrical conductivity on temperature is the same as in the case of supercooled monomeric liquids and glasses. The ionic electrical conductivity of solids and liquids is a characteristic sensitive to the change in the state and structure of the substance.

The study of temperature dependence of electrical conductivity of monomeric liquids and glasses leads to certain conclusions about the continuous change in the short range of the liquid down to the temperature of vitrification and about the presence of fixed structure at lower temperature (46). The temperature dependence of the mobility of the ions in the case of perspex is closely related to the changes in the structure of the medium and the degree of intermolecular interaction of all molecules which form the medium in which the ion appears and moves.

The electrical conductivity of perspex
starts decreasing with field beyond 140 °. This may be on account of the fact that the order - disorder transition may occur in the solid state above this temperature. The dielectric constant shows such type of transition (47).

The conductivity-temperature curves appear similar to that reported by Gehlhoff and Thomas (48) in the case of various types of glasses. \( \log \sigma \) and \( T^{-1} \) curves fitted very well with the formula developed and verified by Rash and Hinrichsen (49) in various types of insulators and semi-conductors. There is deviation from the linear relationship at low fields which is mainly on account of the limitation in the experimental setup.

6. General remarks: The study of electrical conductivity of a nonpolar and a dipolar polymers as discussed above undoubtedly helps us in understanding the mechanism and transformation which take place when they are subjected to high electrical stresses at raised temperature. The basic conduction phenomenon is an ionic one in both the cases. The dipoles do make their contribution in determining the response of a solid dipolar substance when subjected to electrical stress at higher temperature which is absent in a nonpolar substance. Intense dielectric absorption comes into play at high temperature in both the samples which gives rise to hysteresis loop of current variation with
temperature. The possibility of lattice modification giving rise to temperature - current hysteresis cannot be excluded as reported by Palmer in Mn Se (50).
REFERENCES

(2) Gemant, A. - Phil. Mag. 20, 929 (1935).
(9) Gemant, A. - Direct Current. 6, 145 (1953).
<table>
<thead>
<tr>
<th>Reference</th>
<th>Author(s)</th>
<th>Title and Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>(17)</td>
<td>Bhatnagar, C.S.</td>
<td>Thesis accepted for the Ph.D. degree, Saurashtra University, Saurashtra (1956).</td>
</tr>
<tr>
<td>(20)</td>
<td>Gerritsen, A.N. 7</td>
<td>&quot;Hand Buch der Physik &quot; Encyclopedia of Physics, 19, 139 (1956).</td>
</tr>
</tbody>
</table>


(30) Pamphlet - Beckman Ultrameter.


(32) Presnov, V.A. Zh Tekh Fiz. 22, 6 (1952).


(34) Quittner, F. Wien Ber 136 IIA, 151 (1927).


(36) Poole, H.H. Phil. Mag. 32, 112 (1916).


(38) Maurer, R.J. J. Chem. Phys. 9, 579 (1941).


                      Ibid. 39, 153 (1943).
                      Ibid. 40, 443 (1944).


(49) Gehlhoff., and Thomas. - Z. techn Phys. 6, 544 (1925).