On the Electrets[1)]

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Abstract

Some experimental results and their brief discussions are given for the mechanism of electrets. The charges of the electret were measured by a generating voltmeter without touching their surface.

For the case that the temperature of the electret was raised with a rate of 1°C/min., the noise and the external current accompanied with its decay were observed in connection with the net surface charge. Some examinations were performed by the irradiation of γ-ray and by the microscope. The electrets, which were formed without flowing current through it or formed by applying the impulsive field for only one second at various temperatures, were also investigated. In order to explain all our observations, a scheme for the formation and the decay of the electret was proposed, which was somewhat analogous to that of Gross.

I. Introduction

Since the discovery of the electret by Eguchi[(1)], many experiments have been performed on it, and many explanations on its effects have been proposed. Some of them, however, seem to be incompatible with others and the definite interpretation is not yet given.

An electret is a dielectric which can maintain sensibly permanent surface charges. There exist two kinds of charges distinguished in sign, one of which has opposite sign to the charges on the adjacent forming electrode and is thus called the heterocharge, and the other has the same sign as those and is called the homocharge.

Gemant[(2)] postulated that the heterocharge arises from the real ionic charges which are concentrated near the surface of the dielectric under the forming field and the homocharge originates in the dipole orientation of the dielectric by the field of the ionic heterocharge. The dipole orientation remains frozen, while the heterocharge decays in rather short time. On the other hand, Gross[(3)] assumed the coexistence of two independent charges. The heterocharge is attributed to the inner polarization of the dielectric and the homocharge is refered to the breakdown between the electrodes and the dielectric surface. The algebraic sum

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of such two kinds of charges determines the net surface charge density. Gutmann[4] stated, in his report summarized on the many electret effects, as follows : The results of his experiments which showed the discontinuous jumps in the decay of the electret, together with the study by a microscope or X-ray by Nakata[5], suggest that the charges have some relations to the domain structure of the dielectric similar to the ferromagnetism. His opinion seems to support the idea of Gemant. Recently, Robinson[6] has pointed out that the X-ray pattern is independent of the charge of the dielectric. In this regard we have reported previously[7] on the noise accompanied with the decay of the electret and postulated that this noise is attributed to the discharge produced between the electrode and the dielectric surface.

The purpose of the studies described in this paper is to examine the effects of the electret from the various points of view and to clarify the basic mechanism of it. In Sec. II the experimental apparatus and procedure are described briefly, and in Sec. III the experimental results and discussions are given. A new interpretation on the mechanism of electrets, which seems to be somewhat analogous to that of Gross, are attempted in Sec. IV.

II. Experimental Apparatus and Procedure

(A) Preparation of Electret

The electret is prepared by the following procedure : In the first place, the mixture of 50% carnauba wax and 50% rosin is heated and melted. Next, this molten wax is put in a field of about 10 kv/cm, then the wax is cooled and solidified in the field. The shape of electret was a circular disk with thickness of 0.5 cm as shown in Fig. 1. Plates of Cu, Fe, Al, Brass etc. were used as the electrode. The one end of thermocouple was inserted in the electret for the sake of measurements of the temperature.

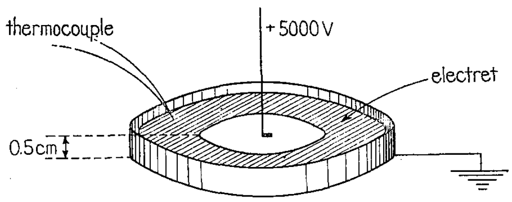


Fig. 1.

(B) Measurement of Charge

The measurements of charges of the electret have been performed by the use of a electrometer up to this time. This method, however, is not desirable because of the effect of rubbing between the electrode and the surface of electret which occurs from lifting off or putting on of the upper electrode.

A new method which makes it possible to measure the charge accurately without touching the surface of the electret was used here. (This was reported briefly in a previous paper[7].) This is the method by the generating voltmeter shown in Fig. 2. If the earthed vane V is rotated at the rate of 25 rounds per second between the electrode A and the electret E, an alternative current of 50 cycles is induced in the electrode A and outer circuit. This current is read with a galvanometer G after the rectification by a vacuum tube T. In order to see whether the induced charge on the electrode is positive or negative, the other electrode B faced to the plate C with a known potential is set up. If the switch S is closed, the algebraic sum of the induced charges on A and B can be measured with G, from which the sign of charge is decided. When the electret is taken off and S is closed, the generating voltmeter indicates the characteristic curve shown in Fig. 3 for various voltages applied on C.

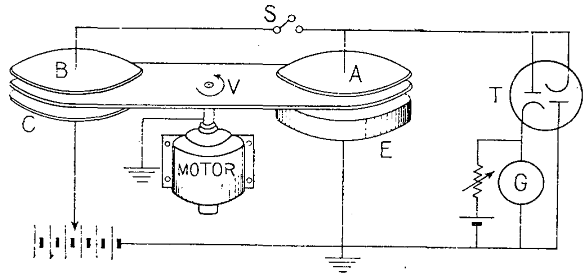


Fig. 2.

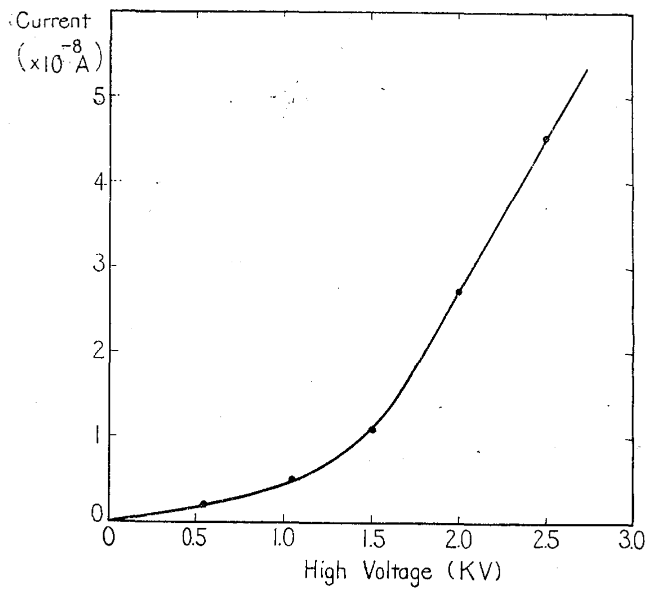


Fig. 3.

(C) Measurement of Noise

The block diagram of the apparatus for measurements of the noise is shown in Fig. 4. The electret was put into the thermostat which was shielded electrically. Discontinuous changes of the voltage produced at the electrode C were amplified, and observed with a cathode ray oscilloscope on the one side, and countered with a thyratron counting device on the other side. The pulse size distribution was determined by changing the bias voltage of the thyratron. The amplifier used is of a resistance-capacity coupling type and works in the frequency range from 200 to 20,000 c/s with a gain

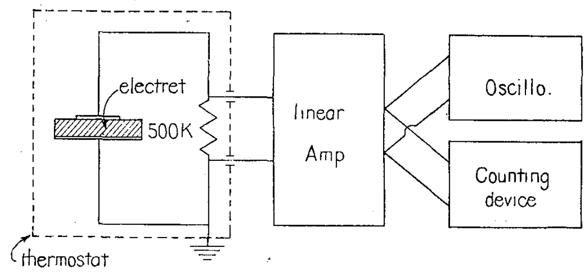


Fig. 4.

of 120 db.

III. Experimental Results and Discussions

(A) Measurement of Charge

1) *Natural decay.* As is well known, the electret decays very slowly under the natural condition. One of the electrets which was kept in the desicator with $CaCl_2$ at the room temperature (5~15°C) decayed as shown in Fig. 5. The heterocharge decreased exponentially with the half life of eleven days in the beginning, but the charge was observed still 5 months later. The observed large fluctuations might be attributed to the change of the temperature, besides the statistical one. In order to increase the decay rate of charge, it is necessary to raise the temperature of the electret.

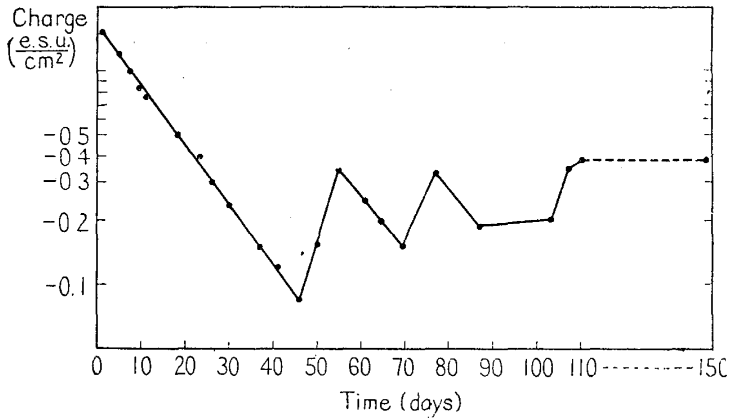


Fig. 5.

2) *Decay by heating.* By raising the temperature from 10°C with a rate of 1°C/min., the variation of the charge was measured for the electret which had initially the charge density of 1.5 e.s.u./cm². As is shown in Fig. 6, the heterocharge decreased rapidly from near 30°C, and converted to the homocharge at 40°C, which began to decay at about 50°C. On the other hand, when the temperature was lowered to 10°C after the reach at 45°C and raised up again to 45°C, the homocharge density retained a constant value as shown in Fig. 7. Afterwards, it decayed in a similar way with the case of Fig. 6, when the temperature was raised up again above 45°C.

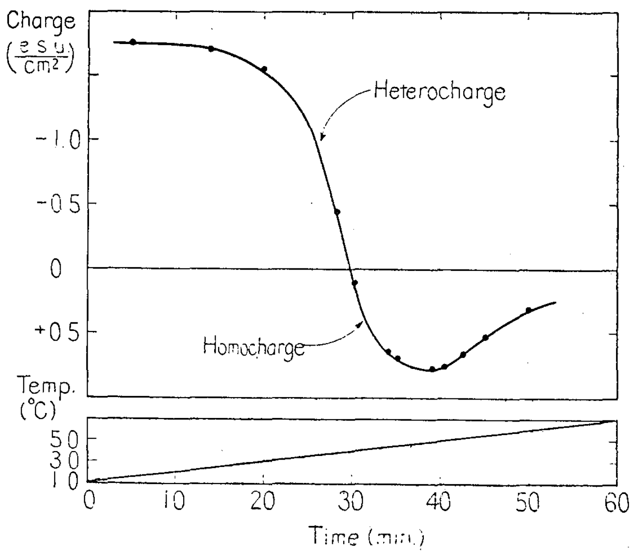


Fig. 6.

When the electret was kept in rather high temperature of about 40°C, the heterocharge decayed out after half an hour and the homocharge after 80 hours.

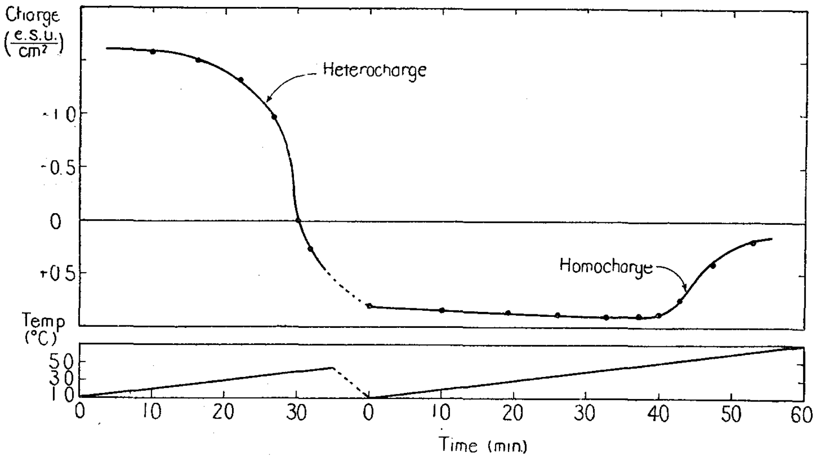


Fig. 7.

It seems to be reasonable to explain these experimental results as follows : Both kinds of charges, hetero- and homocharge, coexist initially in the electret, but as a result of initial excess of the heterocharge, the homocharge is covered until it overcomes the heterocharge. The observed charge is always the difference between the true hetero- and homocharges, which have quite different decay schemes with the temperature each other. This idea is analogous to that of Gross. From the same standpoint, Swann[8] has proposed some analytical interpretations for the decay of charges.

3) *Decay by the irradiation of γ-ray.* If the electret is irradiated by γ-ray from 5 milliculies Ra in atmosphere, the surface charges reduced to zero after half an hour. On the other hand, when the electret was put into a low pressure tank, the charges were only reduced from -0.2 e.s.u./cm^2 to -0.15 e.s.u./cm^2 by the irradiation. (By putting the electret into the low pressure tank, charges were reduced from -1.5 e.s.u./cm^2 to -0.2 e.s.u./cm^2 after half an hour without irradiation. This is observed for the various pressure of air by Sheppered[9].) All the measurements of charges mentioned above were performed in open circuit. (When the both surfaces of the electret are shorted, it is called "in short circuit", and when they are not shorted, "in open circuit"). On the contrary, the measurements for the electret in short circuit, did not show an appreciable change of charges by the irradiation for 30 minutes. From these results it may be thought that the above disappearance of charge is due to the capture of free electrons or ions by the surface of dielectric and not to an inner change of the dielectric.

For the dielectric, the net heterocharge of which were reduced to zero by the irradiation of γ-ray, the net surface charges vary as shown

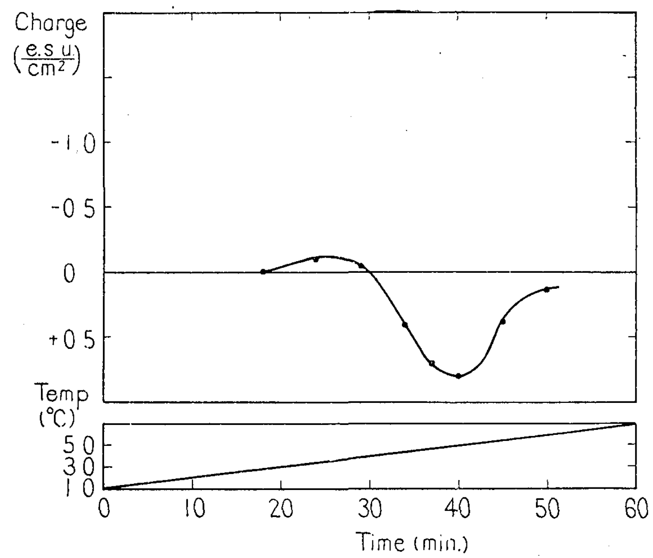


Fig. 8.

in Fig. 8 when the temperature is raised.

The irradiation of γ-ray for the electret, which had shown the homocharge by raising its temperature, also reduced its charges to zero. But, if the temperature of this electret is raised again, the homocharges reappear and begin to decay at 50°C as shown in Fig. 8. In order to explain these results it is favourable to consider that the charges, produced by the sticking of free electrons or ions under the irradiation of γ-ray at room temperature, decay easily at rather low temperature, about 20°C～40°C.

Since it may be thought that the measurement of charges in conducting atmosphere produced by the irradiation of γ-ray is equivalent to the measurement in short circuit, this method was performed for the electret raised its temperature at a rate of 1°C/min. and the results of Fig. 9 were compared with that of Fig. 6.

The net charges are dropped easily below 40°C through external current by the irradiation of γ-ray, but the net homocharge might be so supplied as to over the dropping by a little external current above 40°C.

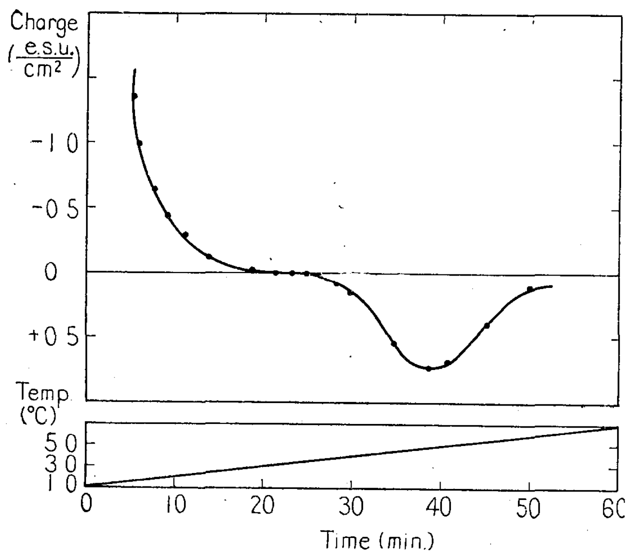


Fig. 9.

(B) Measurement of Noise

As mentioned in a previous paper, one of two electrets prepared simultaneously under the same condition was used to measure the charge, and the other to observe the noise, in order to obtain any relation between charge and noise. In the case that the temperature was raised at a rate of 1°C/min. monotonically, the noise began to appear at 50°C which was just the temperature corresponding to the starting point of decay of the homocharge. After the number of noise pulses arrived at maximum, it tended to zero, as the temperature close to a value which the net homocharge disappeared. (See Fig. 2 of the previous paper[7].) In the region of heterocharge, few noises observed at maximum of the charge density. The noise was not observed by raising and lowering of the temperature so long as it was below 50°C, but it always began to appear with the starting of decay of net homocharges and was maintained till the net homocharge disappeared.

It has been reported already that this noise was due to the discharge in the interface of the electret and the electrode. This phenomena may not be interpreted by the theory of Gemant, but may be by that of Gross. Namely, the real heterocharge is the volume charge so that the noise does not appear by its decay; on the other hand, the real homocharge originates in electrons or ions captured by the breakdown between the dielectric and electrode at 50°C～60°C, (This is clarified later.) so that it is apt to decay through the breakdown, i.e. through the external current with the noise, at the same region of temperature, This breakdown occurs only at rather high temperature, at which the potential barrier might be lowered considerably, and it goes on till the net homocharges almost decay out, i.e. till algebraic sum of real heterocharges and real homocharges tend to zero. It may be noticed that the breakdown occurs only when air gaps exist between electrodes and dielectric surface and the potential difference exhibits between them. So the noise does not always appear with the decay of homocharge. Particularly they can not appear after the net charge becomes zero.

(C) Measurement of Current

The variation of the current with time was measured directly by a galvanometer as shown in Fig. 10, when the temperature was raised with a rate of 1°C/min.. (This was already observed by Kakiuchi[10].) This yielded the result of Fig. 11. The sign of current was positive for the current flowing to the direction of arrow in Fig. 10.

It is found that the negative current flows in the region of temperatures 40°C～60°C which corresponds to the region of net homocharge as shown in the measurement of charge for the identical electret. This current originates to the induced charge in the electrode by the homocharge, so that it is not changed by the insertion of an insulator of mica foil between electrode and dielectric. This means that there exist air gaps between electrode and dielectric, and if not, the negative current might not be observed.

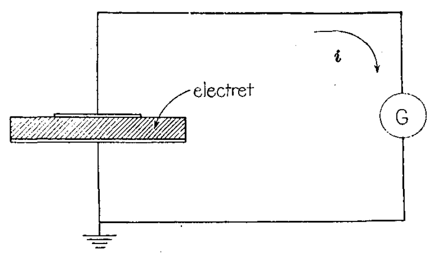


Fig. 10.

The positive external current increases as the electret melts. This current is prevented by the insertion of mica. The current flows on until the dielectric melts out and becomes to a liquid state in which the dielectric has good conductivity. Above 90°C the behavior of the current is governed by the kind of electrode materials. For example, when the upper electrode was made of copper and the bottom was made of iron, the result was shown by the full line in Fig. 11 and when the both electrodes were made of iron, the corresponding result was the dotted line.

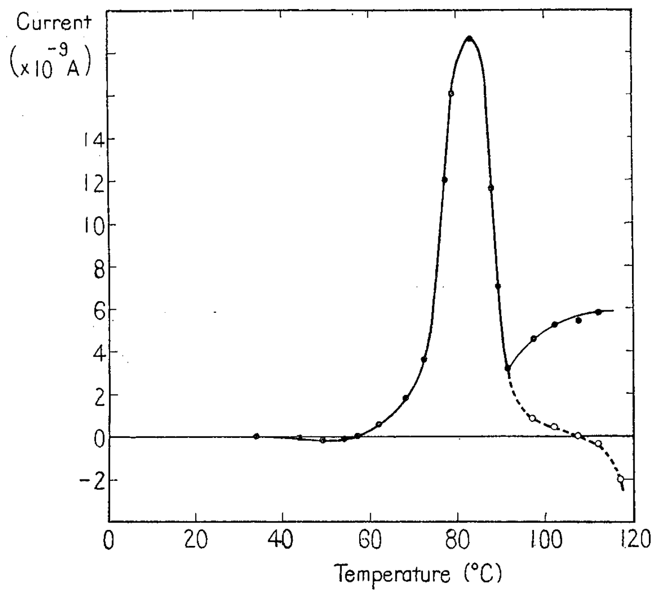


Fig. 11.

It is remarkable that the current increases considerably in the region of temperature above 60°C, at which the apparent charges become nearly zero. This fact seems to show that the real heterocharges and real homocharges are still in existence at such a high temperature.

As soon as some quantity of real heterocharges decay through the internal current, the same quantity of real homocharges may decay through the external current so as to keep the net charges zero. The measurements of conductivity of the dielectric led to the results of Fig. 12. The increase of the internal current with the conductivity leads to the distribution of external current given in Fig. 11.

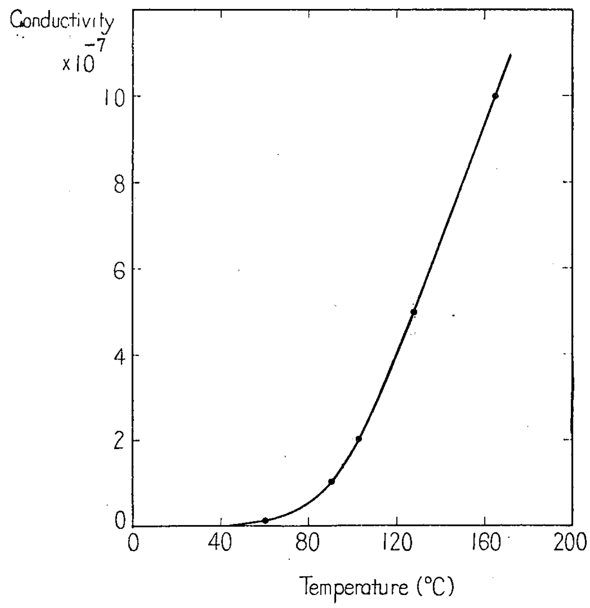
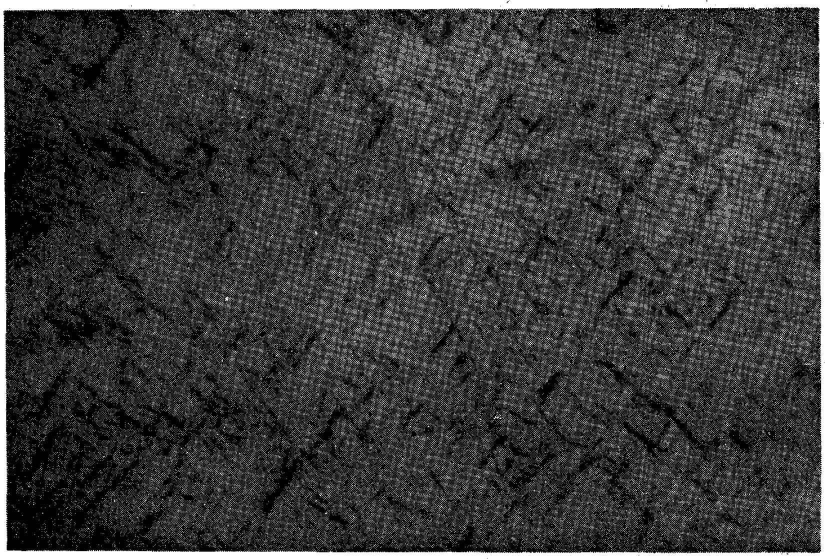


Fig. 12.

(D) Microscopic Examination

The sample was prepared by such a way that the molten wax was inserted between two glass plates and soldified under the forming field. Using a polarizing microscope, the arrangement of spheloite-form was observed as shown in the photograph. It is similar to that of Nakata(5). Since it was verified that the electret nearly decayed after 100 hours at 40°C, microscopic observation was also performed for this dielectric, after keeping of 100 hours at 40°C, and the same pattern as before was observed. Namely, this structure was not changed by the decay of the electret. This result is in agreement with that of Robinson[6] by X-ray. This pattern was not observed with the wax soldified without applying field.



Photograph.

A microscopic observation was also performed while the temperature of the electret was lowered from 90°C to the room temperature. Then a fast transition from a liquid state to the crystalloid polarized for light was observed at about 58°C. It may be thought that the volume polarizations or ions formed in a viscous state are nearly frozen at this transition. The decay of heterocharge may be hastened above this temperature.

(E) Electrets Formed by Applying Field for Very Short Time

In the following experiments the wax was subjected to the field of 5,000 v for only one second at various temperatures, and then was cooled rapidly to the room temperature, at which its surface charges were measured. The wax applied the field in a liquid state at 95°C, did not show any charge after cooling. If the field was applied for the wax in a viscous state at 75°C, a few homocharge was observed. In such case that the wax was subjected to the field at 55°C which was just a temperature of homocharge decay, the homocharge of 0.8 e.s.u./cm^2 arised. The charge was hardly observed when the field applying was at 35°C, at which the wax had been soldified. In these cases, a few heterocharges might be occur, but it decayed likely because of the rather large decay constant. From these results it is found that the homocharge can be formed for rather short time at the temperature at which its decay takes place. The formation of the heterocharge may require the application of field for longer time than that of the homocharge.

When the forming field was applied till the temperature was lowered from 110°C to 60°C and was not applied after that, the resultant electret gave rise to the heterocharge of 1 e.s.u./cm^2 and the homocharge of 0.5 e.s.u./cm^2. But when the forming field was applied during 100°C～50°C, the heterocharge of 3 e.s.u./cm^2 and the homocharge of 1.5 e.s.u./cm^2 arised, and these values were almost the same with those obtained in such case that the field was applied for all time from 100°C to the room temperature. From this, it is found that the almost all charges of the electret are formed till the temperature is lowered to 50°C, and most of these in 60°C～50°C. These facts, together with that mentioned in (D) (i.e. the fact that the transition from a liquid state to the crystalloid occurs at 58°C), seem to show that the "frozen in" of the charges takes place mainly in the region from 60°C to 50°C.

(F) Electrets Formed Without Flowing Current

Some electrets were formed without flowing current through the wax during the formation. Mica foils were inserted between the wax and both electrodes. Then the electret formed by the forming field of 7,000 v gave rise to the heterocharge of 1.3 e.s.u./cm^2, but hardly any homocharge. When the mica foil was inserted between only the upper electrode and the wax, the electret showed the heterocharge of 1.5 e.s.u./cm^2 and the homocharge of 0.2 e.s.u./cm^2 for the forming field of 6,000 v. Contrarily the electret formed without any insertion of mica foil gave rise to the heterocharge of 1.5 e.s.u./cm^2 and the homocharge of 1 e.s.u./cm^2 for the forming field of 4,500 v. The homocharge seems to have a close connection with the current during the formation of electrets. Namely the homocharge formation is attributed to the transfer of charges from electrodes to wax, and it takes place most easily in 50°C～60°C, as cleared by what mentioned previously. On the other hand, the heterocharge seems to be the volume charge which does not require the current flowing during its formation. These results are consistent with the theory of Gross, but not that of Gemant.

IV. Summary

The above experimental results and discussions may be summarized as follows.

(1) *Formation of electret*

When the dielectric is cooled from about 100°C to the room temperature under the forming field, charges of the electret seem to be formed in the following way: As the dielectric turns gradually from a liquid state into a viscous state, the volume polarizations are formed. It is clear that the heterocharges are attributed to these volume polarizations, because of the fact that the heterocharges can appear even for the electret formed without flowing current through it and the fact that it does not give rise to the external current by its decay. By the microscopic examination the dielectric turns rapidly from a liquid state into the crystalloid at about 58°C. Other natures of dielctric also change remarkably at this temperature. So the polarization formed in the temperature region from 100°C to 60°C may be "frozen in" mostly in the region of 60°C~50°C. When the forming field is removed over 60°C~50°C, the quantities of charges frozen in are considerably reduced.

The homocharges originate in electrons or ions transfered from the electrodes to the dielectric. This is found from the fact that the electret formed without flowing current does not yield any homocharge. The dielectric subjected to the forming field for only one second at 55°C yielded a considerably large amount of homocharges, but on the other hand, the dielectric subjected at 75°C, hardly showed any homocharge. So the transformations of the electrons or ions may occur for rather short time, and the charges are "frozen in" mostly in 60°C~50°C similarly with the heterocharge. Thus both kinds of charges are independently formed down to 50°C. In general real homocharges and real heterocharges coexist in the electret, and the algebraic sum of these is observed as the net surface charge.

(2) *Decay of the electret* (On such case that the temperature is raised at a rate of 1°C/min.)

At the beginning, the electret shows the heterocharge as the apparent net charge. As the heterocharge originates in the volume polarization, it begins to decay gradually from 30°C without any external current, while the real homocharge remains still constant up to 50°C as cleared by the result of Sec. III, (A). Consequently the net heterocharge decreases gradually until it becomes zero at 40°C, and after that the net homocharge begins to increase till 50°C. The homocharge is attributed to the electrons or ions which have been stuck in the dielectric and frozen in, so it is rather stable until the temperature of the electret is raised to such a high value that these electrons or ions may be broken out easily from its surface. This is arrived at about 50°C, corresponding to the temperature at which the crystalliod by microscopic observation begins to disappear. From 50°C, the homocharges begin to decay rapidly through the external current and this decay goes on till the excess of the real homocharge over the real heterocharge becomes to zero. If air gaps exist between the electrode and the dielectric the noise may be observed with this decay. After the net charge vanishes the real heterocharge decays through the internal current at an increasing rate with conductivity. Simultaneously the real homocharges decay through the external current so as to keep the net charge to zero. Both kinds of charges continue to decay in the same rate till about 100°C.

Our decay scheme mentioned above is given in Fig. 13.

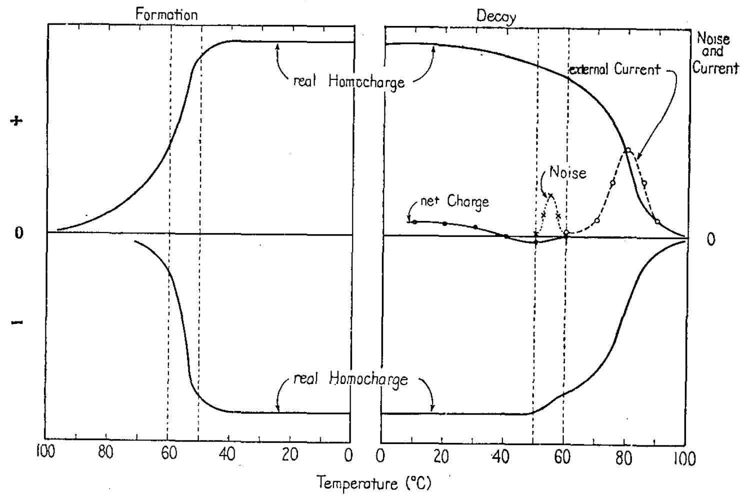


Fig. 13.

Some of our experimental results can not be interpreted by the theory of Gemant, but almost all the results may be explained by the theory mentioned above, somewhat analogous to that of Gross.

Acknowledgment

This study was carried out under the proper guidance of Professor S. Kojima at his Laboratory of the Tokyo University of Education. The author wishes to express her sincere thanks to Professor S. Kojima for his guidance and encouragement. She is also indebted to Dr. Y. Kakiuchi of the Tokyo Institute of Technology for supplying many samples.

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