REVIEWS OF
MODERN PHYSICS

VOLUME 20, NUMBER 3 JULY, 1948

The Electret

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THE term *electret* was coined by Oliver Heaviside to denote a permanently electrified substance exhibiting electrical charges of opposite sign at its extremities. The first man to prepare an electret was Eguchi (1), who reported some experimental results which since have been abundantly confirmed. Eguchi melted equal parts of carnauba wax and resin, with the addition of some beeswax, and permitted the substance to solidify in a strong electric field. He found that disks prepared in this way exhibited a strong negative charge on the face which had been in contact with the anode, and *vice versa*. This initial charge he found to decay within a few days, followed by the building up of charges of opposite sign. These charges, positive towards the anode and negative towards the cathode, Eguchi found to be permanent for all practical means and purposes, no measurable decay having been observed over a period of three years. These electrets, as Eguchi called them, are in many respects the exact electric counterpart of a permanent magnet. If an electret is cut between, let us say, its "poles," it yields merely two complete electrets. If the surface layer is removed from the wax disk by planing or cutting, the remaining body remains an electret. For best results and permanency, it must be kept with its faces short-circuited, exactly as a magnet must be kept with a soft-iron keeper. Eguchi concluded that the electrification, therefore, cannot be merely a surface phenomenon, but must be a volume effect. He found also, that the electrification instantly disappears on irradiation of the electret with x-rays, but reappears after cessation of the irradiation. Remelting destroys the electret.

These were the experimental facts published by Eguchi, who himself attempted no proper hypothesis to account for the phenomenon. Since then, a total of approximately 40 papers have been published on the subject, giving a good deal of experimental facts and a few theories. None of the latter have been universally accepted.

Before entering into a discussion as to the relative merits of these hypotheses, it may be well to present an outline of the physical facts which have emerged.

I. SUBSTANCES CAPABLE OF PERMANENT ELECTRIFICATION

Those substances which are capable of permanent electrification can be roughly subdivided into two classes (20): those which show a reversal of the initial charge, such as mixtures of waxes and resins used in the first experiments, and substances (e.g., resins alone) which do not show such a reversal. (See Table I.) In accordance with Gemant's (5) terminology, a charge on the electret of the same sign as the polarity of the adjacent electrode will be called a *homocharge*, and a charge of a sign opposite to the polarity of the "forming" electrode a *heterocharge*.

It is always the heterocharge which appears initially, but in a number of substances it declines

TABLE I. Characteristics of various substances.

Substances capable of permanent volume polarization		Substances giving	
Yielding heterocharges only	Yielding also homocharges	Surface charges only	No permanent charges
Acidic groups	Carnauba wax	Cetyl alcohol	Paraffin wax
Glass	Beeswax	Cetyl palmitate	Palmitic acid
Resin	Polar hydrocarbons	Non-polar hydrocarbons	Stearic acid
Sulfur	Esters	Stearanilide	1,8-Dinitro-naphthalene
	Alcohols	Seekay wax	
	Asphaltos		

and a permanent homocharge builds up. In other substances there is no sign of any decay of the primary heterocharge.

Homocharges are developed mainly in compounds containing esters and/or alcohols (5), but cetyl alcohol and cetyl palmitate show no permanent volume electrification at all. Hydrocarbons, too, tend to develop homocharges if the compound has a finite dipole moment. Non-polar hydrocarbons, e.g., paraffin wax, yield no electrets. Acidic groups give heterocharges only (5). It was thought that only hard and brittle substances are suitable to become electrets, but it has been found (6), that some very soft and low melting carnauba waxes also form electrets.

Mikola (20) subdivided electrets into two classes, *viz.*, those of comparatively high conductivity yielding heterocharges only and those of much lower conductivity capable of developing homocharges.

Only one systematic attack has been made on the connection between chemical constitution and permanent electrification. Nearly all workers thus far have used waxes and resins or mixtures, which are not definite nor pure compounds. Gemant (5) made some experiments on a few organic compounds related to those making up the usual waxes and resins and it has been confirmed that non-polar substances like paraffin wax do not form electrets (8).

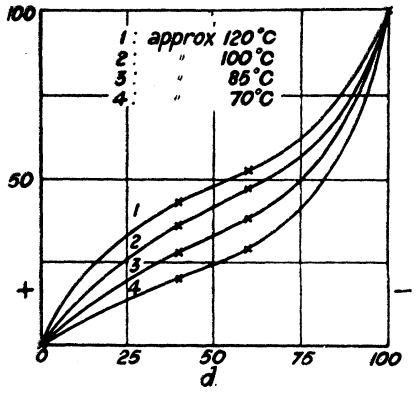

FIG. 1. From Gemant's paper (5). Potential distribution in electrets during making. (Both potential ϕ and distance d are arbitrary units.)

Germant has used the latter fact for the only study involving definite and pure compounds. He dissolved a number of acids in paraffin wax, the neutrality of which had been established, and published a number of curves showing the resulting charges in relation to time, but for a period of eight weeks only. He investigated abietic acid, palmitic acid, and beeswax, asphaltos, resin, and carnauba wax, for comparison. He also gives charge-time curves on a few mixtures of the above substances.

It does not seem to be relevant whether any one of the substances susceptible to permanent electrification is used separately, or in combination with others. Also, the method of mixing, whether dry or in the liquid state, has no influence as long as the resulting mixture is homogeneous (15).

Johnson and Carr (38) report that they succeeded in preparing electrets from molten sulfur. They did not embark upon any investigation of this very interesting result, and the author has been unable to find any further reference to electrets made from molten sulfur.

II. THERMAL AND ELECTRICAL PREPARATION OF ELECTRETS

There are some reports in the literature that permanent electrification has been obtained without heating the dielectric (6), (32), (20), but the electrets formed in this way invariably exhibit a much lower degree of electrification. Also, their permanency has not been established as well as for the conventional ones made by polarization when heated. There seems to be no point in increasing the temperature much above the melting point, but for best results the substance should be thoroughly fluid when the field is applied.

Gross and Denard (36) found that stable electrets of only somewhat lower field strength can be obtained without actually reaching the

melting point of the substance. These authors remark that this is likely to make a qualitative difference only. Groetzinger and Kretsch (32) also prepared electrets without melting the wax.

Tiku (40) found that the generation of charges diminished when the polarizing field was removed while the mixture was not yet completely solidified, or when the field was applied for too long a time after solidification. Best results are obtained when the polarizing field is removed once the wax has thoroughly solidified but still remains at an elevated temperature.

While most workers (following Eguchi's lead) used tinfoil electrodes, since these strip easily from the wax mixture, the choice of the metal for the electrodes has a definite bearing on the problem. Thiessen and others (6) have shown that electrets can be made by allowing the wax resin mixture to solidify between tin electrodes without any external field applied at all. A heterocharge of approximately $\frac{2}{3}$ the magnitude of the charge appearing on electrets prepared with a polarizing field has been observed and found to show no sign of decay over a period of six months. The same authors report that surface charges, of a more or less permanent nature, appear even if the mixture is simply rubbed with a hair brush and kept between tin electrodes, without any heating or external field. The rubbing, of course, will produce a surface electrification. Nickel electrodes, on the other hand, give only a very small charge, decaying practically to zero within a few months.

There is one important difference between the electrified bodies prepared in this way and the true electret prepared with a polarizing field at elevated temperature. The electrification of the true electret is a volume effect, extending throughout the whole of its mass, while the charges appearing without either the thermal or electrical part of the preparation are purely surface charges. Eguchi (1) has shown that the breaking of an electret yields two electrets in exact parallelism to the breaking of a magnet and that the surface of an electret can be planed or cut off without permanently reducing the electrification of the remaining body. Jaeger (4), Thiessen and co-workers (6), and Gemant (5) carefully investigated the distribution of the

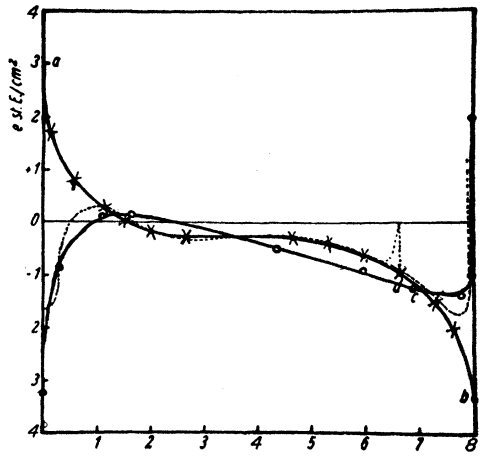

FIG. 2. From the paper by Thiessen, Winkel, and Herrmann (6). The curve x shows the space-charge distribution of an electret polarized with $E<10$ kv/cm. The other curve shows space charges resulting from $E>10$ kv/cm. These curves were obtained by removing layer after layer from the electret and measuring the charge of the remaining dielectric in every case.

charges existing in the interior of electrets. These results are shown in Figs. 1 and 2.

Large space charges were measured while the polarizing field was kept on and after it was removed, and the material was in the solidified state. These charges were found to extend throughout the body of the electret. In contradistinction, charges appearing on the surface of mixture solidified between tin electrodes without a polarizing field were found by Thiessen (6) to be surface charges which do not penetrate the interior of the substance. (See Fig. 3.)

The first investigators all applied fields in

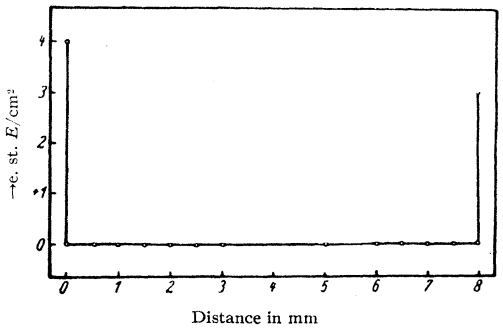

FIG. 3. From the paper by Thiessen, Winkel, and Herrmann (6). Typical space charge diagram of a wax mixture solidified between tin electrodes without application of a polarizing field. The charge is entirely on the surface.

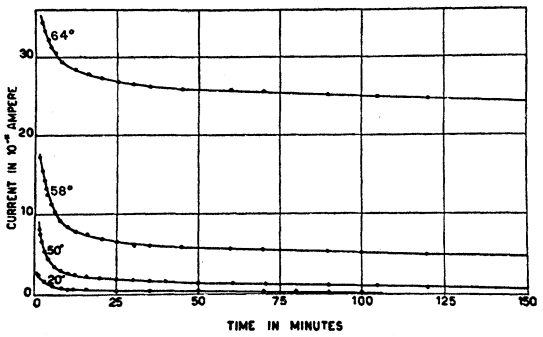

FIG. 4. From the paper by Gross and Denard (36). Isothermal charging currents for carnauba wax at different temperatures.

excess of 10 kv/cm, but Thiessen and co-workers found that electrets can also be prepared with lower fields.

Johnson and Carr (38) report the preparation of electrets with fields as low as a few 100 v/cm. There is one important difference. Electrets prepared with fields below 10 kv/cm give a heterocharge only, which decays slowly to permanent value within 10–20 days.

The magnitude of this charge is proportional to the polarizing field (6), (36). Also the space-charge distribution of the low field electrets is quite different from those made under high fields. An extensive negative space charge appears near the anode, extending approximately to the center of the dielectric. The space charge at the cathode is much less pronounced and also less extensive (Fig. 3).

On the other hand, electrets formed with polarizing fields in excess of 10 kv/cm show a large positive space charge facing the anode, extending only a very narrow distance into the dielectric and going over into a negative space charge of smaller magnitude but extending nearly to the cathode (5), (6), (4). Facing the cathode is a highly negatively charged layer of small thickness. Application of fields in excess of 10–12 kv does not seem to lead to any further increase in the resulting charges. This is not surprising, since the field at the surface of the electrets reaches the maximum value which can be maintained in air at these gradients, that is, approximately 5 abs. e.s.u./cm^2. At the surface of electrets, fields up to 30 kv/cm have been measured (1), (2), (6). A number of workers measured the charging currents passing through the dielectric during its preparation (2), (4), (8), (40), (36). These currents are in the order of a few μa/cm^2 while the dielectric is in the liquid state. They are much smaller when it is solid.

Gross and Denard (36) studied the charging currents under isothermal conditions at various temperatures as well as under rapid changes of temperature (Figs. 4 and 5). All their work was carried out at temperatures below the melting point of wax. Their isothermals show a very pronounced absorption current, which declines

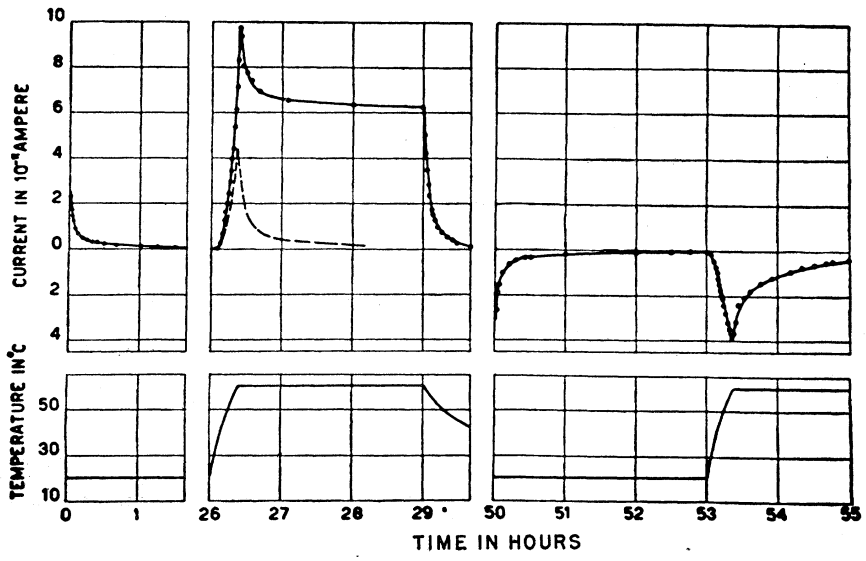

FIG. 5. From the paper by Gross and Denard (36). Absorption current maxima occurring upon rapid change of temperature of the dielectric (carnauba wax).

to a much smaller value within a day, but the curves are shifted rapidly to much higher currents even with small increases in temperature. If the latter is rapidly increased, a transient peak ensues in the charging current, the height of the peak depending on the rapidity of the temperature change.

III. PERMANENCY AND DECAY OF ELECTRETS

Eguchi (1) found no evidence of decay in his electrets after a period of three years. Other workers confirmed this (2), (6), (5), (36). No evidence has been brought to light so far which suggests that properly prepared electrets kept short-circuited and in a dry atmosphere would not keep their electrification for an indefinite time.

The aforementioned two reservations are important. Gemant (5) reports that electrets are exceedingly sensitive to humidity. With humidities below 80 percent, the electret regains its charge when it dries. Very prolonged exposure to humid air produces permanent damage as the result of penetration of water into cracks, especially if the electret has not been kept shorted. Gemant explains the temporary loss of electrification by the assumption of a thin water layer which shields the surface of the electret.

Adams (2) and Gemant stress the importance of keeping the electret short-circuited. The former author finds that the final homocharge on the electret keeps constant no matter how often the short-circuit is applied and removed. If kept open-circuited, the electret shows a decay of charge, but regains its full charge after having been short-circuited for some time.

Gemant reports that any measurements must be carried out immediately after the short has been removed because the charge decays to a considerable extent very soon afterwards. It recovers again on reapplication of the short circuit.

IV. THE ELECTRIFICATION OF THE ELECTRET

The surface charge has been measured by a number of workers. Sheppard and Stranathan (13) measured 10 e.s.u./cm^2, Thiessen and coworkers (6) found up to 8 e.s.u./cm^2, Gemant (5) e.s.u./cm^2, and others report values between 4 and 6 e.s.u./cm^2. The electric field near the surface has been studied by Gemant (11) who obtained values as high as 20,000 v/cm. It also has been studied by Eguchi (1), Adams (2) and Thiessen (6).

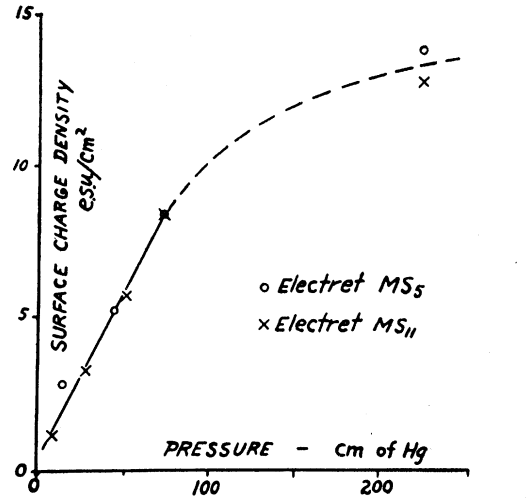

FIG. 6. From the paper by Sheppard and Stranathan (13). Surface charges as a function of the pressure of the surrounding air.

As Eguchi has remarked, the charge on the surface of the electret attains the highest value which can exist without producing a field on the surface sufficient to lead to breakdown of the adjoining layer of air (13).

Thiessen reports fields at the surface of 30 kv/cm, while Gemant (11), (14) measured the field at various distances above the surface. He reports an approximately exponential decrease of the field with distance. It decays to 600 v/cm at 5 mm distance, representing approximately $\frac{1}{5}$ to $\frac{1}{10}$ of its initial value at the surface. This is a smaller magnitude than Thiessen's results, but the difference may be due to the ambiguity in the expression "at the immediate surface" in Thiessen's paper.

As mentioned before, the breakdown strength of the surrounding air limits the field at the surface of the electret. This was tested experimentally by Sheppard and Stranathan (13) who measured the surface charge over a range of pressures between 10 and 228 cm Hg (Fig. 6). The charge density is shown to be proportional to pressure, but the curve flattens out at approximately 110 cm Hg and becomes nearly horizontal

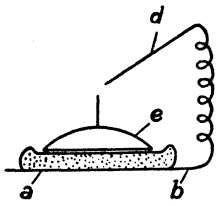

FIG. 7. From Gemant's paper (5). Sparking device for electrets.

at 150 cm Hg pressure where it reaches about 15 e.s.u./cm². Apparently, at these high pressures, the polarizing field was insufficient to produce an electrification capable of yielding a surface potential gradient equal to the breakdown strength of air at that pressure.

The potential distribution within the electret itself is of great theoretical interest and has been studied by Thiessen (6), Jaeger (4), and Gemant (5). Some of the relationships obtained are shown in Figs. 3 and 4, but their theoretical significance will be discussed later.

Jaeger also observed that the electret is not merely a giant dipole but that the body, placed into a Faraday cage, shows a charge as a whole.

Because of the extremely high internal resistance of the solidified electret, the measurement of its charges and of its internal potential distribution is not a simple matter. Eguchi, Adams (2), and others measured the charge by means of an electrometer, while Gemant obtained sparks up to 1 mm length, by the following arrangement.

A metal frame (Fig. 7) with a plate on its bottom and equipped with a needle on its top is dropped on the exposed surface of an electret. The opposite charge is induced at the bottom plate and an equivalent charge collected in the top part. A spark ensues if another needle connected with the other surface of the electret is brought near the fixed needle.

It should be understood, however, that the electret is not a battery and cannot do any work. In Gemant's case, the energy of the spark is supplied by the work done in moving the top electrode.

Eguchi has shown that remelting destroys the electret. Frei and Groetzinger (8) investigated the currents and charges liberated in the remelting process. They found that the quantity of electricity obtained by measuring the current flowing through an external circuit during the remelting is independent of the time lapsed between polarization and remelting and approximately linearly proportional to the polarizing field. The discharge currents are of the order of 10^{-8} A/cm², reaching this maximum value at approximately one-half the total melting time. The current ceases to flow when all the wax has liquefied. The same authors investigated the quantity of electricity liberated from electrified bodies prepared without melting and also from polarized paraffin wax disks. The currents obtained from beeswax electrets, polarized for one hour in the solid state, are one-tenth of those derived from true electrets, and 20 hrs. after polarization only approximately $\frac{1}{10}$ of that charge is liberated which can be obtained by remelting immediately after preparation. Also the maximum current appears after only $\frac{1}{4}$ of the melting time has elapsed. With paraffin wax they find no difference in the currents and charges, whether the substance was polarized in the molten or in the solid state. The magnitude of the charge liberated is about the same as obtained from beeswax polarized in the solid state.

It has to be kept in mind that the currents flowing through an external circuit represent only a fraction of the total quantity of electricity liberated in the molten electret, since the conductivity of the liquid wax is sufficient to allow the passage of quite an appreciable current through the fluid itself.

Groetzinger and Kretsch (32) observed that the depolarization current commences to flow even at temperatures below the melting-point, but a complete depolarization of the dielectric can be achieved only if the highest temperature attained during the polarization is exceeded, or if the wax is completely liquefied.

V. ASSOCIATED EFFECTS

Eguchi found that x-ray irradiation destroys the electrification which, however, gradually reappears. This is probably due to ionization of the air. Nakata (18) took microphotographs which indicated the existence of oriented crystals. This has been confirmed by Ewing (17) and also by the present author (27). The latter obtained

three diffraction rings with characteristic radiation from a Mo target. The middle ring was the most intense. The interatomic spacing indicated was approximately 4 A. It should be mentioned, however, that Bennett (3) found diffraction patterns in paraffin resembling those obtainable with electrets, to a certain degree, although paraffin is an entirely non-polar substance incapable of forming electrets. Good and Stranathan (22) compared x-ray diffraction patterns of freshly prepared electrets with those obtained from electrets which had achieved their final homocharge. These authors conclude that the formation of crystallites has no effect on the final strength of the electret.

The assumption of a crystalline structure in the interior of the electret is made still more probable by Adams' experiments (2) on the piezo- and pyroelectric properties of the electret. The latter effect was observed by Adams to the extent that the rate of growth of charge on removing the short-circuit as well as the maximum charge attained are different depending on whether the electret is heated or cooled. Adams also observed "a large and well reproducible piezoelectric effect." Gemant (5) and Nakata (18) could not find any piezoelectric effects, and Thiessen and co-workers (6) obtained only small deflections of the electrometer upon application of pressure, which they ascribe to capacity changes of the system rather than to piezoelectricity. Adams' electrets were in the form of hollow tubes electrified in a radial direction, and it is conceivable that the constraints set up in the rigid structure of the forming brass tubes might be conducive to the appearance of the piezoelectric effect. Artificial piezoelectric bodies have been prepared by Meissner (23) by suspending quartz powder in wax, and also Turpain and Durepaire (21) report a piezoelectric effect in ebonite, india-rubber, and even paraffin.

Groetzinger (7) investigated the thermal conductivity of electrets by means of Schleiermacher's method. He finds an increase of 71 percent with beeswax, but no result at all with paraffin wax (Fig. 8). The thermal conductivity increases approximately exponentially with the polarizing field. This observation has great theoretical significance, since Groetzinger and Frey (19) found an increase in the thermal conductivity of polar gases and liquids in the presence of an electrostatic field.

Groetzinger (7) also allowed molten beeswax and carnauba wax to solidify in a strong alternating field of 50 cycles. He found a pronounced demixing of the mixture to occur and a subsequent *decrease* in the thermal conductivity of 22 percent. He therefore concludes that the increase in molecular thermal conductivity of electrets is much larger than the observable value, since the demixing which will occur in a non-homogeneous electric field in itself will tend to a decrease of conductivity. The increase in conductivity is independent of the actual field of the electret, that is from short-circuiting it, etc.

A degree of demixing has been noticed by Nakata (18), who also observed a slight difference in the appearance between the cathodic and anodic layers of an electret section, cut parallel to the polarizing field.

The present author (27) found that the decay of the homocharge is not a continuous process, but takes place in discontinuous jumps, which bear a striking similarity to the Barkhausen effect in the magnetic case. The process of decay itself, as well as the magnitude and frequency of these discontinuities, are considerably speeded up by irradiating the electret in a supersonic sound field of approximately 700 kc and rather appreciable intensity.

Groetzinger and Kretsch (32) succeeded in speeding up the decay of the charge by exposing the electret to a strong r-f field, which, however, did not produce discharge currents corresponding to a higher temperature.

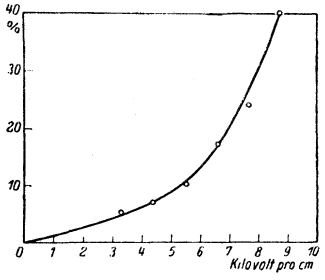

FIG. 8. From the paper by Groetzinger (7). Showing the percentage of increase in thermal conductivity of the dielectric as a function of the polarizing field.

VI. THE PHOTOELECTRET

Before embarking upon a discussion of the theories put forward to explain the electret, it might be of interest to mention electrets produced by Nadjakoff (9), (10) by applying light instead of a change of temperature. He applies a direct field of 470 v/cm to a solid sulfur disk, illuminated with 6000 lux after a dark period of 3 min. The illumination lasts for 12 min. and is removed before the field is disconnected. His *photoelectrets* kept their charges for 15 hours, which was the longest period he investigated, if kept in darkness. Nadjakoff's time-current graphs are shown in Fig. 9. It is seen that the current increases rather suddenly from its very small, dark value to a considerable charging current, which decays approximately exponentially with time. The discharge current appears once the field is removed and the sulfur disk re-illuminated. It flows in opposite direction, but its magnitude and the shape of its decay-curve are very similar to the charging current curve.

Nadjakoff's experiments have not been reproduced as far as the author is aware.

VII. THEORETICAL DISCUSSION

The first attempt towards a theory of the electret was made by Adams (2). He assumes that the electrification is not truly permanent but decays slowly, thereby producing the free charges. The theory is based upon the pyroelectric effect. The latter occurs in asymmetrically crystallizing substances (e.g., quartz) which appear charged immediately upon a change in temperature. These charges gradually disappear, as the temperature of the crystals original environment is again approached. Lord Kelvin assumed the existence within the pyroelectric quartz of permanently polarized molecules, the degree of their polarization being a function of the temperature. If the conductivity of the crystal were zero, any polarization once attained at an elevated temperature would be permanent. Because of the finite conductivity of the crystal this is not the case, but the charges slowly equalize. Adams now assumes a similar mechanish to operate in the case of the electret, but with a rate of decay of charges which is extremely slow.

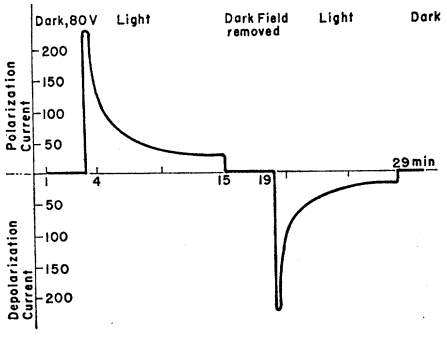

FIG. 9. From Nadjakoff's paper (10). Charge and discharge current curves obtained and photoelectrets (see text).

The homocharge is assumed to be due to compensation of the internal field of the electret by true charges induced upon its surface.

To account for the observed permanency of the homocharge, an initial polarization of such a value would have to be assumed that not even the complete alignment of all dipoles could achieve it. It would also demand that the electret exhibits strong pyro- and piezoelectric properties. These were observed by Adams, but doubts have arisen as to whether Adams mistook changes in the capacity of the system for these effects.

Gemant (5) assumes two entirely different mechanisms for the development of the homocharge and the heterocharge. He considers the latter a purely ionic effect. It is well known that in oils and liquid melts large accumulations of ions occur which form space charges in the regions near the electrodes. Gemant (46) himself has been able to measure such charges ballistically.

Ionization is also known to occur in small voids and adsorbed gas bubbles. This has been shown, e.g., by Tykociner and Raine (29).

Gemant maintains that the ions, which are captured by the solidification of the melt, remain for a certain time in these positions and, because of the very low conductivity of the solid wax, only very slowly drift away and thereby neutralize the space charges. There is little doubt that this concept is essentially true. Gemant himself and a number of other workers (4), (6) found large space charges during the polarization process as well as in the solidified electret. (See

Figs. 1 and 2.) Since the waxes commonly used for the preparation of electrets consist to a large degree of higher organic acids, their dissociation into hydrogen ions and heavy organic anions would be quite feasible. Because of the different mobility of the two ion species, an asymmetrical distribution of charges should result and the electret as a whole should also show an electric charge. This has been found to be the case (4). Gemant also observed, that the asymmetry between cathode and anode space charges increases with the cooling of the electret till in the solidified body only a positive space charge confronting the cathode remains and the anode space charge disappears.

The homocharge is thought to be caused by the presence of a non-dissociable component of finite dipole moment. This contention is supported by the fact that mainly compounds of esters and alcohols show the effect. Gemant assumes that these form crystalline nuclei in an amorphous medium. This again is supported by Ewing (17) and by the present author (21) who found definite evidence for the existence of a crystalline structure in electrets, differing from that obtained by Bennett (3) in paraffin.

Also Nakata's (18) microphotographs show this part of the theory to be substantially correct. This author photographed thin sections of electrets through a powerful microscope in polarized light (Fig. 10). He employed essentially the mineralogical technique. Nakata found a fine fibrous crystal structure in sections cut parallel to the polarizing field and fine spherolites in sections perpendicular to the field. These are crystals growing from a nuclear point forming a fine star. In identical sections of wax which had not been subjected to a polarizing field, but otherwise treated likewise, a completely random distribution of crystals without spherolites was observed.

Gemant assumes that the normally disordered crystallites attain an orientation in the field. Bennett (3) infers from his x-ray experiments that the hydrocarbon chains in paraffin wax which has been allowed to solidify in an electrostatic field remain oriented perpendicular to the polarizing field. This strongly supports Gemant's argument.

Because carnauba wax is very hard, the dipole

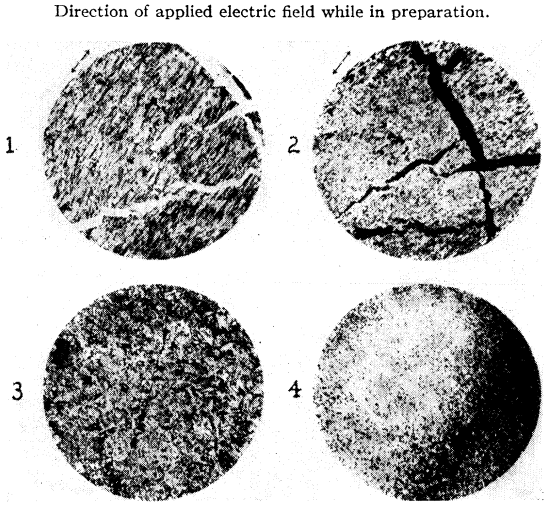

FIG. 10. From Nakata's paper (18). Plates 1 and 2 are taken in a plane parallel to the polarizing field and show crystalline needles aligned with the field. Plate 1: || Nicols (×20); plate 2: ⊥ Nicols (×20); plate 3: ⊥ Nicols (×20); plate 4: ⊥ Nicols (×20). Plate 3 was taken in a plane perpendicular to the polarizing field and shows spherolites appearing in the dielectric. Plate 4 shows the structure of a mixture solidified in the absence of a polarizing field.

moments are "frozen in." Also, since this mechanism would give only a heterocharge, Gemant further assumes that the crystallites are piezoelectric and are hindered in radial contraction in a plane perpendicular to the polarizing field. The crystallites are therefore kept in a state of high radial stress and if they are piezoelectric, a charge should develop on a surface perpendicular to the direction of the stress. This piezoelectric charge would be in opposition to the dipole. Gemant's theory eventually demands the existence of quadrupoles in the electret, but it has since been found that very soft waxes also yield electrets (6), and further, that electrets can be made in a way which precludes the possibility of a radial constraint perpendicular to the direction of the polarizing field (6). This theory also would have difficulties in accounting for the comparatively large discharge currents, which have been observed by a number of workers (8), (36), (32). If Gemant's hypothesis were correct, the charge of the electret should depend on the degree to which the mixture has been strained while cooling, and therefore on the cooling rate. Good and Stranathan (22) report only a very small decrease in the charge density with longer cooling

times up to 24 days. Gemant's theory, as far as the homocharge is concerned, has therefore been discarded but his suggestion of a different mechanism for the homo- and the heterocharge which makes the change of polarity of the electret merely a superposition effect is certainly substantially true. The piezoelectric effect has been observed by Adams (2) and by Meissner (23), but other authors (21), (6) were unable to confirm it.

Thiessen, Winkel, and Herrmann (6) were the first to suggest that differences in the conductivity of the dielectric in the solid and liquid state are responsible for at least part of the effect. They explain the electrification on the basis of Mikola's (20) two classes of dielectrics (Table I) which are both assumed to be present in the wax mixtures: those giving a heterocharge and possessing higher conductivity and those yielding homocharges and exhibiting a lesser degree of conductivity. In the first group space charges are built up from ions. This process is termed "internal polarization." In the second group of dielectrics charges arise either in the interface between wax and electrode or come from the electrode itself. This process Mikola called "external polarization." All dielectrics show external polarization if the applied field exceeds a certain threshold value, due to ionization by collision in the interface. Such ionization processes caused by collisions have been demonstrated in dielectrics, inter alia, by Tykociner and Raine (29).

Thiessen and his co-workers assume that in the liquid state the wax behaves as a dielectric of Mikola's first class, exhibiting internal polarization and building up space charges. As soon as the wax solidifies, it behaves as a dielectric of the second class, and under a high charging field shows external polarization. The different time constants of these two processes account for the change of polarity of the electret. The theory also explains why electrets prepared with weaker fields do not give a homocharge. The value of the threshold field of 10 kv is in fair agreement with Mikola's value of 9 kv for the minimum field necessary to obtain external polarization in glass. The theory is supported by the fact, that space charges can be obtained by charging the cold wax for 10 min. with 25 kv/cm (6). The theory does not account for the necessity of keeping the electret short-circuited, nor does it explain why the same discharge currents are always obtained, no matter when the electret is short-circuited, how often this is done, or at what age the electret is remelted. Furthermore, Groetzinger and Kretsch (32), who obtained electrets without liquefying the wax obtained results difficult to reconcile with this concept.

Groetzinger (7) put forward a very simple explanation for the necessity of keeping the electret short-circuited: Since the conductivity of the electret is finite, the shorting leads to an accumulation of charges on the electrodes and when these are removed, the volume polarization reappears. If kept unshorted, compensating charges will accumulate on the surfaces, which, being unable to escape, "screen" the electret. In a later paper (8), Frey and he assume that the electrification of the electret is due to a shifting of the charges, till compensating charges have accumulated on the electrodes sufficient to cancel exactly the field caused by the volume polarization. They assume that the charges are due to the existence of dipoles with different mobilities. This theory has not been developed sufficiently to permit further discussion, but Grotzinger's explanation of the short-circuiting of the electret seems to be substantially correct.

Gemant (14) presented a mathematical analysis of the field of the electret in a space of finite ionic density, based on a concept similar to the Gouy-Helmholtz double layer in electrolytic reactions. He arrives at a thickness of the ionic layer on top of the electret of 450 A. Outside this distance the field of the electret should be completely shielded. This is in contradiction to experiment, for 5 mm from the surface of the electret there still exists a field of 20 percent of its maximum value.

Gross (16) ascribes the electrification to the enormous increase in the charging and discharging rates of the dielectric with rise of temperature. It is well known that waxes are highly absorptive dielectrics, and Gross has shown in a later paper with Denard (36) that at room temperature it is practically impossible to charge the dielectric completely. He assumes a decay of electrification caused partly by external and partly by internal conduction within the dielec-

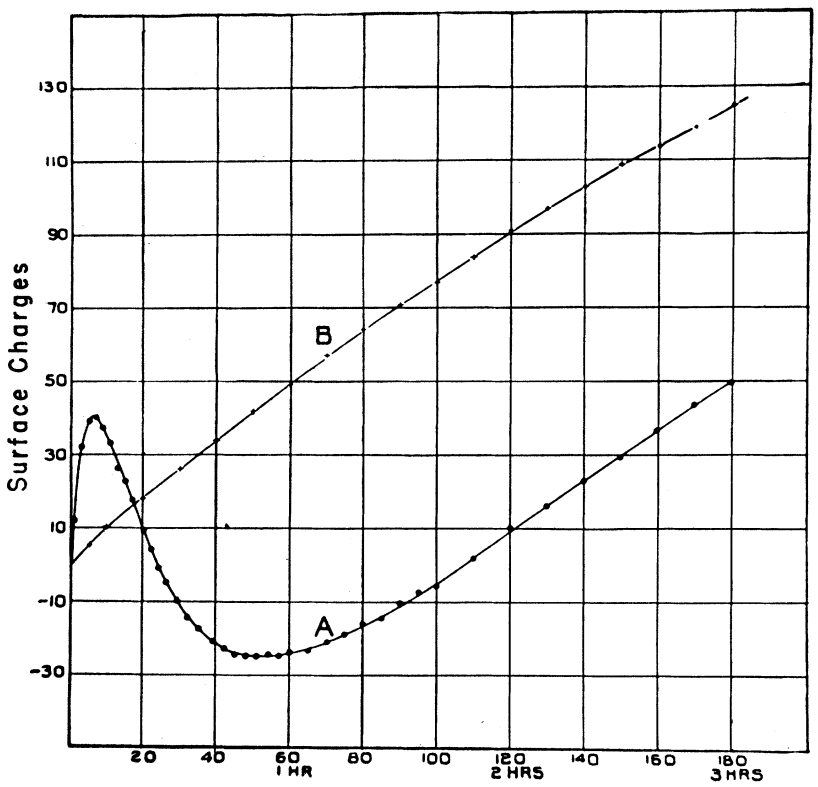

FIG. 11. From the paper by Adams (2). Curve *A* shows the reversal of polarity of charge of an electret which had been heated to 40°C for an hour and then kept at 25°. Curve *B* shows the behavior of an electret kept at 25° for 2 days.

tric itself. If the second kind of conduction is very marked, the direction of the discharge current might reverse. This has been observed.

Gross further assumes the simultaneous occurrence of two processes: First, dielectric absorption involving ions and/or oriented dipoles in the interior of the electret. This produces the heterocharge. Second, conduction currents in the interface between electrode and dielectric produce the homocharge. In polar substances the heterocharge would be caused mainly by dipole orientation in the field. In the interface the field will increase, a conductivity current will flow and ions (or electrons) are fed into or drawn from the electrode. This homocharge initially exists only on the surface, but later tends to spray into the dielectric. Faraday in 1839 visualized such a mechanism. Owing to the short circuit, a part of the polarization in phase with the field, i.e., the heterocharge, disappears immediately and the rest then follows slowly. Eventually, therefore, the homocharge only remains.

Gross's theory is strongly supported by his and Adams experiments on the charging and discharging currents (see Figs. 5 and 11). Since there is no transient peak observable in cooling and since the discharge current depends only on the discharge temperature, he concludes that the absorptive capacitance of the dielectric remains constant at these temperatures while the charging and discharging rates depend largely on temperature. The absorption capacitance as well as the dielectric constant of these waxes is many times higher than commonly thought. From experiments Gross concludes that at room temperatures only about one-half the charge can be absorbed within 100,000 years. This charge can be released within a few minutes at temperatures near the melting point. It therefore seems that the relaxation times of solid absorptive dielectrics are of the order of thousands of years and that such dielectrics can never be completely charged at room temperatures. This Gross compares to the elastic aftereffect, which also exhibits very long relaxation times. Therefore, the static "long-time" dielectric constant of carnauba wax is also much higher than previously assumed. Gross arrives at a figure of approximately 135,

assuming that one could charge the dielectric completely.

Gross's theory is supported by a paper by Cole and Cole (22). These authors derive an expression for the complex dielectric constant of an absorptive dielectric on the basis of Debye's dipole theory. A Fourier development, for the case of a high direct field, also predicts the transients observed by Gross.

At the present juncture, Gross's theory seems not to be in contradiction to any observed facts, but there are quite a few experimental observations which it fails to explain. There can be little doubt that the electret has a characteristic crystalline structure. The x-ray and microphoto evidence (see Fig. 10) cited before all point in this direction. Also Groetzinger's (7) discovery of the abnormally high thermal conductivity of electrets (Fig. 8) and the present author's observation of jumps in the discharge current (27) support the assumption of a crystalline structure. A state of higher thermal conductivity by necessity is equivalent to a state of higher orderliness, and the discontinuities observed in the decay of the heterocharge of electrets point to the existence of electrified subregions within the charged body, similar to the Weiss domains in ferromagnetics, which alter the direction of their electric field vector as a whole. It is known that the magnetic Barkhausen effect increases with the mechanical strain on the magnetic substance and the likewise very hard and brittle electrets are certainly under great mechanical strain.

On the other hand, x-ray patterns have been obtained which indicate a crystalline structure in paraffin wax, a substance which has been shown not to be capable to yield electrets. Paraffin wax is an absorptive dielectric, but perhaps less so than resin and carnauba wax. If Gross's theory were complete, it should also be possible to obtain a volume electrification in paraffin wax. This has been shown to be impossible (5), (8). Paraffin wax also shows (7) no enhanced thermal conductivity if polarized in an electric field. Therefore, it seems that Gross's theory, while so far the most satisfactory which has been put forward, is still incomplete. As far as the heterocharge is concerned, it may well be that Gemant's (5) earlier concept is nearer to the truth than Gross's.

Since Thiessen and his co-workers (6) could obtain no permanent polarization with mixtures containing up to 15 percent palmitic acid, stearic acid, and 1,8-dinitronaphthalene in purified paraffin, all highly polar compounds, it can be concluded that the dipole theory offers no sufficient explanation for the electret.

No attempt has been made to furnish an explanation of Nadjakoff's photoelectret (9), (10). Also Johnson and Carr's experiments (38) on sulfur electrets have not been followed up.

Surface films, prepared after the method of Langmuir and Blodgett, also exhibit a permanent electric moment. Langmuir, Blodgett, and Schaefer published a number of papers on the deposition of multi-molecular layers of long-chain oriented molecules. They distinguish two types: An X type, which can be deposited on glass as well as on metals, and a Y type, which can be deposited on metals only. The X layer exhibits a permanent electric moment, since its molecules are oriented alike. The Y layer is electrically neutral. Goranson and Zisman (34) deposited 340 semicylindrical layers of calcium stearate on an ebonite cylinder which then was suspended in an electric field of 100 v/cm. This resulted in a rotation of the cylinder and a deflection of 16 cm was thus observed. Porter and Wyman (35) measured the potentials and charges of 170 such layers on chromium. They observed a potential of 8.6 v, and a surface charge of 55 e.s.u./cm. No attempt has been made to correlate this effect with the electrets.

Gross treated the electret from the point of view of an absorptive dielectric and in the present author's opinion this is the most promising avenue of approach to the problem. There are many effects known to physicists which, in the writer's opinion, definitely are correlated to the electrification of the electret. There is, e.g., the behavior of anisotropic melts, of which *p*-azoxyanisol is the classical example. Such melts exhibit a definite crystalline structure. Kast (45) has found that their dielectric constant undergoes a change in a not even very strong electric or magnetic field. Since by Coehn's rule (43) a substance with higher dielectric constant becomes positively charged with respect to one of lower dielectric constant, charges should therefore develop in these melts. These melts exhibit

some resemblances to Groetzinger's observations on the thermal conductivity of electrets (7). Groetzinger also observed an increase in the thermal conductivity of meta nitranilin in the presence of electrostatic fields (19).

Piekara (24) observed a discontinuity in the dielectric constant of higher organic acids in the neighborhood of their melting point. It may be significant that palmitic acid, one of the constituents of carnauba wax, exhibits this effect most strongly. The curve relating the conductivity of insulating oils to temperature bears a striking resemblance to that obtained with molten waxes (26). Gemant (26) points out that the transition from the liquid to the solid state does not directly yield a crystalline phase, but that the oils first go over into a glassy amorphous state. Near the melting point they do not represent a true liquid but a glassy amorphous substance. It would be certainly worth while to attempt, at reduced temperatures, the preparation of electrets with oils. W. Jackson (42) found that the highest dielectric absorption in paraffin wax occurred in that transition region which was mentioned above, where the substance apparently is halfway between the true solid and liquid state.

Pre-melting anomalies in long-chain molecules have also been observed by Van Hook and Silver (47). These compounds do not obey Grueneisen's law of constant ratio between specific heat at constant volume and coefficient of expansion. An inordinate expansion of the lattice occurs at a temperature below the melting point.

It can be assumed from Nakata's microphotos and from x-ray studies that the crystalline structure of the electret differs from the structure of the uncharged substance. In this case, a transition point between the two modifications must exist. Since there is some evidence for the piezoelectric property of the electret, Adams' hypothesis that the pyroelectric effect is present in electrets could be taken up, perhaps, in the light of more recent knowledge. Jaffe (33) states that the dielectric constant in the polar direction on transition from the pyroelectric to the non-pyroelectric modification of a crystal approaches infinity, if the transition takes place without latent heat of transition (thermodynamical transition of the second kind). If this quantity is small compared with the anomalous specific heat below the transition point, a sharp but finite maximum is to be expected. This has been observed in the case of another highly anomalous dielectric, i.e., rochelle salt. Therefore, it might well be that the dielectric constant of the electret, which so

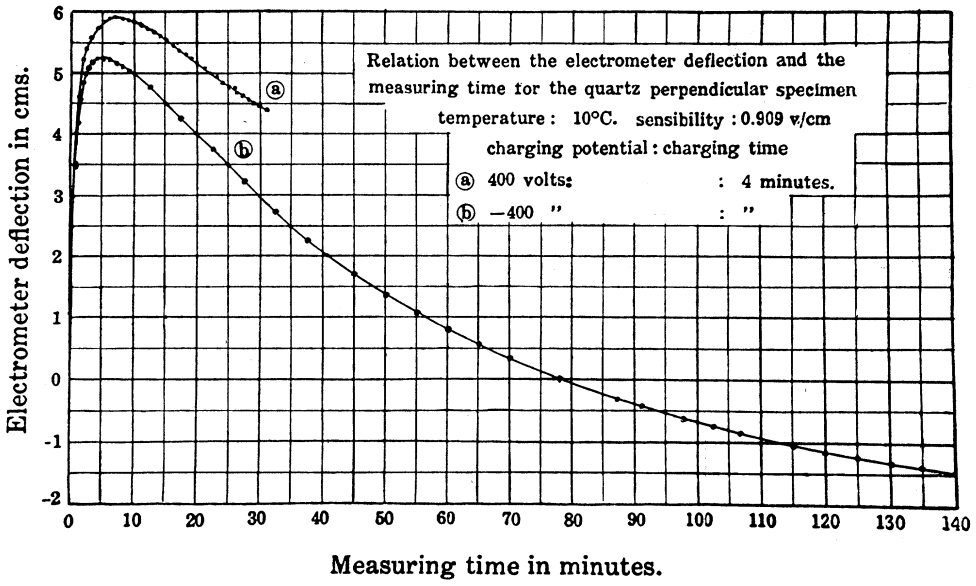

FIG. 12. From Shimizu's paper (44). The ordinate represents residual charge on a quartz disk cut perpendicular to the optical axis.

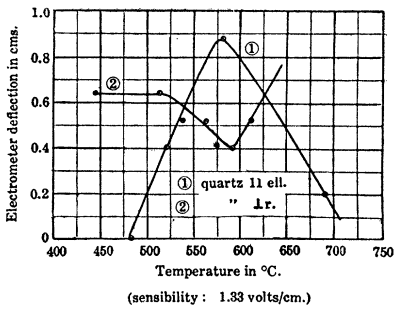

FIG. 13. From Shimizu's paper (44). The ordinate represents residual charge. Curve 1 shows the maximum obtained at the transition temperature (573°) of a disk cut parallel to the optical axis, and curve 2 shows the minimum observed at that temperature with a disk cut perpendicular to the optical axis.

far has not been investigated, will exhibit a maximum at some elevated temperature at or near the transition point.

There are quite a few similarities between the so-called ferro-electric substances like rochelle salt and the electret, but no comparative study of these two subjects has yet been undertaken.

The results obtained by Shimizu (41), (44) are of interest (Figs. 12 and 13). Working with quartz disks, cut parallel or perpendicular to the optical axis, and polarized with approximately 20 kv/cm, he observed a very large increase of the residual charge, followed by its rapid decay and eventual reversal of polarity. The magnitude of the residual charge increases exponentially with temperature. The same author observed a discontinuous increase in the conductivity of quartz at its transition point, 573°C. Furthermore, keeping one electrode earthed, Shimizu found that the disk cut parallel to the optical axis exhibited a sharp maximum of residual charge at the transition point, while the other cut showed a very pronounced minimum at this temperature. The similarities to the behavior of electrets are obvious, but no work has been done in order to link these phenomena. Onsager (37) refers to the lattice structure of electrets and cones to the conclusion that a hexagonal close-packed lattice has a lower energy than any other configuration of spheres carrying electric dipoles. In general, the electric field outside an electret crystal contains an energy comparable to the total proper energy of the molecules, dependent on the shape of the crystal, being negligible for very long lengthwise polarized needles.

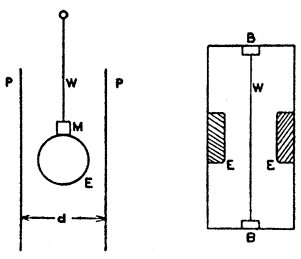

FIG. 14. From Gemant's paper (11). Left: Electrometer with suspended electret. Right: String type instrument.

VIII. PRACTICAL APPLICATIONS

The first suggestion for practical application of electrets was put forward by Adams (2), who thought of utilizing their piezoelectric properties. Gemant (5) built the first measuring instrument incorporating electrets. The electret was suspended between two plates, which were charged by the unknown potential, the whole arrangement being a kind of mirror galvanometer with the electret taking the place of the coil.* He attained a sensitivity of 0.5 v per division. The same author (11) later designed an improved version of the "suspended disk" type of instrument and a string-type voltmeter having a charged wire suspended between two electrets facing each other with opposite charges (Fig. 14). He also evolved an a.c. vibration electrometer incorporating electrets.

In the earlier paper (5) Gemant suggested the employment of electrets in condenser microphones, and during the last war the Japanese apparently took up his suggestion. A number of electret microphones were captured in the Pacific and proved at first rather puzzling to the signallers who tried to fathom their working. It is probable that in the near future electrets, perhaps made from glass or plastics, will be used to a considerable extent in a variety of electrical instruments, wherever a purely electrostatic field is demanded.

* The present author also prepared electrets in the form of lengthwise polarized needle-like cylinders and employed these as the indicating element in a specially built quadrant electrometer.

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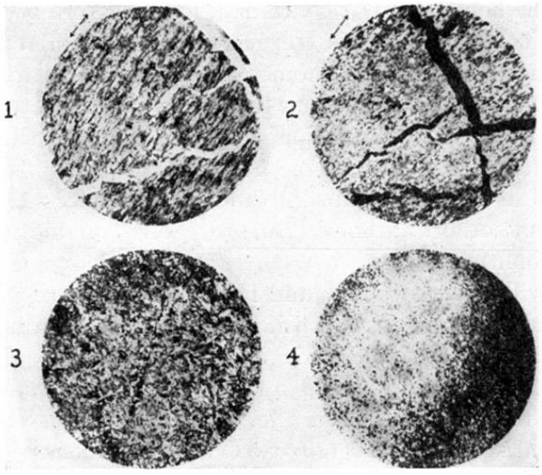
Erratum: Narrow Gaps in Microwave Problems

[Rev. Mod. Phys. **20**, 175 (1948)]
W. R. SMYTHE
California Institute of Technology, Pasadena, California

IN the last two paragraphs of the above article, the approximate formula (25) was erroneously compared with one on page 359 of Schelkunoff's *Electromagnetic Waves*. The latter formula does not apply to this case but in the Phys. Rev. **56**, 313 (1939) Schelkunoff gives a curve (No. 6) which agrees with the dashed curve in Fig. 3. The formula from which this curve was drawn is identical with (25) so the two approximations agree.

Direction of applied electric field while in preparation.



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