The Heterocharge in Carnauba Wax Electrets.

Roy White Clark

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The Department of Chemistry

by
Roy White Clark
B.S., Middle Tennessee State College, 1957
M.S., Louisiana State University, 1959
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ABSTRACT

The heterocharge phenomenon in carnauba wax electrets has never been satisfactorily explained. The purpose of this work was to study the heterocharge phenomenon in the absence of homocharge by using forming fields of less than 2 Kv/cm. The data obtained suggested a previously unproposed mechanism for the heterocharge.

The dielectric constant and dissipation factor were measured for carnauba wax which had been polarized at fields of both 2 Kv/cm and 11.5 Kv/cm. The measurements were continued for thirty-one days after polarization. No significant change in dielectric constant or in dissipation factor was found.

An apparatus was developed which was capable of measuring the electric field above the electrets. This apparatus involved a vibrating electrode to sense the field and an upper electrode to which a voltage was applied to null the field effect of the electret. Thus readings were taken of the electret surface charge and the way in which it changed with time.

Groetzinger's method was also used to find the frozen-in charge of the electrets. Attempts were made to correlate the surface charge data with the thermal discharge current information obtained by Groetzinger's method.
The surface charge measurement apparatus was arranged in such a way that the distance from the vibrating electrode to the electret could be varied. By changing this distance and reading the null voltage required to balance the electret's field, it was possible to test an equation which arises in Gubkin's phenomenological theory of the electret. This technique also permitted calculation of the surface charge on the electret.

Also included in the study, in addition to carnauba wax electrets, were solid solution electrets. These, with carnauba wax as solvent, contained stearic acid and n-octadecyl alcohol as solutes to the extent of 0.45 molal, about 13 percent by weight. Measurements were made on electrets which were coated with conductive paint and also on several which were uncoated.

The rate of decay of the surface charge was not found to be exponential. It did consist of two parts, one a short time constant decay, \( \tau = 40 \) minutes, the other a longer time constant decay, \( \tau = 9.5 \) to 84 hours, depending upon the electret used. The short time constant polarization was also observed without thermal treatment of the electret, but in most cases no frozen-in polarization was found for isothermally treated electrets.

Surface charges were measured to be from 17.5 to 105 nanocoulombs per square centimeter. Electrets painted
with a conductive coat were found to be more stable and reproducible than their uncoated counterparts. Storage of electrets, as well as their behavior when coated, seemed to further verify Gubkin's ideas on the relationship of shorted storage to decay lifetimes.

The added solutes did not change the characteristics of the solution electrets significantly compared to the carnauba wax alone. They did lower the melting point several degrees, however, which caused some difficulties in the Groetzinger method determinations.

An electret which cracked in manufacture was found to have a frozen-in polarization four times that of normal electrets. This "crack effect," and the other data obtained formed the basis for a mechanism proposal for the heterocharge.

The proposed mechanism postulates crystalline domains in the wax which can trap ions by virtue of a potential barrier at their surface. During the thermal formation of the heterocharge, ions are trapped in the domains in such a way as to produce dipolar domains. These dipolar domains then orient in the field, and the long time constant decay is due to their slow disorientation at low temperatures. The short time constant polarization is attributed to the dielectric properties of the amorphous regions of the wax.
CHAPTER I

HISTORICAL BACKGROUND

An electret is a macroscopic electrical dipole formed by exposing a dielectric material to an external electrical field in such a manner that the dipole field remains for a time after the external field is removed. The word electret was suggested by Sir Oliver Heaviside in 1892 when in a volume of Electrical Papers he wrote:

Electrization may be approximately perfectly elastic with reference to the standard zero state, as in a dielectric in which absorption does not occur, so as to disappear on the removal of the exciting cause. There may also be residual electrization, namely, when absorption occurs. This may tend naturally to wholly subside, or a part of it may remain. The body is then permanently electrized. But apart from artificial production of permanent electrization, it exists naturally in pyroelectric crystals, if nowhere else.¹

Heaviside then addressed himself to the task of a name for bodies which were "permanently electrized."

A word is evidently wanted to describe a body which is naturally permanently electrized by internal causes.

He then considered the word "electric" to describe such a

body, but rejected it on the grounds that the word was in common use as an adjective, and also that at one time the word electric simply meant any insulator. He goes on to say:

Another word that suggests itself is electret against which there is nothing to be said except that it sounds strange. That is, however, a mere question of habit. Choosing, at least provisionally, the second word suggested to avoid collision with the adjective, we may then say that certain crystals, if no other bodies, are natural electrets; that solid insulating substances may be made electrets artificially, with a greater or less amount of permanency; that liquid insulators can only be electrets for a minute interval of time, if at all; whilst gases, whose particles are always vigorously wandering about, are never electrets.

Heaviside then went on to speculate on the mechanism of electret formation, even though artificial electrets with a measurable external field had never been made. In fact the first electret was made only in 1920 by a Japanese physicist, Mototaro Eguchi. 2abc Eguchi made an electret by impressing an electrical field across electrodes in molten carnauba wax. He cooled the wax to room temperature so that solidification took place in the presence of the externally applied field. When the field was turned off and the electrodes removed the wax exhibited surface charges. The face

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2b M. Eguchi, Japan J. Phys., I (1922), 10.
2c M. Eguchi, Phil. Mag., IL (1925), 178-192.
of the wax which had been next to the positive electrode was negative, and vice versa. Eguchi also discovered that these surface charges decayed slowly to zero (in about two days), and then most unexpectedly built up a charge of opposite polarity to the original charges.

Aside from this charge reversal phenomenon, an electret made from carnauba wax seemed to be the electrical analog of a permanent magnet. If an electret were kept electrically short circuited, it maintained its electrization for longer periods than it did if it were stored without being short circuited. Presumably if an electret were cut in two, one would have two electrets, showing that the polarization was a volume effect, not simply a surface phenomenon. Eguchi did not actually cut them in two, which would be very difficult with the hard and brittle carnauba wax, but he did plane their surfaces, sometimes removing several millimeters of wax, and always the surface charge was regained after such treatment. Eguchi also irradiated his electrets with X-rays, which caused them to lose their charge. However, with time the charge slowly returned, indicating that the X-radiation had simply ionized the air and temporarily neutralized the surface charges.

Several groups of physicists became interested in these phenomena and by 1948 the related literature comprised about
forty papers. These were summarized at that time in an excellent review article by F. Gutmann. There is no need to review this literature again because the Gutmann review is readily available, but it does seem desirable to summarize some of the theories and ideas concerning electrets which prevailed during this period.

Edwin P. Adams, at Princeton University, performed some experiments on carnauba wax electrets of cylindrical geometry (most workers use discs) wherein he measured the change of surface charge with time. He concluded from his results that the electret effect was a piezoelectric effect in carnauba wax. He reportedly demonstrated that carnauba wax was a piezoelectric material. More will be said later concerning Adams' work.

Eight years later Andrew Gemant, then at Oxford, published his work on electrets. He set out to (1) verify Eguchi's work; (2) clarify the mechanism of the underlying physical process; and (3) estimate the importance of electrets, theoretically and practically. Gemant made surface charge measurements, space charge measurements within the dielectric, and studies of the effect of varying the chemical composition

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5A. Gemant, Phil. Mag., XX (1935), 929-952.
of the electret. He introduced the terminology still used today of \textit{heterocharge} for the initial charge of the electret and \textit{homocharge} for the reversed charge that has the same sign as that of the forming electrodes. He recognized that there must be two different mechanisms, one producing the heterocharge, the other causing the homocharge to appear.

His space charge measurements showed that the field distribution within the electret was not symmetrical. Paraffin alone showed no electret effect, but if he dissolved carnauba wax in paraffin the resulting electret showed a heterocharge and a charge reversal to a homocharge. If he dissolved acid constituents, such as abietic acid in the paraffin, the resulting electret showed only heterocharge. Gemant proposed that the heterocharge was due to ion space charges from the acid constituents of the wax. The asymmetry of the internal field was due to the different mobilities of the hydrogen ion and the anion. The homocharge, he believed, was due to orientation of the dipolar molecules and their solidification into oriented crystallites. However, since this mechanism would also produce heterocharges he further supposed that Adams' ideas of the piezoelectricity of carnauba wax were valid and proposed that upon cooling and contracting the stresses on these oriented crystallites caused them to reverse their polarity due to the piezoelectric effect, and thus a permanent homocharge would be "frozen in."
Gemant's faith in the piezoelectric charge reversal was due in part to his observations of the hardness and the pronounced volume contraction upon cooling of carnauba wax. He ignored the fact that his paraffin electrets with carnauba wax as a solute showed homocharges, although obviously they were not hard and piezoelectric.

The idea of oriented crystallites incorporated in Gemant's theory was in agreement with observations of such microcrystalline structure in carnauba wax electrets. Nakata\textsuperscript{6} photographed thin sections of electrets in a powerful microscope and his microphotographs show needle-like crystals aligned in the direction of the field, whereas these microcrystals were not apparent in unpolarized samples. Ewing\textsuperscript{7} showed with X-ray diffraction that there are some ordering processes or crystalline structure in electrets definitely different from that in paraffin wax.

Gemant's theory of the homocharge was not supported by the following facts: (1) very soft waxes could, under certain conditions, become electrets; (2) other workers could not find the piezoelectric effect in carnauba wax reported by Adams; and (3) electrets can be made in a way that avoids the radial constraint which was proposed as the cause of


the piezoelectric effect. When his theory of the homocharge
was discarded, his theory of the heterocharge was also neg­
lected, and was never fully tested.

The following year Thiessen, Winkel, and Herrmann¹⁸
suggested that differences in the conductivities of the
solid and the liquid states were responsible for the electret
effect. These authors attempted to extend Gemant's obser­
vations but could obtain no permanent polarization with
mixtures of stearic acid, palmitic acid, and 1,8-dinitro­
naphthalene in paraffin. From this they concluded that the
dipole theory, that is the theory that the heterocharge is
due to dipole orientation as suggested by Adams, did not
offer a sufficient explanation for the electret effect.
They were inclined to believe that the heterocharge repre­
sented space charges of ions, much as in Gemant's theory,
but that the homocharge resulted from ions formed at the
electrode-wax interface by the high fields employed. In
effect this was the beginning of the idea that the homo­
charge is "injected charge" whereas the heterocharge is
intrinsic volume polarization.

The idea that the homocharge resulted from surface
ionization, or injected charge, was substantiated by these

¹⁸P. A. Thiessen, A. Winkel, and K. Herrmann, Physik.
Z., XXXVII (1936), 511.
authors' observations that with forming fields of less than 6-8 V/cm homocharges were not observed. With higher forming fields, homocharges were observed. This fact has been abundantly verified.

The difficulties which confronted the theories of Thiessen, Winkel, and Herrmann were mainly: (1) that their theory supposed the heterocharge to be formed in the liquid state by ion motion, although in 1936 Groetzinger and Kretsch obtained electrets without liquifying the wax; and (2) it was difficult to see how the heterocharge and homocharge could coexist and decay independently if they both resulted from ionic mechanisms.

At this time Groetzinger proposed an explanation for the necessity of keeping an electret short-circuited. Essentially he said that an open electret would accumulate compensating charges (from within the electret) on the electret surface and cancel the field of the electret.

More importantly, Groetzinger reported that the thermal conductivity of beeswax electrets was higher than normal in the direction of their polarization. Since it had previously been shown that the thermal conductivity of gases and liquids which contain polar molecules showed a similar effect in an electric field, it was inferred that in beeswax thermo-electrets there are oriented dipoles. It was suggested that

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measurement of this thermal conductivity difference would be a more characteristic measure of the electret effect, since surface charges could be compensated and reduced even while the material remained polarized.

The thermal conductivity of electrets was rarely measured. Instead the method of measuring the discharge current that flowed upon reheating the electret became a powerful tool to measure the frozen in polarization. Bernhard Gross\textsuperscript{10abc} made many careful measurements of isothermal and non-isothermal current measurements on electrets, and correlated the charging and discharging currents with the surface charge behavior as measured by a lifted electrode method. The experimental technique of measuring the current delivered to an external circuit by the electret when reheated to the forming temperature became known as the Groetzinger method; Gross interpreted the integral under the current vs. time curve as a measure of the polarization of the electret. In the present work such current-time plots are referred to as thermal discharge curves.

By 1948 Gross' theories of the mechanism of the heterocharge and the homocharge were well developed. He ascribed

\textsuperscript{10a}B. Gross, \textit{Phys. Rev.}, LVII (1940), 57.  
the electret phenomenon to the enormous increase in charging and discharging rates of the dielectric with rise of temperature. Two processes occur simultaneously. First dielectric absorption involving ions and/or oriented dipoles occurs in the interior of the electret. Second, conduction currents in the interface between electrode and dielectric produce the homocharge. In polar substances he thought that dipole orientation was probably the mechanism of the heterocharge.

Gross and his co-workers in Brazil have done much of the important quantitative work on electrets since 1948. However, Gross' careful experimental work constitutes a description of the phenomenon more than an explanation thereof. To say that the absorptive capacitance of wax dielectrics is higher than is commonly believed is not to explain why it is so high.

The literature since 1948 and up to the year 1960 is reviewed in a book by two Russian physicists, V. M. Fridkin and I. S. Zheludev. Although the book is mainly about photoelectrets, the chapter on thermoelectrets is excellent.

There will be no attempt to review this literature either. The most interesting developments during this period...

follow. By his careful quantitative work Gross and his co-workers proved that the homocharge was indeed an injected charge. In electrets having both heterocharge and homocharge Gross showed how the two types might be demonstrated in thermal discharge curves, and how simultaneous measurement of the surface charge and the discharge current allows the experimenter to distinguish between the contribution to the thermal discharge curve from heterocharge and homocharge. Essentially what Gross did was to demonstrate experimentally that the discharge current could be expressed as $I = i + \frac{d\sigma}{dt}$, that is as the sum of a conduction current (from the homocharge) and a displacement current (from the heterocharge). For electrets made with fields low enough to avoid the homocharge, $i = 0$ and $I = \frac{d\sigma}{dt}$. This possibility was demonstrated experimentally. It follows then that under conditions of no homocharge,

$$\sigma = \int I \, dt$$

which is a statement that the integral of the thermal discharge current-time curve is a measure of the heterocharge.

If an electret has both a heterocharge and a homocharge the surface charge exhibited by the electret depends upon which is greater. If the heterocharge is greater in magnitude than the homocharge, then the electret exhibits a

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heterocharge. If the heterocharge decays more rapidly, as it apparently does, then the surface charge of the electret diminishes to zero and the apparent homocharge appears. This behavior explains the origin of the terminology "intrinsic heterocharge and homocharge," and "apparent charge of the electret."

If one could slow down the decay of the heterocharge, the charge reversal phenomenon might be delayed, according to Gross' ideas. In fact Wiseman and Linden stored electrets at liquid nitrogen temperatures and slowed the decay of the heterocharge.

In 1953 Gemant tried again to explain the mechanism of the electret. Gross' work had shown quite convincingly the nature of the homocharge, i.e. injected charge, but said nothing about the nature of the heterocharge mechanism. Gemant now proposed a combination of three basic processes to explain electret behavior. These were (1) dipole orientation and the collection of these oriented dipoles into domains; (2) ionic displacements within the material; and (3) spray charges from the electrodes during cooling, i.e. injected charge. According to this theory the heterocharge results from both dipole orientation and ion displacements.


\[14\] A. Gemant, Direct Current, I (1953), 145.
The spray charge which would cause a homocharge is initially less than the ion displacement space charges, with which it coexists, and thus the electret shows an initial heterocharge. The heterocharge decay is due to the migration of heterocharge-ions away from the surface, whereas homocharge-ions, or spray charges, remain attached to the domain-like dipolar groups. The homocharge cannot decay until the domains disorient, which fact explains the long lifetime of the homocharge.

This theory of Gemant explains many features of electret decay. However it fails to explain the coexistence of the heterocharge and homocharge if both are ionic. Only by assuming that the heterocharge-ions are more mobile or less attracted to the domains can this theory succeed in explaining the different decay rates. It is difficult to see how spray charge can be other than ions in the dielectric body, and if so why they are not neutralized by the heterocharge-ions. Also it is difficult to understand why the dipolar group attractions do not "lock-in" the heterocharge-ions as well as the homocharge-ions. Although it is interesting in that it combines the ionic and polar orientation theories, and there is experimental evidence for both, this theory cannot be considered to be entirely satisfactory.

Since the publication of Gemant's latest theory there has been further evidence gathered to support the existence
of oriented dipoles or oriented dipolar domains in electrets. This is the work of K. V. Filippova who worked with poly(methylmethacrylate) electrets. She found that thermo-electrets could be formed with heating periods of only 1.5 to 2 hours and optical anisotropy would not appear. When heating time was more than four hours optical anisotropy was observed, and the thermoelectret charges decayed completely in 60-80 days, whereas optical anisotropy was still considerable after 7-10 months.

This work shows, as does X-ray diffraction, that there are definite structural changes in the body of electrets due to the heat treatment in the electric fields. The structural change is not essential to electret formation, nor does it disappear upon decay of the electret at room temperature. Filippova concluded that the polarization of these electrets is due to the orientation of dipole groups which may have been bound to larger aggregates and which rotated those aggregates. The orientation of such aggregates would in turn produce optical anisotropy. The electret decay resulted from the disordering of the dipole groups without disordering the larger aggregates, and thus the optical anisotropy survived the electret field decay.

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Still more evidence that something other than ion motion was involved in electret behavior comes from the work of Froiman and Fridkin\textsuperscript{16} on the heterocharge of electrets. They derived a theoretical expression for the discharge current as a function of temperature and time and compared theoretical discharge curves with experimental ones. Their fundamental theoretical assumption was that the discharge was due to the motion of weakly bound ions in the electret's internal field. The experimental electret thermal discharge curves disagreed with the theoretical in the region beyond the maximum. These workers concluded that the rise of current due to heating was probably due to the motion of ions in internal fields of the thermoelectret and that the slow decay perhaps was due to the presence of an oriented dipole structure.

Much of the reluctance to accept a mechanism for the electret effect which postulated polar molecules orienting, or clusters of polar molecules forming polar domains, was due to the fact that the measured surface charges seemed too large to be attributed to oriented molecules. One can calculate that if all the molecules in a sample of density $10^{22}$ molecules/cm$^3$ were aligned, and each had a dipole moment of one Debye, the resulting surface charge would be

\begin{footnote}
\textsuperscript{16} A. I. Froiman and V. M. Fridkin, \textit{Kristallografiya}, I (1956), 342.
\end{footnote}
about $3 \times 10^{-6}$ coulombs/cm$^2$. Since observed heterocharges are on the order of $10^{-9}$ to $10^{-7}$ coulombs/cm$^2$, one would have to assume that one percent of the molecules or more could be aligned to account for the observed surface charges. This is an unreasonable assumption, since the fraction of molecules aligned with the field should obey a Boltzmann distribution function, and in fact be quite small, too small to account for the observed heterocharge. Also Johnson and Carr's report of sulfur electrets, Baldus' discovery of the electret effect in naphthalene, and Gubkin and Skanavi's results with inorganic titanate electrets all discouraged a dipole theory of the heterocharge.

Baldus first reported in 1954 the heterocharge in naphthalene, and Belyaev, Belikova, Fridkin, and Zheludev in 1958 experimented further with naphthalene. The conclusions were that the electret effect in naphthalene was due to the localization of electrons in deep traps in the crystal structure, and that the mechanism of formation of these naphthalene thermoelectrets was essentially the

18 W. Baldus, Z. angew. Physik, VI (1934), 481.
same as that for photoelectrets of the same material.

If dipolar alignments were responsible for the thermo-electret effect, it seemed reasonable to expect dielectric constant changes in wax electrets due to the polarization. In 1954 Wikstrom reported $\varepsilon$ and $\tan \delta$ the same as in the nonpolarized state. In 1955 Gerson and Rohrbaugh also reported no change. In 1958 Gubkin and Skanavi found no change in $\varepsilon$ and $\tan \delta$ of titinate electrets compared with unpolarized samples. However, in 1955 Chatterjee and Bhadra reported changes of $\varepsilon$ of carnauba wax when electrets were formed; changes of three orders of magnitude were observed. Also they found a rise in $\tan \delta$. In 1958 Bhadra reported $\langle \varepsilon \rangle$, $\langle \varepsilon \rangle$, $\langle \varepsilon \rangle$, where $\varepsilon_1$ is the permittivity along the direction of polarization, and $\varepsilon_2$ is the permittivity perpendicular to the direction of polarization; $\varepsilon$ being the permittivity of an unpolarized sample. Attempts to repeat the experiments of the Indians have failed.

26 See Chapter V, this work.
The two major contributions to the phenomenological theory of electret behavior during the period 1948-60 were those of W. F. G. Swann and A. N. Gubkin. Swann's theory is discussed in Chapter IV and Gubkin's additional contributions, mainly the idea of "degree of short-circuiting," is also explained in this chapter.

The most important paper in the literature since 1960 was one by B. Gross and R. J. de Moraes in 1962. This paper describes a series of experiments designed to determine whether the electret heterocharge is truly a volume charge. The internal charge distribution of heterocharged electrets was measured by a sectioning method and the results showed that "the cause of the heterocharge is a uniform volume polarization." This impressive paper settles the question of whether or not the electret effect is a space charge effect or a volume effect. It is a volume effect of still unknown mechanism.

It has been reported that the consecutive application of direct (constant) fields and alternating electric fields often produces more stable electrets than those obtained without the alternating field. Paraffin wax, naphthalene,

sulfur, Perspex, and Ebonite were used in these experiments by Polovikov. Also, since the book of Fridkin and Zheludev there have been more papers on the ceramic inorganic electrets.  

In 1960 Beeler, Stranathan, and Wiseman reported some effects of certain polar vapors on electret behavior. Vapors used were water and chlorobenzene, the electrets being made of polyvinyl acetate, polyethylene, acrylic resins, and carnauba wax. The vapors reportedly decreased the relaxation time and increased the magnitude of the volume polarization.  

Many of the recent electret papers are concerned with "radioelectrets," which are formed by irradiating the dielectric in an electric field with high-energy beta or gamma radiation. The pioneering paper is from the Brazilian group

Murphy, Costa Ribeiro, Milanez, and de Moraes.\textsuperscript{37} Two years earlier Wolfson and Dyment\textsuperscript{38} had investigated the discharge of electrets by gamma radiation, but not the formation of electrets by this procedure.

Gubkin and Matsonashvili\textsuperscript{39} presented some more data on carnauba wax electrets in 1962, and summarized the present ideas about the persistent polarization. The displacement of electrons and their capture in "traps" is postulated as a mechanism for the heterocharge.

X-rays were used to study orientations at the electrodes when electrets were made of cetyl alcohol in an experiment by Chandy.\textsuperscript{40} He reports preferred orientations but no homocharge.

O'Konski and Bergmann\textsuperscript{41} reported a new electro-optic effect in 1962. They report a shift in color of aqueous methylene blue-montmorillonite complexes in the presence of an electric field. They call this effect "electrometachromism.'


\textsuperscript{40} K. C. Chandy, \textit{Naturwissenschaften}, XLIX (1962), 102.

Although the paper has nothing to do with electrets, this author feels that such an effect may be useful in the future to measure electret fields within transparent electret.

In a most recent development Bhatnagar has reported the production of electrets by magnetic instead of electric fields. In a paper commenting on this report Mathews and Peterson suggest a mechanism. They suggest that heating produces paramagnetism (by free radicals or otherwise) which disappears on cooling, leaving a residue of co-oriented electric polarization. These authors seemed unaware of the note by Chatterjee and Sutradhar reporting paramagnetism in carnauba wax subsequent to its polarization. Although the production of such magnetoelectrets, and even the presence of paramagnetism in electrets, remains unconfirmed by other experimenters, such effects are not impossible. In 1956 McMahon reported that strong magnetic fields affected the dielectric constant change which is observed during the liquid-solid phase change. However, McMahon was not using

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carnauba wax, but 3,4,5,-trichloro-o-xylene and nitrowax.

The wealth of data which electret theories must explain is indeed staggering. Unfortunately, there is little standardization of the procedures used to form or to measure the electrets, so that it is difficult to correlate one effect with another.
CHAPTER II

THE VARIABLES AND THE PROBLEM

For a number of reasons, progress in electret research has been relatively slow compared with that in other fields of solid-state physics. First, work of a quantitative nature with static electric fields is notoriously difficult. Frictional static charges on surfaces, discharge of potentials via the surrounding atmosphere, and complicating surface phenomena are some of the discouraging aspects of such work. Another factor has been that the best electret materials, the classical electrets so to speak, have been carnauba wax and various wax mixtures. These are complicated mixtures of substances, with which one cannot easily work and which are not easily reproduced. Electrets have never found many really good applications, since electric fields are so reliably attainable by other means; this lack of application has probably slowed progress in the field.

The major deterrent to electret research, in the opinion of this author, has been the absence of a clear statement of the variables which must be studied or controlled, and the absence of a terminology for describing these variables. Only by extensive searching of the
literature and complete analysis of the history of electrets can one make intelligent choices of either the conditions best suited for electret formation or the possible variables which must be controlled. Considering this state of affairs, it seems profitable to devote a chapter to clarifying the problem and defining and naming these variables.

The variables are conveniently subdivided into three categories: variables of composition and construction, variables of formation, and variables of measurement. They will be discussed in this order.

A. Variables of composition and construction

The choice of an electret material will depend upon the object of the research, of course, but several guidelines can be given. Carnauba wax itself has become a standard reference substance in electret work, not because it is well suited to be a standard, but because there is a great amount of data on its electret properties with which the performance of other electrets can be compared. Its disadvantages are: its complicated chemical composition; its brittle nature--it is easily cracked or chipped; its large thermal coefficient of expansion (and contraction)

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1Formation is used here to mean the techniques by which a semi-permanent polarization is imparted to the dielectric material.
which makes it difficult to mold; its opacity (which largely rules out spectroscopic studies); and its heterogeneity of crystal structure. Despite all these disadvantages one can hardly choose another standard electret substance without doubts as to whether the mechanism for the phenomenon might be different in this new substance. When electret mechanisms have become clearer, and when one can categorize the different materials as to the mechanism by which they acquire their electret properties, then more suitable standard substances can be chosen.

The plastics, such as polyvinyl acetate, poly(methylmethacrylate), and similar substances have been used as electret materials. They are easily machined to the required shape and are good dielectrics. It is not yet definite that their mechanism of electret formation is similar to that of the carnauba wax electrets, but data collected so far indicates that the mechanisms are similar. If so, one of these may become the standard electret substance in the future.

Another completely uninvestigated possibility is the use of ionomers as electrets. Ionomers are a new type of polymer recently announced by the E. I. du Pont de Nemours Company.² In these polymers the cross-linking is provided

by ionic bonds instead of covalent ones. Although stronger than normal polymers, ionomers are transparent and should possess interesting dielectric properties.

The titanates have been extensively used by the Russians to form electrets. These inorganic electrets are sufficiently different from those made from carnauba wax to suggest the hypothesis that they operate by a different mechanism.

To the chemist it seems reasonable to try a great variety of pure substances as electrets. Whole series of organic compounds suggest themselves, as well as certain inorganic compounds. However, many of these are not practical electret substances because of the physical consistency of their polycrystalline solid form. Masses of fine crystals of some compound would exhibit more surface phenomena than volume polarization. Single crystals of these substances would make interesting electrets, but no work of this kind has been reported. Another possibility is the solution of certain compounds in a binder material which will provide the necessary physical consistency.

The melting point of the substance is of practical importance in the choice of thermal electret material, since the heating process is necessary. If room temperature

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is to serve as the lower of the two temperature limits, the substance must have a melting point appreciably above room temperature for successful electret formation. This point is further discussed in the next section on variables of formation.

The method used for shaping the electret and planing its surfaces also is to be considered along with the material used. If the hardness of the material will permit it, machining of the electret to a desired shape is probably best. In the case of carnauba wax this can be done, but its brittleness discourages this technique. Molding the electret to a desired shape is possible, and probably gives a different sub-surface crystalline structure than machining. A combination of molding and surface polishing was used for the carnauba wax electrets in this research.

B. Variables of Formation

There are at least four distinct techniques which can form electrets. They are:

1. heat treatment during field application--thermo-electrets;

2. light treatment during field application--photo-electrets;

3. exposure to high energy radiation, such as \( \gamma \)-radiation, during field application--radioelectrets;
4. Electric field application alone—no general name other than persistent polarization.

This work is concerned primarily with thermoelectrets, and the other methods will not be discussed. The formation technique within the area of thermoelectrets contains the following variables:

**Applied field.** The electric field applied during formation of the electret is normally a d.c. field. Voltages of 100 to 20,000 volts have been used per centimeter of electret material. Low fields (0-3000 volts/cm) in general produce heterocharges only. Higher fields may produce both heterocharges and homocharges, or only homocharges, depending upon the material used. In fact the 3000 v/cm limit applies to carnauba wax and is probably not applicable in general to other substances.

A d.c. field with a superimposed a.c. component has been used. Very little is known about the effect of the a.c. component. Conceivably a.c. fields without a d.c. component, or waveshapes other than sinusoidal, could be used, but theory at present cannot predict the results of such experiments.

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4See Chapter V under "constant temperature polarization."

Temperature change. The upper and lower temperature limits of the formation program, and their difference, are important variables. No systematic study of the dependence of frozen-in charge on $\Delta T$ has been reported. Indications are that larger $\Delta T$ values produce larger electret effects, other things being equal. A low temperature lower than room temperature multiplies the experimental difficulties of charge measurement.

Exposure to high voltage prior to heating. There was no reason to believe that exposure to high voltage at room temperature would contribute to the subsequent electret effect which was frozen-in thermally. However, data obtained in this research contradict this view. Exposure to high voltage without heating can produce a polarization which can subsequently give a thermal discharge curve. This is a polarization that decays more rapidly than the normal frozen-in polarization. This observation indicates that pre-treatment exposure time can be a factor which affects the overall polarization, and thus this time should be kept constant.

Heating time. The rapidity with which the oven heats the electret material from the low to the high temperature is an important variable. It is controlled in most work by the design of the oven. The heating is customarily done
as rapidly as possible. It is not difficult to keep this variable constant, but it is difficult to cause it to be similar to that in someone else's work. Also, the thermal conductivity of carnauba wax is so low that the time recorded for heating the oven itself may not be the time for heating the interior of the wax. Whether or not heating time has a significant effect on the final frozen-in charge is not known. No systematic investigations of this variable have been reported.

**High temperature exposure time.** Probably there is a minimum time during which an electret should be maintained at the high temperature. Most experimenters seem to feel that after several hours of exposure the cooling should begin. Further exposure to the high temperature is not thought to be effective. Apparently some sort of saturation phenomenon or steady-state condition is envisioned which makes longer exposure unnecessary. There is no real evidence one way or the other, and this author chose a four hour exposure time rather arbitrarily.

**Cooling time.** The rapidity with which the sample is cooled is also a function of the oven geometry in most cases, since cooling is usually accomplished as rapidly as possible. Once again there is very little data on the relationship of this variable to the frozen-in charge.
**Holding time.** After cooling, the electret remains for some time at the low temperature, polarized and still under the influence of the applied field. The question can be raised as to whether an electret "keeps" better stored in this way or stored short-circuited. This holding time probably has little effect because the conditions are similar to the exposure to high voltage before heating. Without definite evidence to support these speculations one should hold this time constant also whenever possible.

**Storage time.** During storage electrets are almost invariably short-circuited. This treatment theoretically reduces the internal field to a minimum and allows the electrets to retain their charge for long periods of time. There is considerable evidence to support this theory. Electrets do maintain their frozen-in polarization best when stored short-circuited. Short-circuited heterocharges can slowly decay and storage time should be considered to be a variable affecting subsequent measurements.

C. **Variables of Measurement**

The measuring process itself introduces many variables into the problem. It is relatively easy to measure the time rate of change of charge on the electret, but it is very difficult to measure its actual charge. The measuring techniques are discussed in the next chapter, but it can
be pointed out that there is only one very reliable technique, and it disturbs conditions within the electret least before the measuring process begins. This technique consists of storing the shorted electret until it is connected to the electrometer through which it is discharged thermally (Groetzinger method). Unfortunately this method requires reheating for measurement of the frozen-in charge, unpolarizes the electret, and destroys the property being measured.

What is needed is a technique for measuring the extent of polarization in the sample by a non-destructive technique which can be accomplished without ever removing the shorting electrodes. Such a technique, although not yet discovered, is very possible and some possibilities are proposed in Chapter VI.

Certainly once the electrodes are removed the electret is never again the same because counter charges are collected from the atmosphere.

Out of this maze of variables the experimenter is required to choose only a few to manipulate. The others must remain constant throughout the research. Since it was desired to learn as much as possible about the mechanism of the heterocharge without the interference of the homocharge, the applied field was more or less dictated. A field of 1000 volts per 0.6 centimeter or about 1700 volts/cm was chosen and used throughout the investigation.
It was thought that insight into the problem, "what is the mechanism of the heterocharge in carnauba wax electrets?", could be gained by the following procedure:

1. Develop techniques to measure and characterize carnauba wax electrets.

2. Take sufficient data on carnauba wax electrets to demonstrate reproducibility.

3. Add selected solutes to the carnauba wax to find out what general type of solute molecule contributes to the heterocharge magnitude, and what solutes discourage the formation of heterocharge.

The composition of carnauba wax is known within certain limits. The major components of the wax are alkyl esters of wax acids, 84-85% by weight. Free acids and alcohols are also present in small percentages. Acids of carbon chain length C\(_{18}\) to C\(_{30}\) are present to the extent of 3-3.5%. The alcohols are C\(_{24}\) to C\(_{34}\) chains, some of which are polyhydroxyl alcohols, and which are present to the extent of 2-3%. Lactides are also present, 2-3%. The remainder of the analysis is: acid-soluble resins, 4-6%; hydrocarbons, 1.5-3%; and moisture and mineral matter, 0.5-1%.

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In view of this analysis a choice of solutes with which to vary the carnauba wax was made. A long-chain acid, a long-chain alcohol, and a long-chain ester were chosen. It was thought that if the acid contributed most to the heterocharge effect one could conclude that ionic conductance was an important factor. It seemed logical to suppose that the free acid molecules would contribute most to the conductivity of the wax, or more precisely, that their solvolysis products would. If both alcohol and acid molecules enhanced the heterocharge one might conclude that the presence of any polar group was the important factor rather than ionization. In this case the added ester should also slightly enhance the effect.

The effect of all these added solutes on the heterocharge decay rate might be further indication of the mechanism. If the acid enrichment resulted in faster decay rates, but the alcohol and ester enrichment did not, then the assumption of acid ionization would be further verified. If all three solutes had no effect on the decay time of the heterocharge one could conclude that either none of these solutes were ionogens in carnauba wax, or that ion conduction was not the mechanism responsible for the heterocharge decay.

This then was the basic plan of the research. As so often happens in relatively unexplored areas there came
to light during the investigation several new phenomena which influenced the interpretation of the data. What these phenomena were, and how their presence was interpreted will be explained in Chapter VI.
CHAPTER III

INSTRUMENTATION FOR ELECTRETS

An open-circuited electret possesses an internal field which results in its decay and an external field which can be directly measured. A short-circuited electret possesses very little field within the body of the electret, no field outside the electret, and intense fields at the dielectric-electrode interfaces. The problem of measuring the electrets' extent of polarization can be approached by attempting to measure:

1. the interfacial field of a short-circuited electret;
2. the external field of an open-circuited electret;
3. the charging current while the electret forms;
4. the discharging current while the electret decays;
5. or some property of the electret material which can be shown to be related to the electret phenomenon.

A. The Lifted Electrode Method

Eguchi measured the interfacial fields of short-circuited electrets.\(^1\) He measured the induced charge on a

\(^1\)M. Eguchi, Phil. Mag., XLIX (1925), 178.
grounded metallic plate that was placed upon the upper electret surface. The opposite side of the electret was always grounded. The plate was connected to an electrometer and a condenser of known capacity. After ungrounding the plate on the electret, this plate was lifted by a string and pulley mechanism to a height, "...such that the influence of the dielectric was no longer sensible," and the voltage on the electrometer was read on a calibrated scale. The surface charge was taken as \( \sigma = CV/4\pi r^2 \).

This lifted electrode method has the advantage of being simple and straightforward; it requires little equipment other than a good electrometer. It has the disadvantages of exposing the surface of the electret during the measurement and of possibly introducing frictional charges during the motion of the electrode.

This author tried a lifted electrode apparatus of simple design. Because an available quartz fiber electrometer could not be made to function, a General Radio type 1230-A electrometer was used. The electret was enclosed in a steel box, a brass electrode on its surface was lifted by means of a solenoid operated by 110 volts a.c., and the induced voltage was read on the electrometer scales. The input resistance of the electrometer could be varied, but was usually \( 10^{11} \) ohms. The method was judged unsatisfactory because the finite load resistance of the electrometer
immediately began draining away the charge across the 1 mfd. capacitor and the peak reading on the voltmeter was determined, at least in part, by the ballistics of the meter movement and not solely by the induced charge on the electrode.

Gross designed a "dissectible capacitor"\(^2\) which was in essence a lifted electrode apparatus. Although he obtained surface charge data he found the thermal discharge current measurements to be more reliable and apparently abandoned this technique.

B. The Vibrating Electrode Method

The use of a vibrating electrode to measure an electric field, or field gradient, is not new. This method was applied to electret field measurement by Freedman and Rosenthal\(^3\) in 1950. Their apparatus is a simple solenoid within which a plunger vibrates at 120 cycles per second. An electrode on the end of this plunger is suspended above the electret surface. Their instrument is practical for recording changes in the field with time, but cannot measure the field nor can it distinguish which polarity the field has.

Physicists have long used a method called the "Zisman method" for measuring contact potentials and work functions

which is essentially a vibrating electrode technique. A study of Zisman methods and field mills suggested that a circuit such as that diagrammed in Figure 1 would be applicable to electrets.

In this circuit $E_c$ represents the electret field voltage, $E_p$ the applied compensating voltage, and $E_o$ the output signal. $M$ is some mechanical means for oscillating the electrode at an audio rate. Without $E_p$ the following circuit analysis is valid:

$$Q = C_0E$$
$$i = \frac{dQ}{dt} = E_c \frac{dC_0}{dt} + C_0 \frac{dE_c}{dt}$$

If $E_c$ is a constant:

$$i = E_c \frac{\partial C_0}{\partial t}.$$  

Now $C = C_0(1 - \delta/d \sin \omega t)$ if $\delta \ll d$, which is the case. Thus

$$i = E_c \frac{dC_0}{dt} = -E_c \omega C_0 \frac{\delta}{d} \cos \omega t ,$$

and if $R \ll l/C$:

$$E_o = -E_c \omega C_0 \frac{\delta}{d} \cos \omega t .$$

In an instrument of this type the output signal is not only a function of $E_c$, but also of $\omega$ (the frequency), and $\delta/d$ (the amplitude of the mechanical vibration). This is

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Figure 1. Circuit of a Field Mill
similar to Freedman's and Rosenthal's apparatus described above.

If \( E_0 \) is reduced to zero by adding \( E_p \) until \( E_p = -E_c \) (null method), then \( E_c \) is measured without the mechanical and frequency variables entering.

Such a null method seemed ideal for electret measurements, and a similar apparatus was constructed. It did not prove satisfactory. It was discovered that in the case of electrets the impressed voltage \( E_p \) would repolarize the electret in such a manner that one could not find an \( E_p \) which would null the apparatus. The measuring process introduced a short time constant polarization into the electret material and changed its field during the measurement process.

The solution to this problem was suggested to this author by Dr. Lloyd W. Morris, Professor of Physics, Louisiana State University. Dr. Morris suggested introducing a third electrode above the vibrating electrode, to which the counter potential would be applied. The vibrating electrode would then shield the electret from the applied counter potential. A diagram of the three electrode system is given in Figure 2. This system worked very well and was used in field measurements in this work. A more complete representation of the apparatus appears in Figure 3.
Figure 2. The Three Electrode System

- Audio oscillator
- Electret
- Sweep box
- 0-±1000V d.c. supply
- Oscilloscope
- 8\" speaker
Figure 3. Vibrating Electrode Apparatus
The counter potential was supplied to the third electrode by a Keithley model 240 regulated d.c. supply. This supply will provide 0 to ±1000 volts in one-volt steps. It was ideal for this application because of its high stability and easy readability. No voltmeters were required.

The mechanical device chosen to vibrate the electrode was an eight inch Norelco permanent magnet speaker which was mounted on top of the oven. A balsa wood suspension from the inner small speaker cone held the vibrating electrode, and the speaker was fed an 80 c.p.s. signal from an audio oscillator. The unbalance signal induced in the vibrating electrode was connected via a flexible wire, and then coaxial cables, to the vertical input of a Tektronix type 53E/54E high sensitivity preamplifier in a type 531 oscilloscope.

The audio oscillator also provided 80 c.p.s. to the sweep box whose circuit is shown in Figure 4a. The purpose of this circuit was to allow adjustment of the phase of this signal before it was fed to the horizontal input of the oscilloscope. Figure 2 illustrates these connections clearly.

When the vibrating electrode apparatus was being used to measure an electret the pattern on the oscilloscope was an ellipse. Theoretically it should have been an ellipse which closed to a horizontal line when the counter potential was adjusted to balance the field of the electret. However,
because the mass of the vibrating electrode suspension could not exactly follow the sine curve variation of the applied 80 c.p.s. signal there was a non-sinusoidal vertical signal whose second harmonic component was sufficient to cause the balance condition to be other than a straight line. The selectable frequency response of the Tektronix preamplifier permitted control of this harmonic content in the vertical signal, and with the vertical response set at 80 c.p.s. to 250 c.p.s., the balance condition pattern was a figure eight. Sketches of the balance signals are shown in Figure 4b.

Since this technique for measuring the surface charge requires exposing the electret surface, the electret and its associated electrodes were enclosed in a controlled atmosphere environment. In this research this requirement was met by placing the electret and electrodes within a small oven. The speaker was mounted on top of the oven, and the oven placed inside a large glove-box of Plexiglas. All the connections to the oven were cabled through the sides of the glove-box by appropriate electrical connectors, and the box was filled with a dry nitrogen atmosphere, the drying agent being phosphorus pentoxide.

Figure 5a is a photograph taken through the glove-box wall with the oven door open. The electret can be seen resting on the foil-covered ground plate. The vibrating
Figure 4a. Sweep Box Circuit

4b. Oscilloscope Patterns
electrode is just above the electret, and the third electrode is visible above it. Figure 5b shows the normal operating condition with the oven door closed. The power supplies, thermistor thermometer and sweep box are on top of the glove-box. The electrometer is to the right.

Figure 6a shows the complete experimental arrangement including the recorder and oscilloscope. In this picture the audio oscillator is the instrument at the upper left. In Figure 6b the two knobs seen above the recorder are used to adjust the recorder span to correspond to the electrometer output.

C. Charging and Discharging Currents

Charging currents. Charging currents during the polarization process have been measured.\(^6\) The shape of such current-time plots depends upon the oven program and oven characteristics, but presumably the area under such curves could be correlated with the total charge within the electret. One major difficulty is that such current measurements are made during the heating process when the conductivity of the wax is highest and the storage of charge is superimposed over a conduction of charge through the electret material. No detailed study has been made of

Figure 5. Photographs of Oven
Figure 6. Photographs of Equipment
this technique. Most experimenters have preferred to make their non-isothermal current measurements without the presence of the polarizing power supply, i.e., to measure the discharge current rather than the charging current.

A short-circuited electret at room temperature does not exhibit a measurable discharge current because it is not discharging. Assuming that the short-circuiting electrodes fit closely, the internal field of the electret is too small for decay to proceed at a detectable rate. There are two basic techniques by which the electret may be caused to discharge so that the discharge current may be measured. One method is isothermal, the other non-isothermal.

Adams' method. In Chapter I the work of E. P. Adams was mentioned. Adams was one of the pioneers in electret research, and his experiments were well-conducted with an interesting and novel measuring technique. This technique was essentially the observation of the change of charge on the electrode covering an electret surface after the electrode was ungrounded and insulated from everything but the electret. The other electrode of the electret was grounded.

Adams' electrets were cylindrical in shape. Three electrodes were involved in his formation and measurement

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technique. Figure 7 is a diagram intended to represent the Adams' method. His electrets were formed at 16,000 v/cm and so exhibited both heterocharges and homocharges. They were polarized from the melt using the inner and outer cylindrical electrodes. The electrets were short-circuited while they were stored. To make a measurement Adams inserted the measuring electrode, which was connected to an electrometer, and then observed the charge on this electrode when the inner concentric electrode was ungrounded. He observed the charge to rise from zero to some value, which then remained unchanged for long periods. Adams' experiments included observations at different temperatures, and he found that the charge increased more rapidly at higher temperatures, and that the final value of the charge observed after 30 minutes was greater at the higher temperatures.

Although it has never been suggested in the literature, it is this author's opinion that Adams misinterpreted his data. He was of the opinion that the rise of charge to a maximum represented a conductivity-controlled charge development and that the maximum was the true polarization charge on the electret. Thus he tried to observe the decay of the electret polarization by observing the change in these maxima over long periods of time (35 days). His data indicated that the polarization decay must have an exponential time constant of about 5000 hours, although he readily
cross section:
geometry is cylindrical.

Figure 7. Adams' Method
admitted that the decay was far from exponential. The charge development process itself he attributed to the "volume and surface conductivities of the electret," and he roughly estimated an average time constant for this decay of 0.22 hours, again explaining that the data did not correspond to a simple exponential decay. At the time it was not understood that short-circuiting the electret reduced the internal field to nearly zero, and in effect concentrated the field at the electrode-material interfaces.

Now, thirty-eight years later, it seems likely that Adams' short time constant charge buildup was the heterocharge decay itself, and the longer time constant data was another aspect of this same decay. This author took field data in many ways similar to Adams, and the interpretation of his data from a more modern viewpoint appears in the next chapter on phenomenological theories.

**Groetzinger's method--thermal discharge curves.** Frei and Groetzinger were originators of the non-isothermal discharge current technique by which much of the later electret work has been done. The extreme simplicity of this technique, combined with the fact that the electret surfaces are never exposed to external counter charges,
is responsible for its wide acceptance and reliability as a measure of the frozen-in charge.

The technique consists of reheating the electret while it is connected to an electrometer that has a finite and known input resistance. The heating hastens the decay of the internal polarization so that the induced charges on the electrodes flow through the external resistance and are recorded as a thermal discharge current. If a plot is made of discharge current versus time the area under this curve is the frozen-in charge, a fact well verified by Gross and coworkers.\(^\text{10}\)

A General Radio type 1230-A d.c. amplifier and electrometer were used in this research. An input resistance of \(10^{11}\) ohms was selected and used throughout the investigations. The method is so simple that the only precautions which must be taken are (1) to keep the connecting leads to the electrometer as short as possible and shielded; (2) to avoid metal-metal junction potentials which might thermally generate spurious responses, and (3) to eliminate switches or other complicating factors from the circuit. Anything else in the circuit, although it may add to convenience of operation, will provide unwanted shunt resistance paths around the electrometer input. The maximum

temperature during the heating process must be less than the melting temperature of the wax in order to minimize current losses through the electret material itself.

In a thermal discharge plot the current rises to a maximum quite rapidly, stays there a short time, and then gradually decreases over many hours to zero. The exact shape of the thermal discharge curve, or TDC, as this author has come to call it, is determined by the oven program and characteristics. However, with these factors fixed the current maxima may be compared between similar electrets as an approximate indication of the relative areas under the curves.

If an electrometer is not available for electret research, it is possible that a pH meter might be used. This idea was tested during the course of this work. It was found that a Beckman Zeromatic pH meter was unsuitable for measuring discharge currents, even though operated on the millivolt ranges. This is probably due to the periodic restandardizing circuit found in this instrument.

It was found that a Beckman model H2 pH meter would give discharge current readings of about twice the voltage value as that of the General Radio Electrometer. Since the General Radio instrument was set on $10^{11}$ ohms input resistance, this implies that the input resistance of the H2 is about $2 \times 10^{11}$ ohms, a good value for electret work.
However, it was found that the H2 responded much slower to changes in the voltage and required much longer to reach an equilibrium value when connected.

This slow response, along with the lack of voltage range selection, indicates that simple pH meters would not be as useful as the General Radio Electrometer for such purposes. It is possible that some of the newer recording pH meters might be more suitable.

Perhaps it should be mentioned that other methods than heating have been used to hasten the depolarization process. F. Gutman used ultrasonic waves\textsuperscript{11} of about 700 kilocycles. Groetzinger and Kretsch\textsuperscript{12} used a strong radio frequency field to depolarize the electret. The frequency was about 60 megacycles, and the depolarization was not caused by dielectric heating.

D. Other Techniques

There are several properties of the electret material which, it would seem, might be altered by its state of electrification and thus become available as indicators of the electret phenomenon. Some of these are thermal conductivity, dielectric constant, magnetic properties, and, for transparent electrets, spectroscopic absorption bands and

\textsuperscript{11} F. Gutman, Revs. Mod. Physics, XX (1948), 463.
\textsuperscript{12} G. Groetzinger and H. Kretsch, Z. Physik., CIII (1936), 337.
optical anisotropy.

Groetzinger\textsuperscript{13} reported that the thermal conductivity was greater in the polarization direction for thermoelectrets. This observation and the attempts to observe a dielectric constant change have been mentioned in Chapter I. If Bhadra's and Chatterjee's experiments\textsuperscript{14} could be repeated this method would serve as a convenient technique. Unfortunately efforts to repeat this experiment have all failed. In Chapter V an attempt to measure dielectric constant change is reported by this author; the results were negative. Gerson and Rohrbaugh\textsuperscript{15} observed dielectric constant changes only for electrets above 50° Centigrade; the effects were small.

Chatterjee and Sutradhar\textsuperscript{16} reported that the magnetic susceptibility of carnauba wax was changed by its polarization, that the carnauba wax in fact became paramagnetic, and that it then slowly reverted to its diamagnetic state in about 30 days. The effect, if verified, would not only be a significant technique for monitoring electret behavior,

\textsuperscript{16}S. D. Chatterjee and N. G. Sutradhar, Note in \textit{Die Naturwissenschaften}, XLII (1955), 366.
but it would have important implications about the formation mechanism. It is not clear if these workers worked with heterocharges or homocharges or both.

This author knows of no work on the electret effect on spectroscopic absorption bands in transparent electrets. K. V. Fillippova reported that poly(methylmethacrylate) electrets developed an optical anisotropy upon polarization. More data must be obtained before any conclusions about this method are drawn. Certainly optical interactions would seem to be ideal tools for investigation of the electret state.

CHAPTER IV

PHENOMENOLOGICAL THEORIES

Since phenomenological theories are essentially descriptions of the behavior of the field and charge distributions around and within electrets as deduced from well known laws of electrostatics, one might conclude that there would be only one phenomenological theory. There are in the literature, however, three phenomenological electret theories which differ from each other in certain respects. The differences arise from differences in basic assumptions about the time-dependence of the heterocharge polarization, and differences in interpretation of the effect of the presence of conducting coatings on electret surfaces.

The three theories are Adams' theory, first proposed in 1927, Swann's theory published in 1950, and Gubkin's theory which appeared in 1957. Let it be understood that these are not hypotheses as to the mechanism of the heterocharge or the homocharge. They are simply deductions of

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1E. P. Adams, J. Franklin Inst., CCIV (1927), 469.
what electrical effects must follow if (1) the heterocharge is a semi-permanent volume polarization that is independent of the conductivity of the wax, and (2) the homocharge is a real charge layer either within or on the exterior of the dielectric substance which decays by ionic conduction either in the surrounding air or in the wax or both.

These three theories will not be restated here because of their general availability in the original sources. However, since an understanding of the basic problems of electret behavior is difficult to attain by reading the literature, an attempt will be made in this chapter to contrast the three theories and explain the relative applicability of each.

A. Adams' Theory

Adams assumed that the polarization (heterocharge) obeyed a first order decay scheme. He assumed $\frac{dP}{dt} = -\alpha P$ where $\alpha$ is a temperature-dependent constant.

Since his electrets were covered with metallic electrodes, even during measurement of their external field, he recognized that the polarization would be partially neutralized by compensating counter charges, $\sigma$, at the surface of the electret. Then $\sigma - P = \eta$ where $\eta$ is the free (uncompensated) charge on the surface.

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4 Adams, loc. cit.
It follows that
\[ \frac{d\eta}{dt} = \frac{d\sigma}{dt} - \frac{dP}{dt}. \]
When the electrodes are short-circuited \( \eta = 0 \). When the short is removed \( \eta \) becomes non-zero and changes with time. Here is where Adams introduced an error into his theory. He assumed that the change of \( \eta \) with time was due to conductivity through and along the surfaces of the electret. The situation described is illustrated in Figure 8.

It has since been shown⁵ that under the conditions shown (short-circuited) the field within the electret is zero, or nearly so. Thus there should be no conductivity through the electret. A modern viewpoint would be that the increase of charge when the short is removed is due to decay of the polarization (heterocharge), leaving the uncompensated induced charge on the electrodes.

Proceeding upon his assumptions Adams put \( d\sigma/dt = -\beta \eta \) in which \( \beta \) is a coefficient the reciprocal of which is the relaxation time of the electret when it is regarded as a condenser; \( \beta \) depends upon the volume and surface conductivities of the electret as well as upon its dielectric constant.

Figure 8. Charges in Adams' Theory
From the differential equation

\[ \frac{dn}{dt} + \beta \eta = \lambda P_0 e^{-\lambda t} \]  \hspace{1cm} (1)

Adams deduced the time dependence of \( \eta \):

\[ \eta = \frac{\lambda P_0}{\beta - \lambda} (e^{-\lambda t} - e^{-\beta t}) \]

He then assumed \( \lambda \) very small compared to \( \beta \). Probably the reverse assumption would have been better. His result was then, for small values of \( t \):

\[ \eta = \frac{\lambda P_0}{\beta} (1 - e^{-\beta t}) \], \hspace{1cm} (2)

but the opposite assumption would have resulted in the same mathematical form, with \( \lambda \) replacing \( \beta \).

From the condition \( \eta = 0 \) when \( t = 0 \), and equation (1), it follows that the initial slope \( (d\eta/dt)_0 \) would be a measure of \( \lambda P_0 \). From equation (2) one can find

\[ \frac{dn}{dt} = \lambda P_0 e^{-\beta t} \],

whereupon a plot of \( \ln(d\eta/dt) \) versus \( t \) should give a straight line of slope \(-\beta\). Adams found that the plot did not give a straight line, and that the initial slope increased rapidly with temperature.

B. Swann's Theory

W. F. G. Swann published his electret theory from 1950 to 1953. By this time there was a great deal more

\[ {^6}Swann, \textit{loc. cit.} \]
understanding of the electret phenomenon. Gross' work had clarified the heterocharge and homocharge concept, and a better choice of basic assumptions was made possible. Thus Swann recognized that the heterocharge was, "a polarization phenomenon or its equivalent," and that the homocharge was "a real charge of electricity which somehow or other, gets into the body of the dielectric during the formation of the electret." Unlike Adams, he supposed that the homocharge does not decay with time, or that if it does, it decays more slowly than the polarization associated with the heterocharge phenomenon.

One of Swann's contributions was the clarification of the role played by conducting surfaces affixed to the electret. He did this by distinguishing between three fields which are superimposed to cause the observable field outside the electret. These are:

1. the field due to the polarization;
2. the field due to the "real" homocharge;
3. the field due to any additional charges which have come to the plates in order to secure initial absence of potential difference between them (i.e., when shorted).

He called this third contribution the pseudo homocharge since it is indistinguishable from the imbedded homocharge as far as its external field effects are concerned. This concept of the pseudo homocharge, which is
really the induced charge on the attached conducting surfaces, is essential to understanding the behavior of electrets that are painted with Aquadag.

Swann's approach was quite general. He assumed a semi-permanent polarization $P_x$, the subscript restricting variation to the axis normal to the plates. He also assumed an induced polarization in an amount $(K - 1)E/4\pi$, where $K$ is the dielectric constant of the electret material.

He assumed a charge distribution (the real homocharge) which is only $x$-dependent and distributed in an arbitrary manner throughout the dielectric. Finally he assumed that real charges had come to the surfaces to produce the pseudo homocharge.

Without making any assumptions about the time dependence of the polarization or the homocharge, he showed that the relationship of the potential difference between the plates and the various field sources was quite generally:

$$V_1 - V_2 = V = \frac{2\pi L}{K} \left[ \sigma_1 - \sigma_2 - \frac{2}{L} \int_0^L Pdx + \int_0^L \rho dx - \frac{2}{L} \int_0^L x\rho dx \right]$$

Here $L$ is the distance between the plates; $K$ is the dielectric constant; $\sigma_1$ and $\sigma_2$ are the surface charges; $P$ is the polarization, and $\rho$ is the volume charge.

The significance of the terms in this equation follows. The first two terms are those due to the surface charges, and if the other terms are zero the electret here reduces to a charged capacitor. The third term is the contribution
to $V$ from the heterocharge polarization and in opposition to $(\sigma_1 - \sigma_2)$ in the sense that it provides "fictitious" charges to maintain $\sigma_1$ and $\sigma_2$ when $V = 0$. The last two terms arise from the imbedded homocharge distribution, which has the same sign as the surface charges.

Swann then introduced time dependence into the homocharge and heterocharge. He assumed decay of the homocharge by ohmic conduction with a time constant $(RC)$ and decay of the heterocharge exponentially with a time constant $(1/\alpha)$. These assumptions transform the previous equation to:

$$V = \frac{4\pi \alpha RC}{(1 - RC\alpha)} \left[ e^{-\alpha t} - e^{-t/RC} \right] \int_0^t P_0 dx + V_0 e^{-t/RC},$$

which is obviously similar to Adams' equation, except for the integral in place of $P_0$, and except for the term $V_0 e^{-t/RC}$ which describes the decay of the heterocharge if at $t = 0$ $V_0$ is not zero, i.e., if the electret is removed from the polarizing voltage without short-circuiting.

If the time constant $RC$ is larger than $1/\alpha$ this equation describes a behavior similar to that of actual electrets made at high voltages. $V$ is originally negative (a minus $V_0$ means a heterocharge), decreases with time, passes through zero, mounts to a positive maximum (the homocharge) and decays eventually to zero. Differentiation of this equation to find the maximum shows that, if $V_0 = 0$:

$$V_m = \frac{4\pi}{K} \left( RC\alpha \right) \frac{1}{1 - RC\alpha} \int_0^1 P_0 dx,$$
which shows that the value $V_m$ is a measure of $P_o$ if $RC > 1/\alpha$.

Swann suggests that a parameter of interest is $\tau_2$, which he defines as the time required for $V$ to change from zero to its positive maximum $V_m$. He considers three cases:

1. Where $R = \infty$ the positive maximum is never reached but is approached asymptotically. Obviously $\tau_2 = \infty$, and he shows that for this case:

$$V_m = \frac{4\tau}{K} \int_0^l P_{ox} \, dx$$

2. Where $RC < 1/\alpha$ the maximum value is reached quickly and:

$$V_m = \frac{4\tau}{K} (RC \alpha) \int_0^l P_{ox} \, dx$$

$$\tau_2 = -RC \ln RC \alpha$$

3. Where $RC = 1/\alpha$:

$$V_m = \frac{4\tau}{Ke} \int_0^l P_{ox} \, dx$$

$$\tau_2 = 1/\alpha$$

Swann's theory is more nearly complete than that of Adams but again there arises the same question which Adams faced. Is the semi-constant polarization lifetime larger or smaller than the electrical conductivity time constant $RC$? Adams assumed it was much larger. Swann makes a similar assumption, choosing as $1/\alpha$ a value of $10^8$ seconds, or about three years. He calculates $RC$ to be roughly $2 \times 10^5$ seconds by using a value of specific resistance for
good paraffin wax of $10^{18}$ ohms/cm. Thus he thought $1/\alpha$ to be about 500 times the value of $RC$.

Swann also concerned himself with the variation of the external field of the electret with distance from the electret surface. He calculated that the field variation external to the electret and along its axis would be much less than had been reported. He explained the disagreement by pointing out that the approach of a metallic plate to the electret surface in order to measure its field will change the fields within and without the electret. In other words, the presence of the field-sensing electrode alters the external field considerably. This explanation is so simple and so important that it is reproduced here in its essentials.

Consider the situation diagrammed in Figure 9. Before the approach of $P$:

$$KF_{oc} = 4\pi \sigma_o$$

in which $F_{oc}$ is the field within the electret. After the approach of $P$ to a distance $\epsilon$ while connected to a large capacitance $C$:

$$\varepsilon F_P = hF_c$$

and

$$F_p + KF_c = 4\pi \sigma_o = KF_{oc}$$

so that

$$\frac{F_p}{F_{oc}} = \frac{Kh}{h + K\varepsilon}$$

or

$$F_p = \frac{4\pi \sigma_o h}{h + K\varepsilon}$$

or

$$F_p = \frac{h + K\varepsilon}{h + K\varepsilon}.$$ (3)
Figure 9. An Electret Approached by a Plate; Swann
Thus $F_p$ depends upon $\varepsilon$ inversely through this capacitance effect. Even more important is the fact that the condition $\varepsilon F_p = hF_c$ indicates that as $\varepsilon$ diminishes $F_c$ must also diminish. The field within the electret diminishes as it is shorted out.

C. Gubkin's Theory

A. N. Gubkin proposed in 1957 a phenomenological theory of electrets which is an improvement over Swann's. Gubkin offers these criticisms of Adams' and Swann's theories:

1. A free electret is considered, i.e., one stored without short-circuiting. Yet the carnauba wax electrets considered in Swann's theories were stored with short-circuiting.

2. In Swann's theory the electret lifetime is taken as $\tau = 1/\alpha = 3$ years, i.e., it is presupposed that the electret long retains a semi-constant polarization which in the main determines the electret effect. However, experiment shows that the heterocharge of an electret may fall to zero in a day or several days, being either completely discharged or changing in polarity.

Gubkin proceeds to demonstrate that, owing primarily to his neglect of the role of short-circuiting, Swann's theories...
theories do not properly predict $1/\alpha$ or $RC$. Although Swann realized that the approach of a conducting plate would decrease the field within the electret, as is shown by his comments on the measured external field, he neglected to take into account the decrease in internal field due to short-circuiting.

Gubkin first gives a more general and complete derivation of the relationships between fields within and without the electret to the distances between the electrodes and the surfaces. Consider Figure 10 in order to understand the symbols used.

One has\[ \varepsilon_2 E_2 - \varepsilon_1 E_1 = 4\pi \sigma_1 \]
\[ \varepsilon_3 E_3 - \varepsilon_2 E_2 = 4\pi \sigma_2 \]

Here $\varepsilon_1$ and $\varepsilon_3$ are the dielectric permittivities of the medium in the gaps between electrodes and electret, $\varepsilon_2$ is the permittivity of the electret material, $E_1$, $E_2$, $E_3$ are the fields in the corresponding regions. Of course, $\sigma_1$ and $\sigma_2$ are the surface charge densities.

\[ V = E_1 d_1 + E_2 L + E_3 d_2 \]

If $E_1 = E_3$ the above equations can be combined to yield:

\[ E_1 = \frac{-\frac{\varepsilon_2 V}{L} - 4\pi \sigma_1 - 4\pi \frac{\varepsilon_1 d_2}{L} \left( \sigma_1 + \sigma_2 \right) \varepsilon_1}{\varepsilon_1 \left[ \frac{\varepsilon_2 \left( \varepsilon_3 d_1 + \varepsilon_1 d_2 \right)}{L \varepsilon_3 \varepsilon_1} + 1 \right]} \]
Figure 10. Symbols Used by Gubkin
When $V = 0$, $\varepsilon_1 = \varepsilon_3 = \varepsilon_{\text{ext}}$, $\sigma_1 = \sigma_2 = \sigma$, $\varepsilon_2 = \varepsilon_{\text{int}}$

Then we get:

$$E_1 = E_{\text{ext}} = -\frac{4\pi \sigma}{\varepsilon_{\text{ext}} \left[ \frac{\varepsilon_{\text{int}} (d_1 + d_2)}{L \varepsilon_{\text{ext}}} + 1 \right]}$$

$$E_2 = E_{\text{int}} = \frac{4\pi \varepsilon_{\text{ext}} L (d_1 + d_2) \sigma}{\varepsilon_{\text{ext}} \left[ \frac{\varepsilon_{\text{int}} (d_1 + d_2)}{L \varepsilon_{\text{ext}}} + 1 \right]}$$

For a free electret $d_1/L = d_2/L \rightarrow \infty$

$$E_{\text{ext}} = -4\pi \varepsilon_1 (\sigma_1 + \sigma_2)$$

$$E_{\text{int}} = \frac{2\pi}{\varepsilon_{\text{int}}} (\sigma_1 - \sigma_2)$$

For an ideally short-circuited electret: $d_1/L = d_2/L \rightarrow 0$

$$E_{\text{ext}} = -\frac{4\pi \varepsilon_{\text{int}} \sigma_1}{\varepsilon_{\text{ext}}}$$

$$E_{\text{int}} = 0$$

Having shown how $E_{\text{int}}$ depends upon the degree of short-circuiting, Gubkin then derives expressions for the time dependence of the electret charge. He makes assumptions similar to Swann's, that is, exponential decay of polarization and conductivity-controlled decay of homocharge. However, he takes into account the fact that the field within the electret will affect the time constants of these
processes. In general he concludes that open-circuiting, thus allowing a large field within the electret, hastens the ohmic processes but slows the polarization decay. Shorting, on the other hand, since it reduces the internal field almost to zero, retards the ohmic processes and causes the RC time constant to be many years. According to his equations shorting also decreases $1/\alpha$, the time constant for the polarization. Thus shorting does not maintain heterocharge but diminishes it, keeping only the homocharge.

For example, Gubkin calculates for open-circuited electrets an electrical (ohmic) time constant of 10 hours and a $1/\alpha$ of greater than 300 years, but for short-circuited electrets where $d_1 = d_2 = 10^{-8}$ cm, the ohmic time constant is greater than 300 years and the $1/\alpha$ almost zero. For a reasonable intermediate case where $d_1 = d_2 = 0.001$ cm, he calculates the electrical time constant to be 3 days, the $1/\alpha$ 1.5 days.

D. Comments on the Theories

As will be apparent in the next chapter, the experimental work by this author supports Gubkin's theory. The heterocharge does decay rapidly. Its decay time does seem dependent upon the degree of short-circuiting. The extreme values for $1/\alpha$ for open-circuited electrets and ideally shorted ones seem unrealistic. This difficulty probably
arises from the approximate nature of several of the mathematical assumptions within the derivations. The lower limit of $1/\alpha$ is probably controlled by the presence of some activation energy barrier to the disorientation process, and the upper limit of $1/\alpha$ is too large because the derivation ignores the second law of thermodynamics. Mechanistic assumptions will have to enter before realistic open- and short-circuited polarization time constants are calculated.

Although the work reported here dealt only with heterocharged electrets, the coated electrets attained a pseudo homocharge by induction. After observing the behavior of many electrets it is difficult for this author to imagine how Adams, Swann, and Gubkin all thought an increase in homocharge could result from ohmic processes. It would seem that ohmic processes, either inside or outside the electret, would decrease the homocharge on the electret, unless the ohmic process represented a heterocharge decay. In this case it could increase the homocharge by leaving uncompensated homocharges on the electrodes, but the decay of the heterocharge is not considered ohmic, for if it were, the heterocharge and homocharge could not coexist. Thus there seems to be no doubt, even from the early data of Adams, that the heterocharge decays rapidly, and that only the homocharge can have a really long time constant, and this can be true only if electrets are stored short-circuited to decrease the internal field.
CHAPTER V

MATERIALS, METHODS AND DATA

In this chapter are presented the results of the experiments with a minimum of hypothesizing. It is hoped in this way to separate the data from the expectations. Also such an arrangement is chronologically correct as far as this author is concerned, since the data were taken almost entirely before the hypotheses offered in Chapter VI were evolved. Many of the experiments were performed on the basis of hypotheses which arose from misconceptions.

The original plan of attack on the problem was:

1. to learn to measure electret properties and to make them in a reproducible manner;

2. to characterize carnauba wax electrets as to surface charge and thermal discharge;

3. to perform similar experiments on electrets containing selected solutes.

It turned out that the first of these tasks was by far the most difficult, and as a result the second and third tasks were not as completely accomplished as one might desire.

The work, other than the development of the vibrating
electrode apparatus, falls into five categories: an attempt to repeat the dielectric constant measurements of Chatterjee and Bhadra; the discovery of the constant temperature polarization phenomenon, hereafter called CTP; the measurement of surface charges; the measurement of thermal discharge curves, hereafter called TDC; and the nuclear magnetic resonance experiment. They will be discussed in that order.

The carnauba wax used was Matheson, Coleman and Bell yellow carnauba wax; the melting range was 82-85 degrees Centigrade. Stearic acid used was C. P. grade from the Matheson Company; the n-octadecyl alcohol was obtained from Eastman Kodak.

A. Dielectric Constant Measurements

In an experiment already mentioned\(^1\) Chatterjee and Bhadra reported very large changes in the dielectric constant of carnauba wax shortly after it was polarized. In comparison with that of a similar unpolarized condenser they found an 18-percent change in the capacitance of a small fixed trimmer air condenser immersed in the molten wax, polarized and cooled. From the observed changes they suggested the presence of free electrons liberated from the polarized molecules during a state of high field perturbation. They also report a change of \(Q\), the loss

factor \( Q = L/(\omega CR) \). The importance of such a result to mechanism postulations for hetero- and homocharges made it desirable to repeat their experiment.

The plate spacing of a twin section air variable capacitor (Hammarlund) of approximately 140 picofarads for each section was measured. A travelling microscope micrometer was used to measure each of the 36 spacings on each half of the dual section condenser. The front section spacing averaged 0.371 mm., the rear section average was 0.390 mm.

The capacitor was mounted on a shelf in the glove box so as to be in a dry atmosphere. The glove box atmosphere was \( \text{N}_2 \) dried with \( \text{P}_2\text{O}_5 \). Fully meshed, the capacitor sections measured 158.5 pf. for the front section and 145.7 pf. for the rear section. The dissipation factor scale read 0.04 for each section. Readings were all made with a General Radio type 1610 capacitance bridge assembly, the connection of which had been cabled through the side of the glove box. The two stators were connected via a selector switch to the "hot" terminal of the bridge in order to make measurements upon the section desired. The rotors were grounded; the shield between the sections was connected to the guard circuit of the assembly. Thus there were no interactions between the sections.

The entire capacitor with its leads was immersed in molten carnauba wax and cooled overnight. The capacitor
and its wax were then remounted in the glove box and readings were taken of the capacitance of each section at a frequency of 1 Kc. Dissipation factor was also read from the bridge. The following day these readings were checked again and the assembly removed to the oven used for forming electrets.

The front stator was connected to +73.5 volts. With the rotor grounded this polarized the front section wax at a field of 2 KV/cm, similar to that in the fields used subsequently in this work. The rear stator was connected to +450 volts, which polarized it at about 11.5 KV/cm, a field strength equal to that which the Indians used. The entire assembly then went through the normal electret program in which the oven is held at 70° C. for four hours.

After polarization the assembly was remounted in the glove box and readings of capacitance and dissipation factor were continued for one month. During this time the room temperature was about 25° C., although it fluctuated a degree or so from day to day. As the data in Figures 12 and 13 indicate, readings were sometimes taken at frequencies other than 1 Kc.

Figure 11 shows the observed values of capacitance plotted for the 31 day observation period. The minor fluctuations are very probably due to room temperature fluctuations. On the sixth day, for example, the air
Figure 11. Capacitance of Polarized Wax at 1 Kc.
Figure 12. Dispersion of Capacitance
Figure L3. Dissipation Factor vs. Frequency

- before polarization
- after polarization

- rear section, 11.5 KV/cm
- front section, 2 KV/cm
conditioning was off and the temperature rose five degrees. There is a general trend downward in the capacitance values which amounts to about 3.5-percent during the month. This change may be caused by crystallinity changes as the wax ages.

Figure 12 shows the frequency dependence of the capacitance, Figure 13 the frequency dependence of the dissipation factor (d.f.). Taking d.f. as equivalent to $\varepsilon''$, and calculating $\varepsilon'$ by dividing the capacitance of the rear section by its capacitance without wax (146 pf.), a crude Cole-Cole plot can be made. Figure 14 shows the result, which does little except show that the relaxation time $\tau$, which is $1/\omega \max$ for such a plot, is certainly greater than $10^{-1}$ sec., and may be many seconds.

The calculated dielectric constant values range from 2.60 at 100 Kc. to 3.11 at 10 c.p.s., in agreement with literature values.\(^2\) Most authors have used 2.8, which is roughly the value at 1 Kc. In contrast to the observations of Chatterjee and Bhadra, almost no change in Q at 1 kilocycle was observed. However, a change of Q ($Q = L/d.f.$) is seen for 100 c.p.s. and 50 c.p.s. The dissipation factor was unreadable for 10 c.p.s.; it was off scale on the General Radio bridge.

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\(^2\)Fridkin and Zheludev, op. cit., p. 39.
B. Constant Temperature Polarization

Early in the research, when the vibrating electrode apparatus was being developed, it was observed that the carnauba wax was polarized by the application of field alone. An experimental arrangement similar to that of Figure 15 was used to study this phenomenon. The wax could be polarized for any desired length of time and at any voltage, then the upper electrode could be switched to the electrometer input. The result was always a large voltage (across $10^{11}$ ohms) which then decayed to zero in what appeared to be an exponential decay. At first it was thought that this was simply charge on the electrodes which remained from the polarization process, and that if the electret were first shorted that this charge would be drained away and the phenomenon would not then be observed.

The result did not support the hypothesis. Shorting before connecting the electrometer kept the deflection from being off-scale initially, but there was still a large voltage which the recorder detected very quickly and which decayed slowly as before. A typical peak reading under these conditions was about one volt, and the decay to zero required about $\frac{1}{4}$ hour or more.

If during the recording of this decaying current the electret was shorted momentarily the reading would fall to zero, of course, but regain its value when the short was
Figure 15. Experiment to Study CTP

Keithley Power Supply

General Radio Electrometer

Recorder
L. & N. Speedomax
removed, and the decay would proceed as before. Figure 16 shows a typical recording of this effect. A logarithmic plot of the readings versus time is not a straight line. In fact no simple function could be found to represent the data from the recorder.

These discoveries caused the author to reread the literature to seek mention of this effect, which seemingly every experimenter would have encountered. Only two definite references to the effect, which this author came to call the constant temperature polarization, or CTP, were found. Gross referred briefly to this effect, saying that the behavior of the time-dependent currents (isothermal charging and discharging) is explained by dielectric absorption and agrees with the conclusions of generally accepted theories of this effect. The theories to which he referred were: (a) hindered dipole orientation (Debye); (b) microscopical heterogeneity of structure (Maxwell-Wagner), a sort of ion-trap theory; and (c) ionic conduction that causes space charges (Jaffe). Gross apparently thought of the thermally produced heterocharge in electrets as the "freezing in" of this dielectric absorption in some unspecified manner.

The other reference was to the experiments of Gerson

Figure 16. Typical Recording of CTP Decay
and Rohrbaugh. They used a measurement of the discharge current through a $10^9$--$10^{12}$ ohm resistance as a measure of the electret effect and gave considerable data on discharge currents (isothermal, not TDC) for their electrets. They wrote the following statement about the CTP effect.

A piece of wax electrified at room temperature exhibits a long-lived discharge current which corresponds, as usual, to either a decreasing heterocharge or a growing homocharge. The initial discharge current from a piece of carnauba wax electrified at room temperature is about the same as that from a thermally treated electret made at the same voltage, but the discharge of the former falls off so rapidly that it is negligible after a few hours.\(^4\)

They go on to say that the fact that the discharge current observed here (low temperature polarization) is different for three electret thicknesses indicates that this effect is not due completely to a volume polarization.

These statements are difficult to understand because their data in the same paper\(^5\) show that for thermally treated and low temperature electrets made at the same field strength there is very little difference at all in the discharge curves. The thermal electret at 5 KV/cm approaches zero discharge current at 600 minutes after the voltage is terminated, and their comparable 5 KV/cm CTP


\(^5\) Ibid.
curve approaches zero at 500 minutes. Their discharge curves for CTP with different dielectric thicknesses are remarkably alike, not different as they claim. A conclusion opposite to theirs is indicated.

It appears that in the case of electrets made at low fields, such as those in this work, Gerson and Rohrbaugh's technique of measuring isothermal discharge currents would not show much, if anything, of the nature of the frozen-in charge. It would seem logical that the application of a short-duration high voltage at room temperature and subsequent recording of its CTP discharge would reveal the state of internal polarization of the wax. If so this would be an excellent, nondestructive way of measuring the internal polarization. However, all attempts to demonstrate such an effect failed. This author polarized carnauba wax thermally and then superimposed the CTP for various short exposure times (15 seconds to 15 minutes) on the charge of the thermal electret, but the CTP discharge on the recorder chart seemed the same for treated and untreated samples. This point will be further discussed in Chapter VI in the light of the hypotheses there proposed.

Perhaps it should be noted that the isothermal discharge current curves of Gerson and Rohrbaugh differ in shape from those obtained in this work. Gerson's plots show almost straight-line approaches to zero current,
whereas the results obtained with the General Radio electrometer and recorder combination used in this work, which in principle is the same arrangement as Gerson's, shows an asymptotic approach to zero.

One aspect of the CTP phenomenon was troublesome from the time of these early experiments with the electrometer to the conclusion of the research. This was the observation that only a short time was required to cause the constant temperature polarization (30 seconds was ample), but the CTP decay required a long time (approximately one hour). This result could not be due to an external RC circuit time constant caused by the $10^{11}$ ohm input resistance of the electrometer because, after shorting, the decay reappeared and continued to follow its previous behavior. It did not seem logical that the difference should be associated with the RC time constant which included the resistance of the electret ($10^{12}$ ohms) because (1) it was not exponential and (2) the charging time seemingly should equal the discharging time.

Many more data were taken on the CTP phenomenon, but these data will be incorporated into the next two sections on surface charges and thermal discharge curves, where the data can be conveniently compared with thermal electret data.
C. Surface Charges

Performance of the instrument. The vibrating electrode instrument for measuring surface charges has been described in Chapter III. It was necessary for most measurements to operate the oscilloscope preamplifier at a sensitivity of 1 millivolt per centimeter and at 80-250 c.p.s. response. External triggering of the oscilloscope was tried, but was found to be unnecessary.

The vibrating electrode was, for most experiments, at a distance of 0.05 inches from the third electrode, and the electret surface was normally an equal distance below it. Inches are used as a distance unit here because the micrometer screw which was used to raise and lower the electret to and from the vibrating electrode was calibrated in inches. One revolution of this micrometer was equivalent to 0.025 inches. This information is pertinent to the distance variation experiments which will be described later.

The sensitivity of the apparatus was all that could be desired. The surface charges were recorded as voltage on the third electrode necessary to null the instrument. When the instrument was operating properly these null voltages could be determined so precisely that the small knob on the Keithley power supply which varied its output voltage between the one-volt increments had to be calibrated. Null voltages were often recorded to four significant
figures. This measurement is indicative of the sensitivity and precision of the instrument. However, the voltage readings were so critically dependent upon the spacing of the electrodes that the significance of the absolute values of the voltages is in some doubt. Once the electret was positioned, the readings were very meaningful relative to each other, but it was difficult to compare one electret with another if the vibrating electrode had been removed and replaced during maintenance, or if the electret thickness varied slightly.

In order to form an uncoated electret the disc had to be raised by means of the micrometer to contact the vibrating electrode. Then when readings were to be taken it was lowered to its original position. Slight changes in the equilibrium position of the speaker cone and its suspended electrode could change the electrode spacings, as could any dimensional changes in the mechanism which held the third electrode in place.

An unplanned experiment served to demonstrate that the vibrating electrode acted as a good shield between the electret and the third electrode. One evening when it was intended that the +1000 volts be applied to the vibrating electrode (not vibrating, of course) to polarize the electret overnight, the potential was inadvertently applied to the third electrode instead. The electret the next morning
was not polarized at all; it had been shielded by the vibrating electrode which was effectively grounded through the oscilloscope input. This point is important, since it means that the decay time of the electret surface charge is not altered by the measuring process. Experiments in which the null voltage was left on between readings and then later turned off between readings also confirmed this fact.

Experiments were also performed which demonstrated that the surface charge on an uncoated electret was unchanged by the temporary placement of a grounded electrode over its surface. This implies that the surface charge is not easily transferred to a conductor; it is a bound charge.

Making the electrets. The electrets were formed by pouring the molten wax into molds. An electret mold consisted of a glass cylinder one centimeter in height of inside diameter 1 7/8 inches, or 4.65 centimeters. These rings of glass were cut from large glass tubing, outside diameter 2 inches.

To make an electret a smooth sheet of aluminum foil was spread on the laboratory bench, a ring was placed on this foil, and molten wax was poured into the mold until it stood higher than the edges of the mold. It was
 allowed to cool undisturbed. When cool the bottom of the electret was usually found to have undergone little shrinkage. Most of the contraction upon cooling took place at the top. The disc was removed from the mold, and its surfaces were planed in the following manner. An electric hot plate with a very nearly flat top was carefully covered with aluminum foil. It was heated to about 90° C. or just above the melting range of the wax. As the hot plate warmed it was desirable for the wax disc to warm with it. This prevented too large a temperature gradient in the wax during the surface polishing.

When the aluminum foil surface was hot enough, as indicated by the melting of the wax, the electret was held with the fingertips on the hot surface and the wax allowed to melt until the surface was completely molten; this usually took just a few seconds. Then the disc was slipped off the hot plate with a quick horizontal motion, leaving molten wax behind. As soon as the disc was removed from the hot surface it was flipped over and held with the just-polished surface up. This whole operation, sliding the disc and flipping it over, was a technique which required much practice, but resulted in smooth and nearly planar surfaces.

If the surface was not perfectly smooth the foil on the hot plate had to be wiped with a lint-free towel or
replaced before the operation was repeated. Molten wax on
the plate spoiled the flatness of the polished surface
because a minimum of molten wax was essential when the
surface was inverted. Three polishings usually sufficed
for the top of the disc, which was initially badly con­
cave. One polishing was frequently enough for the bottom,
which was nearly planar and smooth initially.

Let it be understood that the technique described
above was developed after many attempts to mold or to
machine electrets in various other ways. The discs, after
some practice, could be made with smooth surfaces and
thicknesses of 0.6 centimeters ± ½ millimeter. The surfaces
of such electrets are considerably different in appearance
from those of machined electrets. The heat-polished ones
appear to contain a multitude of tiny crystallites embedded
in a light brown amorphous wax. Machined ones have an
appearance much like that of the interior of wax lumps;
they are more crystalline and have a less waxy appearance.

When completed the discs had a diameter of 4.5 cm.,
and they were always painted on the bottom with Dag, a
colloidal dispersion of graphite in isopropyl alcohol.
Some were not coated on the top and were stored in a des­
iccator; others were also painted on the top with this
conductive coating and are referred to as "coated"
electrets.
A poured and finished carnauba wax electret weighs about 16.9 grams. This work involved nine electrets the composition of which are reported in Table I. Notice the code numbers assigned to the electrets. These will be used throughout this chapter to identify the electrets. The weights given in Table I apply to the mixture before molding, and not to the finished electret. The special circumstances involved in the making of C-4 and C-5 are described later.

An ester was not used as added solute in any of the electrets for two reasons, the principal reason being that so much time was required to characterize the nine electrets used. Also it was thought that added ester would have less effect than the other solutes, since it already constituted a majority component.

The variables. The variables outlined in Chapter II were controlled insofar as circumstances would permit. There were, however, some variations in variables such as pre-treatment exposure time and holding time for unscientific reasons such as the necessity for eating, sleeping, and going to classes. In general the program described below was employed to control these variables.

Forming field. Forming voltage was 1000 volts, positive to top surface or electrode, negative to ground,
# TABLE I

## COMPOSITION OF THE ELECTRETS USED

<table>
<thead>
<tr>
<th>Code Number</th>
<th>Added Solute</th>
<th>Weight Solute</th>
<th>Wt. C-wax</th>
<th>Wt. % Solute</th>
<th>m</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-1 thru 3</td>
<td>0</td>
<td>14.93 g.</td>
<td>12.9</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td>A-18(1)</td>
<td>stearic acid</td>
<td>1.93 g.</td>
<td>12.9</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td></td>
<td>n-octadecyl</td>
<td>2.85 g.</td>
<td>12.8</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td></td>
<td>alcohol</td>
<td>23.2 g.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-18(2)</td>
<td>stearic acid</td>
<td>1.93 g.</td>
<td>12.9</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td></td>
<td>n-octadecyl</td>
<td>2.85 g.</td>
<td>12.8</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td></td>
<td>alcohol</td>
<td>23.2 g.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-4</td>
<td>no solute, but cracked and patched</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-5</td>
<td>no solute, but laminated</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
which was the potential of the bottom coating at all times. For electrets of 0.6 cm. thickness this is a field of 1666 volts per centimeter.

Pre-treatment exposure time. This was usually two hours. A twenty-four hour timer turned the oven on and off, but another one for the high voltage was not available. A more desirable situation would have been to have the voltage automated also.

Temperature change. $25^\circ$ C. to $70^\circ$ C., or $35^\circ$ C. change was used throughout this research. There were a few days when the laboratory was not at $25^\circ$, but the effect was not thought to be significant.

Oven program. The oven was turned on each night from midnight until four A. M. The temperature changes within the oven were measured by a thermistor thermometer and are shown in Figure 17. The thermistor was suspended in the oven about 2 cm. above the electrodes. It could not be allowed to touch the apparatus for this caused great changes in the currents and charges observed.

Holding time. The high voltage was removed at 9:00 A. M. in most cases. This meant a holding time of 3-4 hours.

Storage time. In many cases there was no storage. Instead surface charge readings were begun as soon as the high voltage was removed and continued for several hours.
Figure 17. Oven Program
Surface charge data were infrequently taken on old electrets simply because very little remained. Uncoated electrets either had no charge after one day or had frictional charges from handling. Coated electrets were uncharged and remained that way after unshorting. These electrets were only uncharged on the surface, though, and TDC was still possible after several hours, or even a day. Thus surface charge measurements had priority over TDC and were always made first.

**Uncoated surface charge data.** Figure 18 shows the decay of surface charge with time for two different carnauba wax discs, C-1 and C-2. These two electrets were made one year apart, one in the summer of 1963, the other in the summer of 1964. They did not differ in their dimensions or in any other known way; perhaps the temperature in the laboratory differed when they were poured. C-2 was poured in a dehumidified, air-conditioned laboratory, C-1 in a nonair-conditioned laboratory under conditions not recorded.

The negative sign on the null voltage recorded in the graph means that the surface of the electret was negative. These electrets were all formed at +1000 volts, and thus are showing a decaying heterocharge. All uncoated electrets in this research showed a heterocharge except for two cases in which some of the conducting paint came off the
Figure 18. Surface Charge, Uncoated C-wax
vibrating electrode onto the wax during the heating cycle. These electrets then behaved like the coated electrets that are described in the next section.

The displacement of these decay curves (Fig. 18) from each other in voltage is not particularly significant because of the frequent modification and repair of the apparatus during the intervening periods and the subsequent variations in spacing of the charged surfaces. However, the shape of the decay curve is clearly the same for the three trials of C-2, and different, at least during the first hour, from that for C-1. Figure 19 shows C-1 and C-2 decay curves on an expanded time scale. The C-1 decay seems to be slower than the C-2 decay.

In Figure 18 the discontinuity in one of the C-2 curves was caused by an interruption of readings for repairs of the vibrating electrode connection. The lowest of the C-1 curves ends at 1 hour. This electret was shorted at that time by raising it to the vibrating electrode. After three hours of shorted storage it was lowered and readings were begun again. Figure 19 shows the result which includes a new short time constant decay before the slower decay proceeds.

Many attempts were made to plot the decay curves of uncoated electrets in a manner which would yield straight line plots. Plots of the logarithm of the absolute value
Figure 19. Surface Charge for Longer Times

-1000

-500

volts

C-1

C-1 after unshorting

C-2

Time in hours
of $V$ versus time yield not straight lines but curves similar in shape to the decay curves themselves. Plots of $dV/dt$ versus $V$ also fail to yield straight lines as do plots of $1/V$ versus $t$ and $V$ versus $t$. Something close to a straight line was found only in the case of one electret, Al-18(l), Figure 20, curve C.

The surface charge readings of the electrets with added solutes are shown in Figure 20. There is very little, if any, difference between the rates of decay of pure carnauba wax electrets and those with added solutes. Table II shows detailed data for the curve C (Al-18(l)) in Figure 20. Figure 21 shows the log $V$ plot for this electret on which have been drawn straight lines to correspond to exponential decay times of $\tau = 40$ minutes and $\tau = 9.5$ hours. As mentioned above, other log plots were not as nearly linear, and this one is taken as a rough indicator of the short and long time constant decay scheme.

The CTP. Surface charge readings were made three times on electrets which had no thermal treatment. The decay curves are shown in Figure 22. Curve A is for C-2 exposed for 15 hours to $+1000$ volts. Curve B is for C-4, a freshly made electret, which had never before been polarized either thermally or otherwise. It was exposed for 12 hours to $+1000$ volts. This "virgin" electret seemed to decay more rapidly than the non-virgin ones in the interval one to
Figure 20. Surface Charge, Electrets with Added Solutes, Uncoated
### Table II

**Surface Charge Data for AL-18(1)**

<table>
<thead>
<tr>
<th>Null Voltage (V)</th>
<th>$\log_{10} V$</th>
<th>Time (min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>390</td>
<td>2.591</td>
<td>2</td>
</tr>
<tr>
<td>380</td>
<td>2.580</td>
<td>4</td>
</tr>
<tr>
<td>366</td>
<td>2.564</td>
<td>5</td>
</tr>
<tr>
<td>353</td>
<td>2.548</td>
<td>6</td>
</tr>
<tr>
<td>341</td>
<td>2.533</td>
<td>7</td>
</tr>
<tr>
<td>327</td>
<td>2.515</td>
<td>8</td>
</tr>
<tr>
<td>329</td>
<td>2.517</td>
<td>9</td>
</tr>
<tr>
<td>323</td>
<td>2.509</td>
<td>10</td>
</tr>
<tr>
<td>300</td>
<td>2.477</td>
<td>15</td>
</tr>
<tr>
<td>283</td>
<td>2.452</td>
<td>20</td>
</tr>
<tr>
<td>268</td>
<td>2.428</td>
<td>25</td>
</tr>
<tr>
<td>256</td>
<td>2.408</td>
<td>30</td>
</tr>
<tr>
<td>246</td>
<td>2.391</td>
<td>35</td>
</tr>
<tr>
<td>239</td>
<td>2.378</td>
<td>40</td>
</tr>
<tr>
<td>233</td>
<td>2.367</td>
<td>45</td>
</tr>
<tr>
<td>218</td>
<td>2.338</td>
<td>60</td>
</tr>
<tr>
<td>179</td>
<td>2.253</td>
<td>120</td>
</tr>
<tr>
<td>154</td>
<td>2.187</td>
<td>180</td>
</tr>
<tr>
<td>138</td>
<td>2.140</td>
<td>240</td>
</tr>
<tr>
<td>126</td>
<td>2.101</td>
<td>300</td>
</tr>
<tr>
<td>115</td>
<td>2.061</td>
<td>360</td>
</tr>
</tbody>
</table>
Figure 21. Log Plot of Surface Charge
three hours after readings were begun.

Curve C in Figure 22 is for C-1 exposed for 12 hours. The absence of the initial rapid decay is puzzling. This electret differed from C-2 in curve A only in that it had been coated prior to taking this data. When CTP data were desired on C-1 the conductive paint had been scraped off with a razor blade. Thus the surface of this electret may have had different properties than the normally heat-polished uncoated surfaces.

The value of the surface charge by the method of
distance variation. In Gubkin's theory there arises the
equation (eqn. 4, Chapter IV):

\[ E_l = E_{ext} = \frac{4\pi \sigma}{\varepsilon_{ext} \left( \frac{\varepsilon_{int} (d_1 + d_2)}{L \varepsilon_{ext}} + 1 \right)} \]

Here \( E_{ext} \) is the field outside the electret, in the gap between it and the sensing electrode; \( \sigma \) is the surface charge; \( d_1, d_2, \varepsilon_{int}, \varepsilon_{ext} \), and \( L \) have the significance indicated in Figure 10. In the operation of measuring the charge in this work it was possible to vary \( d_1 \) by the use of the electret micrometer screw. The null voltage was observed to vary, and it was thought that a test of Gubkin's formula should be made. Also this method theoretically can give values of the surface charge.

If one assumes \( \varepsilon_{ext} = 1, \varepsilon_{int} = 2.8 \), Gubkin's
formula reduces to

$$E_{\text{ext}} = \frac{-4\pi \sigma L}{2.8(d_1 + d_2) + L}$$

Note the similarity of this to Swann's equation (eqn. 3, Chapter IV). Upon dividing both sides into unity one finds:

$$\frac{1}{E_{\text{ext}}} = -\frac{2.8d_1}{4\pi\sigma L} + \frac{2.8d_2}{4\pi\sigma L} + \frac{1}{4\pi\sigma}.$$  

If $d_2$ is constant, and $E_{\text{ext}}$ taken as $V_{\text{ext}}/1.3 \times 10^{-7} \text{m}$, considering the distance to the third electrode, and if charge signs are disregarded one has:

$$\frac{1}{V} = \frac{2.8}{4\pi\sigma L(1.3 \times 10^{-7} \text{m})} d_1 + \text{constant} \quad (5)$$

Plots of $V^{-1}$ versus $d_1$ should be linear, a prediction which could be tested experimentally. Figure 23 shows such plots for several carnauba wax electrets. Figure 24 shows similar data for electrets with added solutes. Table III summarizes the conditions and slope determinations for these plots. A typical surface charge calculation is shown in the appendix.

Referring to Figure 23, A and C are for positively charged surfaces, B and D are for negatively charged ones. The sign of $V$ was disregarded in making the plot. Readings of the null voltage were made usually at 2 revolutions of the micrometer, the normal distance, and at successively larger distances. Then the readings were made on the return of the electret back to normal position. This explains
Figure 24. Distance Variation Plot for Electrets with Added Solutes
<table>
<thead>
<tr>
<th>Figure Identification</th>
<th>Electret Identification</th>
<th>V at 2 rev.</th>
<th>$\sigma$ (from slope)</th>
<th>Coul. $\times 10^3$</th>
<th>Special Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>23-A</td>
<td>C-1</td>
<td>+77</td>
<td>17.5</td>
<td></td>
<td>accidentally coated</td>
</tr>
<tr>
<td>23-B</td>
<td>C-1</td>
<td>-210</td>
<td>46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23-C</td>
<td>C-2</td>
<td>+360</td>
<td>55</td>
<td></td>
<td>polarized with -1000 V</td>
</tr>
<tr>
<td>23-D</td>
<td>C-1</td>
<td>-573</td>
<td>88</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24-E</td>
<td>A1-18</td>
<td>-259</td>
<td>38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24-F</td>
<td>A-18</td>
<td>-217</td>
<td>57</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24-G</td>
<td>A-18</td>
<td>-245</td>
<td>57</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24-H</td>
<td>C-1</td>
<td>-606</td>
<td>105</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
the arrows and double curve in Figures 23 and 24. Disagree-
ment of the readings on the forward and return trips can be
attributed to two causes. Any mechanical play in the mi-
crometer mechanism will cause such an effect. A more im-
portant reason was that the surface charge was not always
constant during the measurement, but was still changing
slowly. In the case of uncoated electrets it was decreas-
ing. In the case of curve A, Figure 23, which was acci-
dentally coated and showed a heterocharge, it was increasing.

Figure 24 shows the surface charge of two trials of
A-18(1), F and G, which were in very good agreement.
Al-18(1) gave the rather erratic curve E, and H shows a
C-L curve for similar circumstances.

Figure 25 has a different scale than that of the other
plots. It shows in curve A a surface charge by distance
variation for a carnauba wax electret the slope of which
corresponds to about 100 nanocoulombs. Curve B in this
figure is a plot of null voltage versus distance when the
top surface of the electret was coated and connected to a
separate power supply providing -1000 volts. The connec-
tion was made through a small phosphor bronze contact that
rode on top of the electret. The auxiliary supply was a
Gyra Electronics V-200. Due to 120 cycle ripple in the
output of this supply it was necessary to operate the entire
instrument at 60 c.p.s. during this measurement in order
Figure 25. Constant Surface Voltage Compared to Constant Surface Charge
to stabilize the null pattern.

The significance of this experiment is that such a plot is not as nearly linear as the normal surface charge plots. This is to be expected because an electret with 1000 volts applied to its surface and maintained by an external source should not behave as does an electret the voltage of which varies with the degree of short-circuiting according to Gubkin's equation. It is apparent in the figure that the voltage on the surface of a real electret, and thus the field within it, increases as the distance $d_1$ increases. Gubkin's equation is not exactly obeyed because it was derived for infinitely extended electrets with no edge effects. In other words the electret plots are not linear because of flux loss as $d_1$ increases and becomes appreciable compared to the electret diameter.

**Coated surface charges.** Electrets the top surfaces of which were painted with Dag exhibited a completely different surface charge behavior than those that were left uncoated. Coated electrets have an apparent homocharge. If the polarizing high voltage is removed from the top surface without grounding it, the surface charge (+) behaves as in Figure 26, curves A and C. Curve B shows the buildup of surface charge on the electret when the surface in curve A was shorted momentarily after 5½ hours. Curve
Figure 26. Surface Charge, Never-shorted Coated Electrets
C is that of an electret which was never shorted and was enclosed in a glass ring (its forming mold) during the readings. The decrease in charge was due to the resistive path provided by this ring which drained away the charge, which would otherwise have been slowly increasing with time.

Figure 27 shows how the surface of a coated electret behaved when it was shorted upon removal of the polarizing voltage. This was the case when the polarizing supply was turned to zero volts before it was disconnected; such a procedure is much safer than the previous one. At time zero on the figure the short was removed. A and B in this figure are both C-2 thermally polarized under the usual conditions. In A only +500 volts of polarizing voltage was used; in B the usual +1000 volts was used. The B curve also shows the results of shorting again at one hour.

Figure 28 gives a more complete picture of the effect of short-circuiting the electret at various times after the high voltage was removed. Curve A, the same as B in Figure 26, shows the increase of charge after a momentary short for C-2 which had been open-circuited and never shorted after the high voltage was removed. Note the definite short time constant for the charge increase.

Curve B is the same as B in Figure 27, except that the B' part is shown for longer times; B' is the charge increase after momentary shorting at one hour. C is essentially the
Figure 27. Surface Charge, Coated C-wax
Figure 28. Some Effects of Shorting on Coated Electrets
same situation, but the electret was shorted at ½ hour; C' is the continuation of the charge increase after shorting. D is a different electret, C-1, and it was polarized at -1000 volts instead of +1000 volts. The null voltages plotted were negative, but the sign is disregarded in order to display them on the same graph. D' is the continuation after shorting at ½ hour. The line E shows the charge increase on C-2 when the electret had been short-circuited for five hours, after the removal of high voltage until readings began. Note the difference between this gradual rise and that of curve A.

After 4½ hours of taking readings for E this electret was shorted and left overnight. Then, 22½ hours after the removal of high voltage the short was again removed and curve F resulted. The gradual rise indicates that the heterocharge is still decaying.

Figure 29 shows decay curves for seven different electrets, three of carnauba wax and two each of electrets with added solutes. These are grouped together in one figure because they were all formed and measured under nearly identical conditions. After forming them thermally by the usual process, the high voltage was removed without shorting them and the positive surface charge was read for five minutes. These initial data are given by the primed set of points. The electrets were shorted at five minutes.
Figure 29. Surface Charge, Electrets with Added Solutes, Coated
The short was removed at 5½ minutes, and the results appear in the figure.

Curve A is the old C-1 which always showed a slower initial decay than did any of the other electrets in this work. Curve B is C-3, an electret freshly made at the time of the reading. Curve C is C-5, a carnauba wax electret that was slightly thicker than most of the electrets and formed in two layers that were sandwiched together. D and E are Al-18(1) and Al-18(2) respectively. These electrets were made a year apart, although these data were taken within a few days of each other. The agreement is surprisingly good for two different discs. F and G are A-18(1) and A-18(2) respectively. The same remarks apply, and agreement in this case is even better. Reproducibility in these experiments was aided considerably by the fact that the electret spacing did not have to be altered between experiments. With coated electrets a wire was used to connect the vibrating electrode to the electret surface during polarization; thus the electret did not have to be raised. The shorting wire had an insulated handle that enabled it to be removed, leaving the coated and charged surface at the standard distance from the vibrating electrode.

The shapes of all the curves in this figure are similar except for that of C-3. For some reason C-3 has a more
rapid early decay. Also the curve for C-3 (curve B) becomes horizontal much sooner than most. C-5 (curve C) shows a larger charge probably because of its greater thickness, not because of its greater polarization. Since, in this series of experiments, the electret holder was not moved this thicker electret was closer to the vibrating electrode. It is unfortunate that this fact was not appreciated at the time and that the experiment was not repeated at the proper spacing.

It should be pointed out here that these surface charge plots on coated electrets are identical in shape to those published by Adams in 1927.6 Like Adams' curves, these do not fit any exponential scheme. Plots of log \((V_\infty - V)\) versus time were tried for several curves that approached a horizontal asymptote which could be assigned as \(V_\infty\), but the results were not straight lines.

Figure 30 was plotted for the purpose of comparing the coated surface charge rise with the uncoated surface charge fall, since both presumably represent the decay of the heterocharge. In this figure curves A and B represent the results from the uncoated electrets C-1 and C-2; the left-hand ordinate values are applicable. C and D give results from coated electrets; these results are plotted upside

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6 Adams, op cit., p. 475.
Figure 30. Surface Charge, Comparison of Uncoated and Coated Decay
down; the right-hand ordinate values are applicable. Curve C is for the electret C-3 and appears dissimilar to the others, but D is for C-5, the laminated electret, which illustrates the expected great similarity to the decay of uncoated electrets. However, even C-5 becomes horizontal after two hours (there is more data which lies beyond three hours), whereas the uncoated decay schemes proceed downward eventually to zero.

Figure 31 shows surface charges for C-2 under similar conditions in two experiments. The only difference is that curve A is for a non-thermal electret (CTP) and curve B for the usual 4-hour oven cycle. Thus the curves compare CTP with an identical thermal electret. The electrets were initially shorted, and the dotted line represents a short circuit. It is apparent that the non-thermal electret has a heterocharge which decays more rapidly than does the thermal electret. A faster CTP discharge was also observed with uncoated electrets. In addition this figure illustrates the fact that these surface charge readings on coated electrets give almost no information about the frozen-in charge. They provide instead only a reproducible measure of the short time constant decay that is characteristic of both thermal and non-thermal electrets.
Figure 31. Surface Charge, Coated, CTP Compared with Thermal
D. Thermal Discharge Curves

The apparatus used for thermal discharge current measurement had been described in Chapter III. Although the equipment and the procedure are simple, some discussion of the difficulties involved is in order.

First the choice of $10^{11}$ ohms as an electrometer input resistance for the measurements was dictated by the upper limit of the calibrated resistances in the General Radio electrometer. It was thought that the higher the resistance the better the result because this arrangement magnified the voltage readings for a given current. Gerson and Rohrbaugh had used approximately this resistance. However, it is now felt that a lower resistance would have been a better choice, perhaps $10^{10}$ or $10^9$ ohms. The fraction of the discharge current lost by conduction within the body of the electret was probably higher for the resistance used than it would have been for lower external resistances.

The General Radio electrometer proved a stable and dependable instrument, and it is recommended for use in this application. After an hour of warm-up the zero-drift of this instrument was never more than a few millivolts. General Radio connectors were used at the instrument but standard coaxial connectors elsewhere. The input cables

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7 Gerson and Rohrbaugh, *op. cit.*, p. 2382.
were all high-quality coaxial cables. Well-grounded instrumen-
t was essential in such experiments; in one case dificulty was caused by an ungrounded thermistor probe
from the battery operated thermistor thermometer.

It is important that connecting wires inside the oven
be bare, uninsulated, solid copper wire. During one summer
about fifty thermal discharge curves were recorded for a
series of electrets, mostly C-l, paraffin wax, pure stearic
acid, and electrets A-18(l) and Al-18(1); the curves later
had to be thrown away. It was discovered that although
the apparatus gave no TDC when a control experiment was run
at normal temperature, it did give a TDC when the apparatus
was run through a control polarization cycle. This obser-
vation meant that parts of the apparatus other than the
sample were behaving as electrets. The cause of this inter-
ference was finally found to be a shielded wire which had
been used in the oven between the coaxial connector and the
vibrating electrode. It was an old type of shielded wire,
the kind with cloth insulation, and the shield was grounded,
of course. The cloth insulation gave excellent thermal
discharge curves which had a peak current of about $2 \times 10^{-11}$
amperes. When the shielded wire was replaced with a bare
wire all of the apparatus TDC disappeared.

Thermal discharge curves could not be run immediately
after the high voltage was turned off, and the electrometer
was connected to the coated electrets. If this procedure were attempted there would appear on the electrometer a high positive voltage which then decayed toward zero. This was again the CTP phenomenon which was reported in part B of this chapter. After 30 minutes this current had usually diminished sufficiently to begin the TDC by turning on the oven. Thus "immediate TDC" in the text to follow really means discharge after 30 minutes.

The final electrometer reading after this CTP decay was not zero. It varied from -40 to -120 millivolts across 10 ohms. This voltage was thought to be a contact potential characteristic of the apparatus or of the Dag-wax surfaces because it always was present. The only difficulty it caused was the inconvenience that the TDC's did not begin at zero.

Uncoated TDC. If an electret was polarized thermally without conducting paint on its surface, that is by raising the electret to the electrode, it showed a surface charge behavior which has previously been described. However, uncoated electrets gave very little or no effect in the TDC experiment. Figure 32 shows thermal discharge curves for coated and uncoated carnauba wax electrets. Curve A is for an uncoated electret two hours after the polarizing voltage was turned off. Curve B is for an uncoated electret 30 minutes after the high voltage was turned off. Curves
Figure 32. The Effect of Coating on TDC
C and D are for coated electrets.

The vast difference between the curves A, B and those C, D raises the question, do uncoated electrets not acquire a frozen-in charge or do they acquire one which does not get to the electrometer in the TDC experiment? This question was answered by a series of three experiments. In two of these experiments uncoated electrets were exposed isothermally for twelve hours to the high voltage; then surface charges were read as usual. After this operation the electrets were painted with Dag and the TDC experiment was run. They both showed no TDC and gave a line similar to curve A in Figure 32. The third uncoated electret was polarized in the usual manner, thermally, and after the surface charges were determined, the electret was coated and TDC was run. Curve E is the result.

These data indicate that electrets which were polarized uncoated did acquire a frozen-in charge, a fact which their surface charge behavior also indicated. However, if the TDC experiment was attempted without coating, very little or none of the discharge current got to the electrometer. Presumably it was dissipated within the electret because the contact resistance to the electrode was too great. If the electret was coated before TDC it showed a proper thermal discharge curve when there was a frozen-in charge. In the case of isothermal electrets there was apparently no
frozen-in charge. All of the remaining TDC's are for coated electrets.

Reproducibility and effect of storage. Figure 33 shows TDC's for two carnauba wax electrets. All these curves except D are for the electret C-2. Curve D is for C-1 after 4 days storage. Curves A and B show the good reproducibility that is obtainable when the same coated electret is used in two experiments. A third curve could have been drawn for C-2 under these conditions, which were immediate TDC with no storage time, but the data are so close to those of curve B that one curve suffices for both sets of data.

C, D, and E are all for electrets that were stored while shorted. Curve C is for C-2 after 4 hours storage. Curve E is for C-2 after 5 days storage. These curves show that the frozen-in charge in shorted electrets decays only very slowly during storage. They also show that in comparison to immediate TDC's the current rise during the TDC is significantly delayed after storage. For example curve E acquires a positive slope only after fifteen minutes, whereas A and B do so within the first five minutes. Time zero in these plots is the moment at which the oven was turned on.

It would be interesting to see an immediate TDC for C-1 with which to compare curve D. Unfortunately this
Figure 33. TDC of C-wax Immediately and After Storage
experiment was not done; C-1 was uncoated throughout most of the work and was coated only during the final experiments. The dotted portion of D and the arrows indicate that here the electrometer readings were erratic and fluctuated up and down abruptly. This happened frequently with stored electrets. It is not known if this variation was characteristic of the electrets or due to some poor contact in the equipment.

The effect of storage was determined more quantitatively by weighing the areas under the TDC's of Figure 34. These are results from the electret A-18(I) that were obtained immediately after the high voltage was removed, curve A, and after 34 hours of storage while the electret was shorted, curve B. These data were taken for a sufficiently long time so that they could be extrapolated to zero current. Then they were integrated by weighing and the frozen-in charge calculated in each case. The immediate TDC represented $4.1 \times 10^{-2}$ microcoulombs of charge, or 41 nanocoulombs. The 34 hour TDC represented 27.4 nanocoulombs of charge. If one assumes an exponential decay of the form:

$$P = P_0 e^{-\alpha t}$$

these data then correspond to $\alpha = 1.19 \times 10^{-2}$ hr.$^{-1}$, or $\tau = 1/\alpha = 84$ hours = 3.5 days.

Data on the C-2 electret which was stored 5 days
Figure 34. Effect of Storage on TDC of Shorted Electrets

Millivolts across $10^{11}$ ohms
(shown in Figure 33) were not observed for a sufficient time to make integration by weighing possible. It is apparent, however, that $T$ for storage of shorted C-2 is much longer, and it is estimated at 16 days.

**Electrets with added solutes.** Figure 35 shows TDC for the solution electrets. The curves are labeled by their electret code numbers. They were all formed and measured under similar circumstances. A-18(1) and A-18(2) did not agree well with each other. A1-18(1) and A1-18(2) also did not agree. The data on Al-18(2) are erratic because the surface of the electret was melting at about $t = \frac{1}{2}$ hour. The oven was no hotter than usual, but the melting point of this electret was apparently too close to 70 degrees.

About the only conclusion one can draw from this figure is that all the solution electrets seemed to have more frozen-in charge than C-2, but considering that the pure electret C-1 also did, one cannot attach much significance to this fact. The major conclusion to be drawn is that, although one electret's TDC may be reproduced quite satisfactorily later under similar conditions, the TDC of two different electrets are generally different, regardless of their similarity of composition.

**The crack effect.** Electret C-4 was unique due to an accident during its preparation. During surface polishing
(shown in Figure 33) were not observed for a sufficient
time to make integration by weighing possible. It is
apparent, however, that $T$ for storage of shorted C-2 is
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factorily later under similar conditions, the TDC of two
different electrets are generally different, regardless of
their similarity of composition.

**The crack effect.** Electret C-4 was unique due to an
accident during its preparation. During surface polishing
Figure 35. TDC for Electrets with Added Solutes
it cracked due to thermal stresses. The crack ran across the electret diameter but not vertically through it, at an angle of perhaps 60 degrees. C-4 was patched together and used. The pieces fit together well, and the surfaces were polished in such a way that the surface melt would hold the electret together. After the polishing it had the outward appearance of a normal electret. It was coated and polarized normally.

The surface charge increase of C-4 was normal and is shown in Figure 36. After surface charge readings were taken it was connected to the electrometer for TDC. It gave a very large peak of current which decayed more slowly than the usual fast CTP current. In fact it seemed it wouldn't be ready for the TDC run that afternoon. The electret C-4 still read +300 mv. at the usual time for TDC to begin, and it was wrapped in aluminum foil and stored in the desiccator. The next day this electret was connected into the apparatus and TDC was begun at the usual time, or rather 24 hours after the usual time. The discharge current from this electret was many times larger than that of any previous electret. The relative TDC's are shown in Figure 37. Notice the larger values of voltage than usual on the ordinate of this graph. The peak reading of C-4 is five times that of C-2; the area under the curves is about in a ratio of 3.7 to 1, perhaps 4 to 1 if extrapolated to
Figure 36. Surface Charge of Cracked Electret
Figure 37. The Crack Effect
zero current.

Figure 38 shows another TDC from this electret, C-4, which was taken nine months later. It is not quite as large, but it is still significantly larger than normal TDC's. The large frozen-in polarization could be attributed only to the crack built into this electret--thus the terminology "crack effect," with which Figure 37 is titled. This writer feels that the discovery of the crack effect is a significant one for electret heterocharge theory. It is unfortunate that at this writing it is not substantiated by more data than those in Figures 37 and 38.

Several unsuccessful attempts were made to manufacture other cracked electrets. In one attempt a laminated electret, C-5, was made by making two polished discs of carnauba wax of about 0.4 cm. thickness. These were "glued" together by light melting of one surface and sticking them together. This C-5, as has been apparent earlier in the data presentation, was a rather normal electret. Its peak electrometer reading during TDC was +530 mv., a very normal value. Various attempts were made to crack electrets longitudinally, that is, in a plane parallel to their surfaces. Such discs shattered into many pieces. Several other techniques for cracking electrets remain untried. These are included in the next chapter, but experience has shown that the closely fitted crack necessary is not easy to deliberately produce.
Figure 38. TDC of Thermal and Isothermal Electrets
TDC from CTP. Constant temperature polarization can produce some frozen-in charge. This is illustrated in Figure 38. Curve A results from electret C-1 formed thermally, and A' represents data from this electret after it was exposed to the field for 12 hours isothermally. Curve B comes from C-2 formed thermally, and B' resulted when this electret was formed isothermally for 11.5 hours. Curve C is from the cracked electret, C-4, formed thermally, and C' is from this electret after isothermal exposure for 48 hours to the high voltage. It must be remembered that the normal thermal program includes about eight hours of isothermal exposure. The results show that isothermal exposure can produce electrets. It would be interesting to know if the polarization represented by the primed curves in Figure 38 would decay at the same or a faster rate as that in the unprimed curves. Data have not yet been obtained on this problem.

E. NMR Experiment

An experiment was performed to determine if the nuclear magnetic resonance spectrum of carnauba wax was in any way affected by the polarization process. It was expected that the wax would have a broad proton resonance, although no literature research was done on this point.

An afternoon was assigned for the use of the Varian n.m.r. equipment, and so two samples were prepared. This
was done by selecting soft glass tubing the diameter of the n.m.r. sample tubes. The glass tubing was inserted into molten carnauba wax which was then allowed to cool with the glass tubing still in the pot. When the wax had hardened the glass tubes were removed and the cylindrical wax pieces in their interior carefully removed. Two cylinders of wax 6 cm. long and having a diameter of 2 mm. were selected so as to be free of air bubbles in the wax.

One of these samples was placed in a section of tubing previously sealed at the bottom to form an unpolarized sample. The other sample was inserted into a glass tube 14 cm. long and fitted with electrodes at each end made of No. 12 solid copper wire. The wires were taped in place with electrical tape. Both samples were placed in the oven to be treated thermally. The sample with copper electrodes was subjected during the cycle to 10,000 volts d.c. from a Dumont type 263-B power supply.

The following day the polarized sample was placed in a tube similar to the unpolarized one. Both were used as samples in the Varian n.m.r. equipment. Neither the polarized nor the unpolarized sample showed any resonance over the entire range of the magnetic field available to the instrument. The search for the resonance was conducted both with and without the sample spinning.
The absence of a resonance is puzzling. Liquids give good proton resonance peaks, as is well known, and it would seem that an amorphous solid would be similar. Perhaps there is too much crystalline character to carnauba wax and the peak is broadened to invisibility.

In the light of Chatterjee's and Sutradas's report of paramagnetism in carnauba wax electrets, the electron spin resonance experiment would seem to be a logical next step.

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8 S. D. Chatterjee and J. G. Sutradhar, Die Naturwissenschaften, XLII (1955), 366
A. Discussion of Results

The data reported in the preceding chapter provide the following facts:

1. Polarization does not significantly change the dielectric constant of carnauba wax.

2. The relaxation time of the molecules in carnauba wax is greater than $10^{-1}$ seconds.

3. Exposure of carnauba wax to electric fields of 1-2 KV/cm. causes a slowly decaying polarization (the CTP). This polarization can be caused in a shorter time than is required for its decay.

4. The surface charge of uncoated electrets exhibits a rapid decay superimposed upon a slow decay. The rapid decay appears again, in part, after storage while shorted.

5. Isothermal polarization produces surface charges that are very similar to those of thermal electrets, except that perhaps they have a more rapid long time constant decay.

6. The surface charges on solution electrets are usually slightly smaller in magnitude than those shown by
the carnauba wax electrets, but the decay scheme seems very similar.

7. Surface charges are measured to be from $10^{-7}$ to $10^{-8}$ coulombs/cm².

8. Coated electrets exhibit surface homocharges. If these electrets are never shorted these charges are constant or decrease with time. If the electrets are shorted the charge builds up to a constant value and remains constant until the electret is shorted again.

9. Coated electrets which have never been shorted show the short time constant rise in charge when they are momentarily shorted, whereas coated electrets which have been stored while shorted no longer exhibit this short time constant rise upon unshorting.

10. Coated solution electrets show a charge rise similar to that shown by carnauba wax electrets. For both types of electrets the short time constant rise is similar to the short time constant decay of uncoated electrets.

11. Non-thermal electrets exhibit a similar short time constant rise, which is perhaps slightly more rapid in character.

12. Uncoated electrets give no thermal discharge curves, unless they are coated after formation. Coated electrets give thermal discharge curves corresponding to a frozen-in charge of $10^{-8}$ to $10^{-9}$ coulombs. A short time constant
polarization must decay before thermal discharge curves are run.

13. Thermal discharge curves are reproducible only on the same electret. Other electrets of the same composition give significantly different results.

14. Solution electrets show frozen-in charges of the same order of magnitude as those of pure carnauba wax. In a few cases the frozen-in charge seems larger, but the data are insufficient for reaching any definite conclusion on this point.

15. The frozen-in polarization of a stored carnauba wax electret decayed at a slower rate than that of an electret containing acid.

16. The TDC of electrets stored short-circuited differs from the TDC of electrets recently polarized in that the current rise begins later. This displaces the TDC of stored electrets as much as ten minutes to the right of recently polarized electrets.

17. Isothermal exposure can cause frozen-in polarization, but the extent is much smaller than that resulting from the thermal treatment.

18. A cracked electret exhibited similar surface charge behavior to that of normal electrets, but it showed a significantly greater frozen-in polarization.
These results, along with the previously reported properties of electrets, should all be explained by a proper mechanistic theory of the heterocharge. Such a theory has been evolving slowly since the discovery of electrets forty-five years ago.

The discovery of the crack effect has provided one more important clue to a realistic choice of mechanism from the multitude available. The result is that there can now be proposed a new theory which is a natural culmination of existing theories and also explains the crack effect. In the next section this theory will be put forth in some detail, using the data of Chapter V as an example of how it can be applied. Of course the theory was induced from these data and can only be tested by testing the validity of its deductions. Some proposals as to how this might be done are presented in a section that follows the theory.

B. A Theory Proposed

The large internal polarization of the cracked electret suggests that a well-fitted crack can act as a barrier to the passage of ions at low temperatures but not at higher temperatures. In other words, the crack is a two-dimensional potential barrier to the passage of ions in the wax. It is not an infinite barrier because room temperature exposure of the cracked electret causes a partial appearance of the crack effect.
When the cracked electret was heated in the field ions migrated across the barrier, heterocharging the electret. When the electret was cooled in the field there was a charge separation across the crack which constituted a frozen-in polarization. When the field was removed and the electret was shorted, this field caused induced charges on the conducting coatings of opposite sign. When the electret was reheated so that ions could move across the potential barrier of the crack, the induced charge on the conducting costs was liberated and flowed through the electrometer circuit, causing the large thermal discharge current. According to this theory only the horizontal component of the crack contributed to the polarization. If such an ion barrier could be introduced horizontally across the entire electret, what an extraordinary electret might result!

The idea of a potential barrier to the passage of ions seemed to be the key to the troublesome question of how the heterocharge and the admittedly ionic homocharge could exist in the same region of the electret without neutralizing one another. One only has to suppose that a similar potential barrier to the passage of ions might exist at the boundaries of the crystallites, or domains, in the carnauba wax. Polar waxes such as carnauba wax possess such crystallites, microcrystals, domains, or whatever one wishes to call them, distributed throughout the wax. These
crystallites are regions of crystalline solidity in a sea of amorphous but viscous fluidity. Nakata's\textsuperscript{1} microphotographs actually show these crystallites, at least the larger ones, and show them oriented by the field.

The amorphous binder which holds all the crystallites together certainly must have different physical properties than those of the crystallites. It does not seem unreasonable to postulate a potential barrier at the interface of the crystallite and the amorphous region, a barrier to the passage of ions or polar molecules at room temperature. This is equivalent to saying that more energy is required for an ion or polar molecule to leave or enter the crystallite, than to move in the amorphous binder at room temperature. Another way to put it would be to state that the rate of exchange of ions and molecules between the crystalline and non-crystalline regions is low at room temperature.

It is apparent that on the basis of such assumptions one can picture ions becoming trapped in the crystallites in the same way that they are trapped in the cracked electret. When cooled in the field, then, the crystallites might have a net charge, or they might be neutral and dipolar. If dipolar they might well orient in the field

during the cooling process, and the frozen-in charge would consist of either (1) ionic space charges locked into the domains or (2) dipolar domains which could disorient only slowly or exchange ions with the amorphous region only slowly at room temperature.

Both the mobility of ions and relaxation time of dipolar molecules would be entirely different in the amorphous region than in the domains. Ion mobility in the domains would be practically nonexistent, whereas in the amorphous region it would be finite. At room temperature polar crystallites would have a very large relaxation time, whereas the molecules in the amorphous region would have relatively short relaxation times. This suggests an explanation of the long and short time constant decay schemes exhibited by the electrets.

In terms of the experiments reported here this means that the CTP is a characteristic of the amorphous region, whereas the frozen-in polarization is characteristic of the domains and their associated potential barrier.

At this point in the theory two choices must be made. Is the domain heterocharge due to domains with a net charge, and thus a locked-in ion space charge, or is it due to dipolar domains? Also, what is the mechanism of the CTP in the amorphous region, ionic or dipolar?
The first of these choices is the easier. Nakata's microphotographs, X-ray studies, the noise of decaying electrets, and the large but finite decay time of the frozen-in charge seem to point to the dipolar domain idea. If rotation is still possible at temperatures where the ions cease crossing the barrier into the domains then the dipolar domain theory is certainly plausible. In fact it could coexist with a net charged domain theory. The permanence and characteristics of the homocharge are readily accounted for on the assumption that the injected charge becomes frozen into the domains. Thus the homocharge can coexist with the ions of the amorphous matrix and not be neutralized.

The second question as to the nature of the polarization in the amorphous region is more difficult. Either ionic space charges or dipolar orientations are possible and perhaps have the correct lifetime. The data presented here show that, although the CTP decay is not exponential, an approximate time constant of 40 minutes can be assigned. Swann and Gubkin take as the specific conductance of carnauba wax $10^{-18} \text{ ohm}^{-1} \text{ cm}^{-1}$. Using this for a disc electret gives $RC = 2 \times 10^5$ seconds. This is 55 hours, or 2.3 days. Unless the value for specific conductivity is very wrong an ohmic mechanism for the CTP is not indicated.

A dipole orientation mechanism is feasible to account
for the CTP, since the relaxation times are completely unknown. In face a distribution of relaxation times would be expected in such a medium, and this would account for the fact that a simple exponential function does not fit the decay scheme. In the experiment in which a coated electret had its conducting coat scraped off and was then polarized uncoated, the CTP seemed much less than usual, in fact almost absent. This suggests that the dipolar orientation responsible for the CTP takes place mainly near the surfaces and perhaps is not a true volume polarization. On the other hand, Gross' machined electrets showed a CTP similar to the normal surface polished ones in this work, so the preceding inference may not be valid.

In order to clarify further the ideas which follow from the theory above, the eighteen phenomena listed in the "discussion of results" will be explained one at a time. In doing so the term CTP or CTP decay will be used to refer to the short time constant polarization or its decay, since it is obvious that this polarization does not require the heating process.


\[3\] B. Gross, J. Chem. Phys., XVII (1949), 869, Figure 4a.
1. Free electrons, or electrons in "traps," are not involved in the theory. The dielectric constant as determined at 1 Kc. or similar audio frequencies is that of the amorphous binder, and it is not appreciably affected by the domain polarization. It should be pointed out that the dielectric constant experiment reported in this work differed in one way from that of Chatterjee's and Bhadra's experiment. This wax was polarized without melting; their's was polarized from the melt. This may account for the result that contradicts that of the Indians. Polarization from the melt was not attempted here because of the danger of arcing across the small gaps of the condenser which would cause conditions unlike that of normal polarization.

The theory proposed here would not predict any paramagnetism, and the magnetic data now need to be determined by ESR to decide this point.

2. The CTP mechanism rests on the assumption that relaxation times for molecules in the amorphous binder can be as great as 40 minutes, and that there is a dispersion of decay times due to local field inhomogeneities throughout the wax. Gerson and Rohrbaugh are of the opinion that such a time constant for molecules in carnauba wax is too high.

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4Gerson and Rohrbaugh, op. cit., p. 2387.
3. The CTP is thought to be polarization of the molecules of the amorphous phase of the wax. It can be created faster than its decay rate because during application of the field the rate of polarization is large due to the large field within the electret. However, due to the absence of field when a coated electret is short-circuited, this polarization decays more slowly than the time required for its formation. When the electret is open-circuited this CTP decay is more rapid, and this explains why it was so difficult to get surface charge readings on uncoated electrets during the first two minutes. Because of the rapid change in CTP the instrument could rarely be nulled until two to three minutes after high voltage was removed.

4. The rapid CTP decay is superimposed on the slower decay processes. After a period of storage while shorted the CTP again shows in part, because during the short the strong field near the electret surfaces tends to align molecules near the surface, the disorientation of which causes the reappearance of the CTP upon removing the short.

5. Isothermal polarization is just as effective in causing the polarization of the amorphous phase as is heat treatment. In fact heat treatment probably disorients much of the amorphous phase polarization, and at higher temperature the CTP would tend to disappear. In effect it shows
after heat treatment only because of the low temperature exposure after the oven has cooled.

6. Electrets containing the 18-carbon chain alcohol and acid should show a faster CTP decay because these hydrocarbon chains are somewhat smaller than those that naturally occur in the wax. It is difficult to tell from the experiments with the uncoated solution electrets if this expectation is so or not. Why these solutes would lower the surface charge due to the domains is not apparent. Perhaps their presence affects the height of the domain potential barrier.

7. The surface charges measured by the distance variation method seem high compared to the integrated frozen-in charges observed, and they are higher than those surface charges reported for carnauba wax electrets made at higher voltages.

However, these are not unreasonable values of the surface charge. Gross reports greater charges in at least one paper. Other workers may have not sufficiently dried the atmosphere over the electret, or it may be that in other cases much of the heterocharge was masked by homocharge.

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5Gross, op. cit., p. 869, Figure 4b.
8. and 9. It is not unusual that the coated electrets exhibit the opposite sign to that of the surface beneath them. A coated electret in effect never has its electrode removed. After formation, without even shorting it, this electrode will have a positive charge on it placed there by the polarizing power supply. As the heterocharge beneath it decays this positive charge should actually increase, since there are more charges not neutralized by heterocharge. This does happen (Figure 26). The CTP phenomenon is absent if the coat has never been shorted because the field is still in the electret, and the polar molecules are still aligned. Only if there is an ohmic leakage will the charge decrease with time. This was the case in curve C in Figure 26. In this experiment the glass ring around the electret acted as a leakage resistance across the electret. When the ring was not used, as in all other experiments, this decrease in charge was not observed.

If the surface is ever shorted, either immediately or later, Figure 28, the CTP begins its rapid decay. If the short is removed immediately this rapid decay is observed as a rise in the liberated induced charge on the surface, i.e., curves in Figure 27. If the short is maintained until the CTP decay is essentially complete, the surface charge rises only slowly from zero upon removal of the short. This slow rise represents the slow decay of the
domain polarization.

One would expect, in view of the above discussion, that the homocharge rise on coated electrets would be virtually identical to the heterocharge decay. However there are some differences. In Figure 30 where coated surface charge rise is plotted upside down along with uncoated decay, it is apparent that the long time constant decay is absent from the coated decay. If it were proceeding one would expect a gradual rise of about the same slope, but of opposite sign, as the uncoated decay after many hours. This leveling off of the coated charge rise to essentially a horizontal can be explained. If any ohmic leakage is present in uncoated electrets it acts in the same direction as the heterocharge decay, that is it decreases the observed charge. On the other hand, for coated electrets an ohmic leakage path would decrease the observed charge in opposition to the heterocharge decay which would increase the observed charge. It is possible that leakage would just about counter-balance the slow decay of the heterocharge. This often seems to be the case. It isn't so much that this is fortuitous as that a self-regulating mechanism sets in at high field values.

The leakage current of course depends upon the voltage of the coated surface. If the CTP decay is included in the charge increase then the leakage current goes up also. Eventually an equilibrium is reached in which leakage drains
away the charge on the coat at the same rate at which it is liberated by the decay beneath the coat. Thus, if the short is maintained beyond the CTP decay time or if the surface is reheated at this later time, then the heterocharge decay again becomes observable as a slow rise of the coated surface charge (see, for example, curves E and F, Figure 28). Thus the behavior of coated electrets is completely explained by the theory.

10. The surface charge behavior of coated solution electrets is not sufficiently different from carnauba wax electrets to permit any conclusions. Apparently the presence of the excess alcohol or acid molecules does not affect the characteristics of the amorphous region very much. It may be, of course, that these extra additives were incorporated into the crystalline domains primarily. If so they would not affect the CTP decay.

11. As in the case of uncoated electrets, the surface charge data, except that taken for very long times, do not show much about the frozen-in polarization. They mainly show the CTP and its decay.

12. Uncoated electrets do acquire a frozen-in charge when they are polarized. If TDC is attempted without coating the electret the contact resistance to the electrode is so large in most cases that most of the discharge is
lost internally. If the electret is coated before TDC the frozen-in charge can be seen. From the standpoint of reproducibility electrets are best polarized and measured when they are coated.

The integrated charge represented by the TDC is smaller than the surface charge would indicate, but it is comparable to the charges obtained from thermal discharge curves reported elsewhere. It may well be that the choice of $10^{11}$ ohms as electrometer resistance caused the internal loss of an appreciable fraction of the current. At room temperature the electret resistance is certainly much greater than $10^{11}$ ohms, but at 60-70 degrees this may not be true.

Because the CTP has apparently been discharged before the TDC is run, the TDC is a good measure of the part of the polarization which is not well measured by surface charge data. Thus the two methods complement each other in this study.

13. On the theory that domain dipoles are the cause of the frozen-in polarization it is understandable that reproducing this effect from one electret to another would be difficult. Very probably the domain sizes and number of domains per unit volume vary from one electret to another. The variation in domain size would cause a dispersion in relaxation times for the domains and a non-exponential decay (observed), and it might well cause the frozen-in
charge behavior to be a function of the past history of the electret.

If conditions were sufficiently controlled it is understandable that one particular electret could acquire very nearly the same quantity of frozen-in charge in two experiments, and what is more important to the shape of the TDC, it would liberate it at a reproducible rate each time as long as the reheating did not greatly alter the domains.

14. The way in which the additives affect the growth, size or population of the domains is not predictable, nor is it apparent from these data. Apparently the Al-18 electret had a sufficiently lower melting point than the pure carnauba wax so that its surface melted. This caused the Al-18(2) curve to be extremely unreliable. The solution electrets were more unreliable as far as TDC is concerned than the carnauba wax. This erratic behavior did not arise when the surface charges were measured; it occurred only when TDC was obtained. The theory cannot say why such behavior should be typical of solution electrets, but it can be pointed out that TDC taken too close to the softening temperature or melting point of these waxes may always be unreliable, and the solutes may have simply lowered the melting point.

15. If the observed trend, that electrets containing
acid decay more rapidly than carnauba wax electrets, is valid, it would mean that the domain size is smaller in the former, or that the potential barrier to rotation of the domains is less. This effect was not predicted.

It could be proposed that the more rapid decay was due to greater ion conductivity and that the long time constant heterocharge decay was thus indicated to be an ionic mechanism. This explanation is not supported by the fact that on the surface charge rise plots for coated A-18 electrets (curves F and G, Figure 29) there is the least indication of leakage of the surface charge. Surely a greater conductivity in the amorphous binder would have leveled these curves off as in curve B in this figure. Conductivity within the domains seems improbable. This author suggest that the addition of these solutes made little difference in the conductivity of the wax.

The delayed rise of discharge current for stored samples possibly means that the domains which remain oriented longest are those deeper in the electret rather than those near the surface. This is reasonable if the short-circuit decreases the field to zero in the interior, but not quite to zero near the electrodes because of the finite, even though small, electrode-dielectric gap. If the surface domains are disordered when the oven is turned on, the first discharge current must await the penetration of the heat
into the electret interior.

17. Isothermal exposure can cause frozen-in polarization only if the domains can be oriented to an appreciable extent at room temperature or if the domain surface barrier can be crossed by ions at this temperature. The theory supposes that neither process would be rapid at room temperature, although sufficiently long exposure (several days) should orient domains which still are polar. A two-day isothermal exposure was tried once, but this experiment employed the cracked electret (Figure 38), and the resulting frozen-in polarization may not have been characteristic of normal electrets. More work needs to be done on the temperature dependence of the rate at which an electret acquires the frozen-in polarization.

18. The behavior of the cracked electret has been discussed prior to the theory proposal. No other reasonable explanation of the crack effect has occurred to this author.

The above discussion relates the theory proposed to the data presented. The theory also is compatible with much of the data collected over the past forty years; this correlation can be seen by reviewing Chapter I. For example the greater permanence of the homocharge relative to the heterocharge is easily seen. It is easier for a dipolar
domain to rotate than for a domain with a net charge to move through the wax matrix and approach oppositely charged domains. Such net charged domains would be neutralized by ions from the binder grouping about them if the electret were left open so that the homocharge field was uncompensated. However, if the electrets were stored while shorted, such homocharges would have a great permanence because of their neutralization by the induced charge on the shorting electrodes and the absence of ion conduction in the electret due to absence of a field.

Gemant's experiments\textsuperscript{6} in which he dissolved abietic acid in paraffin are understandable on the basis of this theory. Any very polar substance in paraffin would be likely to be dispersed more in colloidal domains rather than in true solution in the nonpolar solvent. Gemant proposed long ago that such domains were the cause of the electret effect, but his idea was that the dipolar domains were the cause of the homocharge. He imagined that the stresses in the wax on the domains could reverse their polarity by a piezoelectric effect. He attributed the heterocharge to ion space charges.

In recent years Gemant has proposed a different theory\textsuperscript{7}

\textsuperscript{6}A. Gemant, \textit{Phil. Mag.}, XXIX (1935), 929.
\textsuperscript{7}A. Gemant, \textit{Direct Current}, I (1953), 145.
which was also mentioned in Chapter I. In it the oriented dipoles form domains which are responsible for the heterocharge. Then through a complex series of ion movements the heterocharge changes to homocharge. Although admittedly close to the theory proposed here, this mechanism would yield domains which were no more polar that the molecules of which they were composed. In the proposed theory the domains could have a very large dipole moment, since they could have a many-electron charge at each end of the domain.

Fillipova's results\(^8\) on the optical anisotropy of poly(methylmethacrylate) electrets is compatible with the proposed theory. So are the X-ray diffraction results of several authors, and the conclusions of Froiman and Fridkin.\(^9\)

If electrets can be produced by the application of magnetic fields, as Bhatnagar\(^10\) has reported, the theory proposed here is not capable of explaining the fact. No electrons in traps, free-radicals, or other causes of paramagnetism are postulated in the theory. Of course radio electrets or photoelectrets may well have a completely different formation mechanism and such magnetic


\(^9\)A. I. Froiman and V. M. Fridkin, Kristallografiya, I (1956), 342.

effects would not be surprising in this case.

C. For the Future

Although the gradual accumulation of knowledge about the probable mechanism by which substances become electrets has dispelled much of the mystery which once surrounded these objects, the field is still barely out of its infancy. If the electret effect is ever to be added to the many other field effects which are reported in textbooks with confidence, much more certainty must accompany the mechanism conclusions. Experimental techniques must become more sophisticated and reproducible. Forming of the electrets must be done in a much better way.

This section then offers suggestions for (1) experiments which would serve as tests for the theory proposed, (2) lines of investigation suggested by the theory, and (3) various other experiments which seem plausible.

Experiments which would test the theory. The most rigorous test of the dipolar domain theory would be an experiment designed to reorient the domains in an electret without heating them to as high a temperature as the formation temperature. If a polarized but decayed electret could be more easily repolarized at lower temperatures than a "virgin" electret which had never been polarized at all, then the polar domains would be strongly indicated.
Of course the previously polarized electret would have to have decayed at room temperature so as not to lose its ionic charges to the amorphous binder.

If the mechanism seemed to explain the behavior of plastic electrets, then the actual observation of the domains by some photomicrographic technique might be possible to settle the question of their orientation in the field.

Finally preparation of electrets might be attempted with single crystals of organic substances which were pure simple substances. This theory would predict that homogeneous single crystals would not attain a long time constant heterocharge as does carnauba wax. However, sandwiches of carefully machined single-crystal pieces fitted together might become electrets by the crack effect.

In order to study the crack effect further, a study which would not necessarily test the theory of normal electrets, many experiments can be suggested. Long thin cylindrical electrets which have been cracked in several places across their small dimension could be produced. Another easier method would be the production of ordinary disc electrets without coatings. Cracking them across the disc, as they naturally crack, and painting the electrodes on each piece, rather than on the top and bottom, would simulate a horizontally cracked electret. It has also
been suggested that sealing a thin dielectric film, such as Saran wrap, into the wax might produce the effect.

**Lines of investigation suggested by the theory.** If a simpler and better characterized binder substance were found to act as the amorphous phase, then polar substances could perhaps be dispersed in this binder colloidal so as to act as the domains. This would not be easy to do.

Infrared studies of transparent electrets are long overdue. Since in a reasonably thick electret almost no infrared energy could be transmitted, perhaps this study could be accomplished by imbedding tiny thermistor elements in various positions in the electret to act as infrared detectors when selected wavelengths were focused on the electret surfaces.

It is not inconceivable that techniques could be developed by which the domains could be separated from the matrix in carnauba wax. Perhaps a solvent extraction technique might do this. This line of investigation admittedly sounds like more trouble than it is worth.

**Other suggestions.** In transparent electrets many interesting studies are possible. One which suggests itself is to look for the Kerr effect within the body of

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11 Private communication from P. E. Koenig.
the electret. In all such optical studies it is important to remember that the internal field of the electret is low when it is shorted, high when open-circuited. This suggests that coated electrets would not be as suitable for such work as would uncoated ones from which the electrodes could be completely removed.

Although no differences were found in CTP decay before and after polarization, it seems probable that there must be some difference. A more sophisticated technique for studying the CTP, i.e., the electrical characteristics of the amorphous binder, seems to be indicated. Perhaps the application of short duration electrical pulses of 100 volts or sc, followed by an oscilloscopic study of the inter-pulse currents would be an effective tool. Modern electronics should be able to devise circuitry for a non-destructive measure of the frozen-in polarization via the response of the binder to some sort of low frequency signals.

Continuing TDC studies to test the validity of the ideas presented in this work, and the design of electronic measuring techniques as described above constitute the future plans of this author.
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APPENDIX
The Calculation of Surface Charge
from Distance Variation Data

From equation (5), page 111, the slope of the $V^{-1}$ versus $d_1$ plots should be:

$$slope = \frac{2.8}{4\pi \varepsilon_0 L(1.3 \times 10^{-7} \text{ m})}$$

The $1.3 \times 10^{-7}$ meters which appears here is the distance from the vibrating electrode to the third electrode. This distance entered the equation because it is assumed that the null condition, which for the listed $V$ is valid, is as follows:

$$E_{\text{ext}} = E_{\text{null}}$$

where $E_{\text{ext}}$ is the field at the vibrating electrode due to the electret, and $E_{\text{null}}$ is the field at the vibrating electrode due to the voltage on the third electrode. Since

$$E_{\text{null}} = \frac{V_{\text{null}}}{1.3 \times 10^{-7} \text{ meters}}$$

then

$$E_1 = E_{\text{null}} = \frac{V}{1.3 \times 10^{-7}}.$$

Now taking a typical example, the slope of Figure 23, curve D is about:

$$slope \approx \frac{(8 - 2) \times 10^{-3} \text{ volts}^{-1}}{(7 - 2) \text{ revolutions}} = \frac{6 \times 10^{-3} \text{ volts}^{-1} x 10 \text{ cm/m}}{5 \text{ rev} x .025 \text{ in/rev} x 2.54 \text{ cm/in}}$$
slope = 19 volts $^{-1}$ m $^{-1}$

Now we can put:

$$19 \text{ volts }^{-1} \text{ m }^{-1} = \frac{2.8}{4\pi \sigma L (1.3 \times 10^{-7} \text{ m})}$$

$$\sigma = \frac{2.8 \text{ volts m}}{4\pi L (1.3 \times 10^{-7} \text{ m})(19)}$$

$$\sigma = \frac{2.8 \times 8.85 \times 10^{-12} \text{ C}^2/\text{Nm}^2 \times \text{Joules/C}}{4 \times 3.14 \times 6 \times 10^{-3} \text{m} \times 1.96 \times 10^{-3} \times 19}$$

where $L = 0.6 \text{ cm} = 6 \times 10^{-3} \text{ m}$.

and $8.85 \times 10^{-12} \text{ C}^2/\text{Nm}^2$ is the permittivity of free space.

Finally

$$\sigma = 8.8 \times 10^{-8} \text{ C/cm}^2$$

$$\sigma = 88 \text{ nanocoulombs/cm}^2$$
VITA

Roy White Clark was born in Oak Park, Illinois on November 11, 1930. When he was nine his family moved to Shelbyville, Tennessee, where he graduated from Bedford County Central High School in June, 1948.

He served in the United States Air Force from 1948 through 1952 as an enlisted man where he was trained to be a radio mechanic. In June, 1952 he was honorably discharged, and soon passed the examination to receive a first class commercial radio operators license.

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Title of Thesis: The Heterocharge in Carnauba Wax Electrets

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