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PROPERTIES OF ELECTRETS

by

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A thesis submitted to the Faculty of
Graduate Studies in partial fulfilment
of the requirements for the degree of
Doctor of Philosophy

Carleton University

Ottawa, Ontario.

May, 1964

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ABSTRACT

The results of an investigation of the electret properties of 1-tetradecanol are presented. Measurements were made of the charging and discharging currents, the macroscopic dipole moment, and the internal potential differences of the electrets. The results are explained in terms of a two charge theory; the observed dipole moment being due to the superposition of a real surface charge and space charges within the volume of the electret. The discharge current arises from the decay of the surface charge.

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CONTENTS

	<u>PAGE</u>
CHAPTER 1 <u>PURPOSE OF THE INVESTIGATION</u>	1
CHAPTER 2 <u>INTRODUCTION</u>	2
2.1 Historical Outline	2
2.2 Theories of the Nature of Electrets	10
2.3 Experimental Methods	15
2.4 Choice of Substance to be Studied	21
2.5 The Scope of the Investigation	22
CHAPTER 3 <u>APPARATUS</u>	24
3.1 Torsion Balance	24
3.2 Current Measurements	31
3.3 Probe Measurements	33
3.4 The Controlled Temperature Chamber	38
CHAPTER 4 <u>EXPERIMENTAL PROCEDURE</u>	42
4.1 Preparation of Samples	42
4.2 Electrification	42
4.3 Measurement of Discharge Current	43
4.4 Torque Measurements	47
4.5 Probe Measurements	49
CHAPTER 5 <u>RESULTS</u>	51
5.1 Current Measurements	51
5.2 Torque Measurements	81
5.3 Probe Measurements	102

5.4 Reliability of Experimental Results	131
CHAPTER 5 DISCUSSION OF RESULTS AND CONCLUSIONS	133
BIBLIOGRAPHY	155
APPENDIX A	157
APPENDIX B	159
APPENDIX C	160
APPENDIX D	160

LIST OF TABLES

<u>TABLE</u>		<u>PAGE</u>
1	Discharge current as a function of time for 11 and 4 hour electrification.	44
2	Charging current as a function of time (+26.0°C).	52
3	Charging current as a function of time (+14.0°C).	53
4	Charging current as a function of time (+8.5°C).	54
5	Charging current as a function of time (-3.0°C).	55
6	Charging current as a function of time (-11.0°C).	56
7	Charging current as a function of time (-28.0°C).	57
8	Discharge current as a function of time (+26.0°C).	64
9	Discharge current as a function of time (+20.0°C).	65
10	Discharge current as a function of time (+15.0°C).	66
11	Discharge current as a function of time (+8.5°C).	67
12	Discharge current as a function of time (-3.0°C).	68
13	Discharge current as a function of time (-11.0°C).	69
14	Discharge current as a function of time (-28.0°C).	70
15	Charging current at +14.0°C, 10kV/cm. Discharge current at -15.0°C and reheating at 1.0°C/min.	73

<u>TABLE</u>		<u>PAGE</u>
16	Charging current at +14.0°C, 10kV/cm. Discharge current at -15.0°C and reheating at 0.5°C/min.	74
17	Charging current at +14.0°C, 10kV/cm. Discharge current at -15.0°C and reheating at 2.0°C/min.	75
18	Charging current at +10.0°C, 3.3kV/cm. Discharge current at -15.0°C and reheating at 0.5°C/min.	76
19	Dipole moment of an electret, forming field 10kV/cm, temperature -15.0°C.	82
20	Dipole moment of an electret, forming field 5kV/cm, temperature -15.0°C.	83
21	Dipole moment of an electret, forming field 7kV/cm, temperature -15.0°C.	84
22	Dipole moment of an electret, forming field 5kV/cm, temperature -7.5°C.	85
23	Dipole moment of an electret, forming field 7kV/cm, temperature -7.5°C.	86
24	Dipole moment of an electret, forming field 5kV/cm, temperature +0.6°C.	87
25	Dipole moment of an electret, forming field 6kV/cm, temperature +0.6°C.	88
26	Dipole moment of an electret, forming field 7kV/cm, temperature +0.6°C.	89
27	Dipole moment of an electret, forming field 10kV/cm, temperature +0.6°C.	90

<u>TABLE</u>		<u>PAGE</u>
28	Dipole moment of an electret, forming field 1kV/cm, temperature +8.8°C.	91
29	Dipole moment of an electret, forming field 3.5kV/cm, temperature +8.8°C.	92
30	Dipole moment of an electret, forming field 10kV/cm, temperature +8.8°C.	93
31	Dipole moment of an electret, forming field 5kV/cm, temperature +16.0°C.	94
32	Dipole moment of an electret, forming field 6kV/cm, temperature +16.0°C.	95
33	Dipole moment of an electret, forming field 10kV/cm, temperature +16.0°C.	96
34	Probe potential during electri- fication, forming field 10kV/cm, temperature -7.5°C.	103
35	Probe potential during discharge, forming field 10kV/cm, temperature -7.5°C.	104
36	Probe potential during electri- fication, forming field 5kV/cm, temperature -7.5°C.	105
37	Probe potential during electri- fication, forming field 5kV/cm, temperature +0.5°C.	106
38	Probe potential during electri- fication, forming field 10kV/cm, temperature +0.5°C.	107
39	Probe potential during electri- fication, forming field 7kV/cm, temperature +0.5°C.	108

TABLEPAGE

40	Probe potential during discharge, forming field 7kV/cm, temperature +0.5°C.	109
41	Probe potential during electri- fication, forming field 10kV/cm, temperature +8.5°C.	110
42	Probe potential during electri- fication, forming field 5kV/cm, temperature +8.5°C.	111
43	Probe potential during electri- fication, forming field 10kV/cm, temperature +15.0°C.	112

LIST OF FIGURES

<u>FIGURE</u>		<u>PAGE</u>
1	A short circuited electret.	4
2	Graph of electret surface charge: due to Eguchi.	5
3	Diagram of internal polarization and surface charge: due to Adams.	10
4	Potential distribution in electrets during formation: due to Gemant.	12
5	Circuit used in current measurements.	18
6	Diagram of electret in the field of the torsion balance.	25
7	Photograph of torsion balance in the controlled temperature chamber.	27
8	Photograph of the interior of the torsion balance.	28
9	Line drawing of the torsion balance.	29
10	A modified coaxial connector.	33
11	The electrostatic null detector.	35
12	The potential divider circuit.	36
13	Teflon mold with probes.	39
14	Discharge current as a function of time for 11 and 4 hour electrification.	45
15	Charging current as a function of time (+26.0°C).	58
16	Charging current as a function of time (+14.0°C).	59
17	Charging current as a function of time (+8.5°C).	60
18	Charging current as a function of time (-3.0°C).	61

<u>FIGURE</u>		<u>PAGE</u>
19	Charging current as a function of time (-11.0°C).	62
20	Charging current as a function of time (-28.0°C).	63
21	Discharge current as a function of the reciprocal of time for varying temperatures.	71
22	Discharge current as a function of time at -15.0°C and during reheating at $1.0^{\circ}\text{C}/\text{min}$. (forming field $10\text{kV}/\text{cm}$).	77
23	Discharge current as a function of time at -15.0°C and during reheating at $0.5^{\circ}\text{C}/\text{min}$. (forming field $10\text{kV}/\text{cm}$).	78
24	Discharge current as a function of time at -15.0°C and during reheating at $2.0^{\circ}\text{C}/\text{min}$. (forming field $10\text{kV}/\text{cm}$).	79
25	Discharge current as a function of time at -15.0°C and during reheating at $0.5^{\circ}\text{C}/\text{min}$. (forming field $3.3\text{kV}/\text{cm}$).	80
26	Dipole moment of an electret at -15.0°C for forming fields of 5, 7, and $10\text{kV}/\text{cm}$.	97
27	Dipole moment of an electret at -7.5°C for forming fields of 5, 6, 7, and $10\text{kV}/\text{cm}$.	98
28	Dipole moment of an electret at $+0.6^{\circ}\text{C}$ for forming fields of 5, 6, 7, and $10\text{kV}/\text{cm}$.	99
29	Dipole moment of an electret at $+8.8^{\circ}\text{C}$ for forming fields of 1, 3.5, and $10\text{kV}/\text{cm}$.	100
30	Dipole moment of an electret at $+16.0^{\circ}\text{C}$ for forming fields of 5, 6, and $10\text{kV}/\text{cm}$.	101

FIGUREPAGE

31	Probe Potential during electrification 10kV/cm; -7.5°C .	113
32	Potential distribution during electrification 10kV/cm; -7.5°C ; at times of 120 minutes and 240 minutes.	114
33	Probe potential during discharge 10kV/cm; -7.5°C .	115
34	Probe potential during electrification 5kV/cm; -7.5°C .	116
35	Probe distribution during electrification 5kV/cm; -7.5°C ; at times of 60 minutes, 120 minutes and 240 minutes.	117
36	Probe potential during electrification 5kV/cm; $+0.5^{\circ}\text{C}$.	118
37	Probe distribution during electrification 5kV/cm; $+0.5^{\circ}\text{C}$; at times of 60 minutes, 120 minutes and 240 minutes.	119
38	Probe potential during electrification 10kV/cm; $+0.5^{\circ}\text{C}$.	120
39	Probe distribution during electrification 10kV/cm; $+0.5^{\circ}\text{C}$; at times of 60 minutes, 120 minutes and 240 minutes.	121
40	Probe potential during electrification 7kV/cm; $+0.5^{\circ}\text{C}$.	122
41	Probe distribution during electrification 7kV/cm; $+0.5^{\circ}\text{C}$; at times of 60 minutes, 120 minutes and 240 minutes.	123
42	Probe potential during discharge 7kV/cm; $+0.5^{\circ}\text{C}$.	124
43	Probe potential during electrification 10kV/cm; $+8.5^{\circ}\text{C}$.	125
44	Potential distribution during electrification, 10kV/cm; $+8.5^{\circ}\text{C}$; at times of 60 minutes, 120 minutes and 240 minutes.	126

<u>FIGURE</u>		<u>PAGE</u>
45	Probe potential during electrification 5kV/cm; +8.5°C.	127
46	Potential distribution during electrification 5kV/cm; +8.5°C; at times of 60 minutes, 120 minutes and 240 minutes.	128
47	Probe potential during electrification 10kV/cm; +15.0°C.	129
48	Potential distribution during electrification 10kV/cm; +15.0°C; at times of 60 minutes, 120 minutes and 240 minutes.	130
49	Temperature of Cabinet as a function of time.	48
50	Charge distribution within an electret.	147

CHAPTER 1

PURPOSE OF THE INVESTIGATION

The aim of the investigation was to study the behaviour of electrets formed from a substance of known structure in order to determine the location of charges that give rise to the electret effect.

CHAPTER 2

INTRODUCTION

2.1 Historical Outline

The term electret was coined by Heaviside in his Electrical Papers (1885). He used the term to describe any material that, after the removal of an applied field, retained an electric polarization. He made no distinction between substances that retain their polarization for a fraction of a second and those that retain it for many hours.

In 1919 Eguchi (1919, 1920, 1921, 1925) manufactured the first example of what is now known as an electret. He had been investigating the conductivity of waxes and he observed that some samples had an appreciable conductivity when liquid, but practically zero conductivity when solid. He suspected that if these substances were allowed to solidify in an electric field there would be some retention of polarization. He gave no reason for this supposition, but it seems likely that he thought the charge carriers responsible for conduction in the liquid state would be trapped in an uneven distribution when the wax solidified. Eguchi took a mixture of equal parts of carnauba wax and resin with a small addition of beeswax and allowed this to solidify in an electric field. On removal of the field Eguchi found that the wax exhibited a charge on its faces, a negative charge on the face that

had been in contact with the anode and a positive charge on the surface that had been in contact with the cathode. The charges were measured by measuring the induced charge on a metal plate placed on the surface of the wax. When not being used for measurements of the surface charge, the disc was stored between two short circuited metal plates (Fig. 1). The measured surface charge on the wax decayed with time to zero and then increased in the opposite direction; that is, to a positive charge on the surface that had been in contact with the anode and a negative charge on the surface that had been in contact with the cathode. The magnitude of these charges rose towards an approximately uniform limited value, the value remaining almost constant after two days (Fig. 2).

After this growth the charge was found to remain constant for as long as three years. Eguchi carried out a series of tests on the wax samples to determine how this charge was stored. He found that planing the surfaces, washing the surface with solvents, and irradiation with x-rays temporarily removed the charge, but after a few hours it recovered its previous value. Cutting a charged disc laterally between its poles produced two charged discs of lower charge. Eguchi found that if the shielding electrodes were removed from the wax the surface charge decayed to a lower value which then remained constant. Replacing the shield restored the original charge. From these observations Eguchi concluded that the electrification was not wholly a surface phenomenon and must be in part a

FIG. 1

A short circuited electret.

FIG. 2

Surface charge on electret due to Eguchi.

volume effect. As there seemed to be some similarity between this electrical polarization of the wax and the magnetization of ferromagnetic materials, Eguchi chose Heaviside's term "electret" analogous to "magnet" to characterize these new effects. Eguchi's results have been well confirmed over the years, and this long term charge retention has been observed in many dielectrics. Eguchi's original mixture contained the materials that he had been investigating in conduction experiments and it had the advantage that, unlike the separate waxes, the resin-wax mixture was easily cast into a flaw-free sample. Unfortunately, this original choice of materials seems to have been blindly followed by later workers, who have almost exclusively used complex and indeterminate compounds. This has led to an impression, even among specialists, that the electret effect is a strange phenomenon, not the behaviour to be expected from a "normal dielectric".

To simplify the description of the electret phenomenon the following convention has been adopted: A homocharge is a surface charge of the same polarity as the adjacent forming electrode and a heterocharge is a surface charge of the opposite polarity to the adjacent forming electrode. This nomenclature was originally introduced by Gemant (1935).

Mikola (1925) classified dielectrics by their reaction to D.C. fields, using four classifications:

- i) Those materials showing heterocharge only

- ii) Those materials showing heterocharge and homoccharge
- iii) Those materials showing a surface charge only
- iv) Those materials showing no persistent charge.

In more recent work Wiseman and Feaster (1957) state that all solid insulators exhibit the electret effect, however, the rate of change of the charge distribution is often too fast or too slow to measure with conventional apparatus.

This statement is valid if the term electret is taken to mean any substance that exhibits charges of opposite polarity on its faces as Heaviside coined the word. However, the word electret has come to mean a body that retains these charges for times of the order of many minutes (as in the case of Eguchi's first electrets) and it seems likely that there is some charge-separation mechanism common to the substances that form electrets at room temperatures, obscured by the nature of substances previously used.

When an electric field is applied to an electret forming substance, or indeed, to any dielectric, a current flows and this current decays with time. If, after the removal of the forming field, from an electret, the electrodes are connected together, a current flows between them in the opposite direction to the charging current. This current, referred to as the discharge current, decays with time, and provides means of investigating the behaviour

of electrets. Measurements of these currents have been made in many of the investigations of electrets; for example, E.P. Adams (1927), G. Gross (1949), P. Jaeger (1935), H. Frei and A. Groetzinger (1936), and R. Gerson and J. Rohrbaugh (1955).

The earlier workers followed Eguchi's example and allowed the chosen material to solidify from a melt in an electric field between two electrodes. This procedure is not entirely satisfactory, as many of the substances chosen do not form flawless samples when allowed to solidify in this manner and conditions are not reproducible. Some workers, such as Mikola (1925), attempted to produce electrets by electrification at room temperature but did not pursue the investigation when they found that the measured surface charges on these electrets was much smaller than on electrets produced by Eguchi's method. This concern with producing a large effect rather than a reproducible effect with a minimum of complicating factors is typical of the approach of the earlier investigations. In an attempt to produce a large electret effect with samples that could be more carefully prepared Gross (1949) applied an electric field to solid carnauba wax at a temperature just below the softening point of the wax and allowed the wax to cool in this field. This produced electrets as highly charged and permanent as those produced from liquid wax. As the electrification of solid samples permits more careful preparation and repeated

use of one sample, yielding more closely reproducible results than those previously reported, electrification of solid samples has been used in all recent investigations, for example, Gross and DeMoraes (1962), Gerson and Rohrbaugh (1955), Perlman (1960), Wiseman and Feaster (1957), Cross and Hart (1964).

In fact it is not necessary to allow the samples to cool in the electric field. It has been shown (e.g. Wiseman and Feaster, and Perlman) that the application of an electric field to an electret-forming substance maintained at a constant temperature produces electrets. These electrets are not as highly charged as those produced by Gross's method, but it is sufficient that the charges be measurable. The use of a constant temperature controls one parameter to which the electret effects are highly susceptible. The lower charge separation achieved is not of any great importance provided that the study is not directed towards a practical application.

2.2 Theories of the Nature of Electrets

The first theory of the electret effect was suggested by Adams (1927). He assumed that the heterocharge was the result of the orientation of dipoles with long relaxation times and the homocharge was due to real surface charges that collected to compensate the heterocharge (Fig. 3). He supposed that the internal alignment of

FIG. 3

dipoles gradually becomes random after the removal of the forming field, leaving the homocharge predominating.

Gemant (1955) pointed out that a basic fault in Adams' theory was the need to assume an extremely high value of initial polarization to explain the magnitude of the observed homocharge; the polarization necessary could not be produced even by the total alignment of all the molecular dipoles in the sample.

As an alternative explanation of the homocharge, Gemant proposed that there was a strain set up in the wax as it cooled and this produced piezoelectric charges on the surface. This idea must be rejected, as electrets have been made from very soft waxes that could not possibly show piezoelectric effects. Moreover, it is possible to produce electrets without cooling the samples, and in these cases no mechanical strain develops. Gemant (1935) considered it likely that the heterocharge was due, not to an alignment of dipoles, but to the formation of space charges near the electrodes. He placed metal probes in carnauba wax and measured the potential of the probes by a null method. His results are shown in Figure 4. The curves indicate for the liquid wax (M.P. 80°C) that there are space charges developed near both electrodes and for the solid wax at the cathode only. Thiesen, Winkel and Herman (1936) electrified carnauba wax and made measurements of the surface charge by lifted electrode techniques. They planed off layers of the wax and measured the remaining

FIG. 4

Potential distribution in electrets during formation. (after Gemant)

charge on the wax after each layer was removed. They obtained results similar to those of Gemant but the experimental technique involves such drastic treatment of the sample that the results must be regarded as dubious.

In 1936 Thiesen, Winkel and Herman published the results of an investigation into the space charge distribution and surface charges of electrets. They proposed that the measured surface charge resulted from a superposition of two processes; one an internal polarization due to ion displacement and the other a surface charge due to ionization of the air gap between the electrodes and the surface of the sample. This theory was developed more fully by Gross (1949). He investigated the behaviour of carnauba wax electrets measuring the surface charge and the charging and discharging currents. He found evidence of conduction between the electrodes and the sample at high field strengths and in these samples the homocharge appeared. At lower field strengths there was no evidence of breakdown and the samples showed only a heterocharge. His results support the theory that the measured surface charge of an electret is due to the superposition of two effects one a volume polarization and the other a true surface charge arising from breakdown in the air gap between the electrode and the dielectric. This theory, referred to as the "two charge theory" is usually attributed to Gross although his work was a development of the work of Thiesen, Winkel and Herman. The nature of the so-called volume polarization is a point of disagreement between various

workers. In a later paper (1962) Gross and DeMoraes investigated the total charge liberated when sections of differing thickness from different regions of the electret were discharged. He found that the total charge liberated by a section was independent of its thickness and its original position in the electret. He concluded therefore, that the discharge current was due to the collapse of a uniform volume polarization. However, the probe measurements of Gemant (1935), Antennen (1955) and Van der Linde (1959) and the measurements of the surface charge after removing layers of the electrets (Thiessen, Winkel, and Herman - 1936) all indicate that space charges exist near the electrodes.

Gerson and Rohrbaugh (1955) investigated the dielectric constant of carnauba wax electrets and found that it was not significantly different from the value for non-electrified wax. This evidence is also in contradiction to theories that the electrification process produces a uniform volume polarization due to dipole alignment. They found that if a carnauba wax electret was stored until its discharge current was almost zero and then sprinkled with iron filings the discharge current was increased by a factor of a thousand. This result was not discussed in any detail but they stated that it was not readily explicable on the basis of either space charge or dipole theory and they suggested that some electron trap mechanism was responsible for the polarization. However, this explanation ignores the possibility

that the discharge current might be a surface effect and then a granular conducting material could be expected to change the surface conditions considerably.

The present opinion expressed in several papers on the subject (Gross - 1962, Perlman - 1960, Van der Linde - 1959, Gerson and Rohrbaugh - 1955) is that the observed surface charges are due to the superposition of a surface charge and a volume polarization, and the discharge current is said to be due to the decay of the volume polarization. Opinion is divided on whether the volume polarization is due to dipole alignment, electron trapping, or some other trapping or ionization mechanism.

2.3 Experimental Methods

The investigations of electret properties have principally involved measurement of the surface charge, charging and discharging currents and internal potential differences in the sample.

2.3.a Shielding

The changes taking place in an electret depend upon the electric fields acting. In a dielectric with a surface the internal field depends upon the shielding conditions. If a metal electrode is placed on each face

and the two electrodes short circuited the internal field is very close to zero (Appendix A). If the surfaces are uncovered the internal field is given by

$$E = \frac{\sigma}{\epsilon_0}$$

In earlier work the aim seemed to be to maintain as high a measured surface charge as possible. It was found that in the short circuited state the measured surface charge was highest and therefore the electrets were normally stored between short circuited metal electrodes. If, as in the present investigation, the aim is to throw some light upon the mechanism of the electret process it is not essential to use the system that produces the highest surface charge and therefore measurements of unshielded electrets are suitable; however, if the shielding conditions are changed often during the experiment it is difficult to assess the effect of the changing internal field and therefore measuring techniques of this type should be avoided wherever possible.

2.3.b Current Measurements

The measurement of charging and discharging currents necessitates the fitting of metal electrodes to the sample. During these measurements the electrodes need not be moved and the shielding conditions can remain unaltered during the measurements.

To measure the currents flowing a direct-

current measuring device is inserted in series with the sample (fig. 5). If the resistance of the device is low compared with the resistance of the sample the measuring procedure does not affect the electrifying or shielding conditions. As the electret impedance is usually of the order of 10^{10} ohm this condition is easily met.

2.3.c Probe Measurements

Measurement of the internal potential differences have been measured only by the use of metal probes. This technique is likely to alter the condition of the electret and great care has to be exercised. To keep the disturbance to a minimum the probes must be as small as possible and limited in number, and the potential measuring device must draw as near to zero current as possible. The probe method provides direct information on the interior conditions of the electret and is an invaluable tool.

2.3.d Surface Charge Measurements

The measurement of the surface charge is usually carried out by the "lifted electrode" technique. Two electrodes are placed on the surface of an electret and an electrometer is connected between them. One electrode is then lifted from the surface of the electret and

FIG. 5

Circuit used in current measurements.

the potential reading of the electrometer is noted. The induced charge on the electrode can then be calculated if the capacitance of the measuring system is known.

There are two disadvantages to this technique. Firstly the shielding conditions of the electret are changed when the measurement is made, and secondly the charge measured is the charge on the electrode and this is not necessarily equal to the surface charge on the electret. There is no way of overcoming the change in shielding conditions. If the electret is being investigated in the shielded state, its shielding must be removed during the period of measurements; and if in the unshielded state, it must be shielded when the electrodes are placed on the surface to accumulate charge. If the changes in the electret take place slowly, then the disturbance may not be too severe, but this system would be unsatisfactory for a rapidly changing electret. The second difficulty can lead to serious errors in the results. As the electrode is removed from the surface of the electret it is possible for the field between the electrode and the surface to exceed the breakdown potential of the air, and if this happens there is a loss of charge from the electrode. The result is that the maximum measured charge on an electret depends upon the breakdown field of the atmosphere surrounding the sample. This has been demonstrated by Wild and Strathan (1957) who studied the variation of the measured electret surface

charge with air pressure. They found that the graph of measured surface charge against air pressure was the same shape as a graph of the breakdown field of air against air pressure. By connecting a suitable capacitor in parallel with the electrometer it is possible to reduce the potential of the electrode and make this method more reliable. Another factor which can make the charge on the electrode different from the electret surface charge is the accumulation of static charges when the electrode slides against the surface of the sample. This electrification process is discussed by Loeb (1958). To avoid this trouble the lifted electrode must be very carefully controlled so that no sliding can take place and this greatly complicates the construction of the apparatus. Because of these difficulties it seemed advisable for us to look for further methods of investigating the charge distribution.

2.3.e Torque Measurements

An electret exhibits charges of opposite polarity on its faces and therefore is an electric dipole. If a dipole is placed in an electric field it experiences a torque, the magnitude and direction of which is given

by
$$\underline{\tau} = \underline{\mu} \times \underline{E}$$

where $\underline{\tau}$ is the torque, $\underline{\mu}$ is the dipole moment of the electret, and $\underline{E}$ is the electric field.

This property of an electret was used by Gemant (1940) to construct an electrometer in which the unknown potential provided the field and the deflection of an electret suspended by a torsion suspension indicated the magnitude of the potential. If the electret is placed in a known field, and the torque on it is measured, the dipole moment can be calculated. This technique can be used to measure the macroscopic dipole moment, and hence the apparent surface charge, of an electret, without disturbing the electret. The method is most suitable for studying unshielded samples and we have used it only in this form. The apparatus for measuring the dipole moment can be easily and cheaply constructed and it does not have the disadvantages of the lifted electrode method. A simple form of the apparatus is described in an earlier note by Cross and Hart (1964) and the apparatus used in this investigation is further described in Chapter (3).

2.4 Choice of Substance to be Studied

The material most widely studied in work on electrets is carnauba wax. This is a very hard wax, extensively used in commercial polishes, and it was one component of Eguchi's original mixture. These properties however, are hardly sufficient qualifications for its selection as a material for detailed study. As the wax is

a natural product obtained by very primitive processes from palm leaves, the chemical composition varies from batch to batch. The impurity content of the wax is extremely high and with a sample of "best yellow carnauba wax", fine filtering extracted a considerable quantity of gross impurities, including insect wings. The other materials investigated have almost all been quite complex natural or artificial polymers.

If one hopes to throw some light on the mechanism of the electret effect it is advisable to choose a material with as simple a composition as possible. As the constituents of carnauba wax are long chain alcohols (for example, of analysis, Appendix B) it seemed probable that a single pure alcohol would exhibit the electret effect and these compounds can be readily obtained in a pure state from commercial sources.

The structure and dielectric properties of these compounds have been widely studied. These considerations led us to choose a solid primary alcohol, 1-tetradecanol, as the subject of our investigation. This alcohol $\text{CH}_3(\text{CH}_2)_{12}\text{CH}_2\text{OH}$ melts at 36.0°C and is the simplest member of the series that is solid at room temperature.

2.5 The Scope of the Investigation

From the considerations in the previous para-

graphs, we decided to investigate the electret behaviour of 1-tetradecanol by measuring the charging and discharging currents, the torque on the electret and the internal potential differences, varying the temperature of electrification and storage, and the strength of the forming field.

CHAPTER 3

APPARATUS

3.1 Torsion Balance

3.1.a Principle of Operation

If a disc with an electric dipole moment in the direction of its axis is placed in an electric field it will, in general, experience a torque. If such a disc is suspended in a uniform electric field, so that it can rotate about a diameter, it will rotate until it is at equilibrium under three torques due to the interaction of the electric field with the intrinsic dipole moment of the disc, the induced charges due to the measuring field, and the twist of the suspension.

In general the magnitude of the torque due to induced charges is difficult to estimate, but when the axis of the disc is at right angles to the field, the geometry is symmetrical and there is no torque resulting from these charges; and the torque due to the intrinsic dipole moment is a maximum. Measurements are, therefore, made with the disc in this position. See Fig. (6).

The disc is suspended by a torsion suspension in a uniform electric field and the torsion head is rotated until the axis of the disc is at right angles

FIG. 6

Diagram of electret in the field of the torsion balance.

to the field. The direction of the field is then reversed and the torsion head moved until the axis of the electret is again at right angles to the field. The difference between the two positions of the torsion head is twice the angle of twist of the suspension needed to counteract the torque on the electret due to the interaction of the applied field with the dipole moment in the direction of the axis of the disc.

3.1.b Construction

The torsion balance was so constructed that in addition to measuring the torque on an electret it provided a cell in which the sample could be held while all other measurements were made.

The balance is illustrated in figure (7), (8) and (9). The torsion head is graduated in minutes of arc and is practically free from "backlash". The sliding electrodes can be moved from outside the temperature chamber by means of rods, in such a way that the electrode faces remain parallel. The electrical connection to these electrodes is made with coaxial leads. The two parallel brass plates, referred to as the field plates, provide an approximately uniform field in which the sample can be suspended. The suspension used is a 0.0015" gold strip Leeds and Northrup Galvanometer suspension, which can be easily replaced

FIG. 7

FIG. 8

FIG. 9
Torsion balance.

by another having the same torsion constant if one should be broken. The torsion constant of these suspensions is 0.09 dyne cm/radian. The sample is fitted into a Teflon ring attached to the lower end of a bakelite rod which is a push fit into the brass fitting which terminates the suspension. This brass fitting can be held by the clamp shown. When the clamp is closed, the sample is lifted so that it lies between the two sliding electrodes and the weight is removed from the suspension. Plane mirrors are attached to the sample holder and the front field plate. When these mirrors are parallel the axis of the sample is at right angles to the field produced by the field plates.

3.1.c Operating Procedure

To determine the torque on an electret in the electric field of the balance, a measurement is made of the angle of twist of the suspension required to hold the electret with its axis at right angles to the field. The light from a lamp and scale system is allowed to fall on the mirrors on the sample holder and the front field plate. When these two mirrors are parallel the axis of the electret is at right angles to the field and the two reflected light beams coincide. A potential difference is applied to the field plates and the tension head adjusted until the mirrors are parallel. The direction of the field is then reversed and the mirrors

again brought parallel. The reading of the torsion head is noted for each case. The smallest dipole moment that can be measured with the balance is approximately 10^{-3} e.s.u. (For calculation see Appendix C).

3.2 Current Measurements

The charging and discharging currents of the samples are measured using a simple two terminal system (Fig. 5). As the currents are small it is necessary to use an electrometer technique. The electrometer used was a General Radio, Type 1230-A D.C. Amplifier and electrometer. This instrument has an input resistance variable in steps of 10 from 10^4 to 10^{10} ohm, and voltage ranges from 30mV to 10V and therefore can be used to measure currents in the range 10^{-14} to 10^{-3} Amperes. The connection from the sample to the electrometer is a coaxial lead with a polyethelene dielectric and teflon dielectric in the fittings; this has a leakage resistance of approximately 10^{13} ohm; the leakage current can be ignored as the highest input impedance used is 10^{10} ohm.

During measurements it is necessary to check the zero of the electrometer at intervals. The "zero check" button on the instrument opens the input circuit. When the electrometer is being used to measure currents opening the input circuit allows the full source potential to develop across the input terminals and interrupts

the current flow. This could cause damage to the instrument and is an undesirable interruption of the current, therefore it is preferable to provide a means of short circuiting the input terminals. A simple effective means of short circuiting the input terminals and power supply for discharge current measurements is provided by the modification of a coaxial connector shown in Fig. (10). When the screw is screwed in, the lead is short circuited without otherwise disturbing the circuit or the shielding. (As the outer case is at ground potential it is also a safe procedure.) To provide a continuous record of the currents the electrometer deflection was recorded by an Esterline Angus Graphic Recorder Type A W.

When shunted with a 350 ohm resistance this recorder requires the same current for full scale deflection as does the meter of the electrometer.

3.3 Probe Measurements

3.3.a General Comments

To measure the potential differences within an electret by means of probe techniques, it is essential to use a measuring system that draws a minimum current from the sample. If a null method is used, at balance no current will be drawn from the electret by the probe. If an electrostatic null detector is used,

FIG. 10

the amount of current flowing from the probe in an unbalanced system will depend upon the leakage resistance of the detector and leads. The apparatus we used consisted of a Kelvin Varley potential divider network with the variable tapping point connected to the probe through an electrostatic null detector designed by Hart and Mungall (Fig. 11). The potential divider (Fig. 12) draws a constant current from the high voltage supply and the voltage drop across the component resistors is low enough to permit the use of ordinary carbon resistors. The voltage applied to the null detector was measured with a voltmeter consisting of a microammeter in series with a 10^8 ohm series resistor.

3.3.b. The Null Detector

If a conductor is placed between two metal plates with a potential difference applied between them there will be a force acting between the conductor and each of the plates. The magnitude of the forces depends upon the position of the conductor and the potential of the conductor relative to the plates. If the potential of the conductor lies between the potentials of the plates, the conductor can be so placed that there is no net force acting upon it. If the conductor is unrestrained, any change in its potential will result in a net force upon it which will move it

FIG. 11

The electrostatic Null detector.

Fig 12

The switches are shown in the measuring position. Position 2 is used to establish the zero position of the leaf.

out of equilibrium into contact with one plate. If there is a constraint on the conductor a small change in potential will cause it to move towards one plate until the electrostatic force is balanced by the constraining force. If the potential is increased above a certain value the conductor moves out of equilibrium and into contact with one plate; for a fuller discussion see Hart and Mungall. This system is used in the null detector. The conductor takes the form of a brass leaf 0.001" thick and 1.5 cm² in area placed between two brass plates. An extension of the leaf 0.2 cm wide is used to support the leaf. The elastic properties of this strip provide the constraining force for the conductor. The plates are supported in a Lucite case and the leaf is further insulated from the plates with Teflon. A battery of dry cells is used to apply a potential difference of 225 volts to the brass plates. A potential divider R is also connected across the plates (Figs. 11 and 12).

To prepare the null detector for use the plates are moved until the leaf is situated approximately midway between them. The potential difference of 225 volts is then applied to the plates and the leaf is connected to the variable point P of the potential divider R (Fig. 12). By changing the setting of P the potential of the leaf with respect to the plates is changed until the leaf is brought to an equilibrium position between the plates. Two sighting

pins are used to determine this position. After setting up the detector in this manner the leaf is switched to the probe in the sample and the point P is switched to the output point of the Kelvin Varley potential divider. The Kelvin Varley divider is then adjusted until the leaf returns to the equilibrium position. When the leaf is in the equilibrium position the point P is at the same potential as the probe within the limits of the detector. The potential difference between P and the cathode is measured with the high resistance voltmeter V and this is equal to the potential difference between the cathode and the probe. If there is no leakage from the leaf, this system draws no current from the probe apart from charging the capacitance of the system. With the detector used it was possible to detect a difference of potential between point P and the leaf of approximately 2 volts.

3.3.c The Probe System

To keep the disturbance of the electret to a minimum the probes must be limited in number. In this investigation three probes were used at distances of 0.5mm, 1.8mm, and 2.5mm from the cathode. The sample was cast in a teflon mould (Fig. 13) with the probes fitted into the mould. The probes were 0.005" diameter brass wire, spaced at 120° intervals around the circumference. The leads from the probes were taken out of the cell and constant temperature chamber

SECTION

PLAN

FIG. 13

Teflon mould with probes.

through three teflon tubes. The lead from the null detector to the probes was stiff copper wire and was connected to the desired probe by means of a push-on connector. This system provides an extremely high resistance between the leads and ground. With no sample in the mount and the null detector balanced, the resistance between any probe and the cathode is greater than 10^{16} ohm. Within the detector there are two leakage paths, one from the leaf terminal to the plates and one from the leaf to the nearest plate when the system is out of equilibrium. The first leakage is very small as the leaf terminal is separated from the plates by a teflon insulator and several centimeters of Lucite; the second was reduced by facing the brass plates with teflon sheet. The total resistance of the unbalanced null detector was of the order of 10^{16} ohm.

3.4 The Controlled Temperature Chamber

The behaviour of electrets is strongly dependent upon temperature and therefore, the measurements must be carried out at a controlled temperature. In this investigation the cell containing the sample was placed in a Delta Design Company Environmental Test Chamber Model 1060 R. This chamber provides controlled temperatures from -60°C to $+350^{\circ}\text{C}$. The temperature is controlled to within $\pm 0.2^{\circ}\text{C}$ and if

necessary the temperature can be changed very rapidly. The temperature control system of the chamber proved to be badly designed. The control depends upon the e.m.f. from a copper-constantan thermocouple with one junction in the chamber. No provision had been made to maintain the other junction at a controlled temperature and therefore the cabinet temperature varied with room temperature by several degrees. This fault was corrected by extending the thermocouple leads and placing the second junction in a controlled temperature bath. This modification also provided an alternative means of controlling the temperature of the cabinet. By uniformly heating the external junction the temperature of the cabinet can be made to rise uniformly. Fig. 7 shows the constant temperature chamber with the cell fitted in it.

CHAPTER 4

EXPERIMENTAL PROCEDURE

4.1 Preparation of Sample

The samples were made from 1-tetradecanol produced by Eastman Organic Chemicals Ltd. and supplied by Fisher Scientific Company and classified as "highest purity". The alcohol was melted and poured into a Plexiglas mould and allowed to solidify in a dessicator at room temperature. When solid the upper surface was machined level with the top of the mould. This produced disc-shaped samples 3mm thick and 12.7mm in diameter. The samples were then fitted into the cell and left in the dry atmosphere for sixteen hours before measurements were made. In the cell and the dessicator silica gel was used as a dessicant.

4.2 Electrification

The controlled temperature chamber was set to the desired temperature and to electrify the alcohol the sliding electrodes were brought into contact with the surface of the sample. A period of thirty minutes was allowed for the cell and sample to come to thermal equilibrium with the chamber and then the forming field was applied using the circuit shown in Figure (5).

During the electrification process I wanted the

sample to reach its equilibrium state for the applied field, but to save time I did not wish to continue electrification long after the equilibrium had been reached. To determine the minimum electrification time, the charging and discharging currents were measured for samples electrified for different periods. It was found that there was no significant change in the discharge current if the electrification was continued for more than four hours (Fig. 14 and Table 1) and therefore all samples were electrified for four hours. The charging current was recorded during the electrification of all samples.

4.3 Measurement of Discharge Current

The discharge current was measured for two types of thermal treatment of the sample. In the first case the sample was held at one temperature during electrification and discharge and in the second case the sample was electrified at one temperature, cooled rapidly with the field still applied, and then discharged at the lower temperature. When the discharge current at the lower temperature had fallen to a negligible value the sample was heated uniformly and the discharge current measured during the heating.

4.3.a Discharge Current Measurements at Constant Temps.

The discharge currents were measured using the circuit shown in Fig. (5) for temperatures varying from

TABLE 1DATA FOR FIG. 14

<u>Forming Field 10kV/cm</u>		<u>Temperature 26.0°C</u>	
<u>Time Since Field Removed</u>		<u>Discharge Current</u>	
<u>Minutes</u>		<u>Amperes, x 10⁺¹¹</u>	
		<u>Electrification</u>	
		<u>4 hr.</u>	<u>11 hr.</u>
1		21.0	19.0
3		7.6	7.0
5		4.8	4.5
10		2.7	2.6
15		1.9	1.8
20		1.4	1.3
30		1.0	1.0
60		0.6	0.6
120		0.4	0.4

FIG. 14

Discharge current as a function of time.

-30.0°C to 25.0°C. In all cases a charging potential of 3kV was used, giving a charging field of 10kV/cm.

For the measured discharge current to be a representation of the current that would flow from a short circuited electret the input resistance of the electrometer must be small compared with the internal resistance of the sample. To minimize the fluctuations in the electrometer reading due to pick up in the leads it is advisable to use the higher voltage ranges wherever possible. As it is possible to vary both the input resistance and voltage range of the electrometer by factors of ten it is a simple matter to check that the chosen value of the input resistance is suitable. If the input resistance is low compared to the internal resistance of the sample, lowering the input resistance will have no effect upon the value of the current. If both the input resistance and the voltage range of the electrometer are lowered by a factor of ten the recorder pen will take up the same position as before the change was made. This check was carried out in all current measurements.

4.3.b Discharge Current Measurements with the Temperature Varied

The samples were electrified at temperatures between 10.0°C and 15.0°C for four hours and then cooled to -15.0°C with the field still applied. The samples were then held in a shielded condition at -15.0°C until the

discharge current had practically ceased. The controlled temperature chamber was then heated at a uniform rate to 40.0°C and the discharge current was measured during this time. Forming fields of 10kV/cm and 3.3kV/cm were applied and heating rates of 0.5°C/min. , 1.0°C/min. and 2.0°C/min. were used. A constant rate of heating was achieved by placing the reference junction of the controlled temperature chamber thermocouple in an oil filled dewar flask and adding heat to the oil at a constant rate by means of an electric immersion heater. The temperature of the controlled temperature chamber follows the temperature of the reference junction and as is shown by Fig. (49) the temperature of the cell, as determined by a thermocouple attached to it, rises at an approximately constant rate.

4.4 Torque Measurements

To measure the torque on an electret in an approximately uniform electric field the sample was first placed in the cell and electrified as previously described in 4.2. During these experiments the temperature remained the same for electrification and measurement. After electrification the sliding electrodes were removed from the sample and the suspension clamp released so that the sample hung freely from the gold suspension between the field plates. The dipole moment was then measured as described in section 3.4. Measurements were continued for approximately four hours, this being in most cases sufficient time

FIG. 49

Temperature of cabinet as a function of time.

for the dipole moment to become too small for satisfactory measurement. Measurements were made at temperatures of -15.0°C , -7.5°C , 0.5°C , 8.5°C , and 15.0°C with forming fields from 1 to 10kV/cm.

4.5 Probe Measurements

4.5.a Probe Measurements During Electrification

The sample was prepared and the apparatus set up as described in Chapter 3. The chosen electrifying field was applied to the sample and the charging current was recorded throughout the measurements as a check on the system. The potential differences were measured for forming fields of 10, 7 and 5kV/cm. The temperature was constant throughout each experiment and temperatures below -7.5°C and 25.0°C were used. At temperatures below -7.5°C the charging current is very small (of the order of 10^{-11}). As the leakage resistance of the null detector in an unbalanced condition is of the order of 10^{16} ohm then a current of 10^{-13} ampere is necessary to maintain the detector leaf at 1kV. This is a large percentage of the available current to be collected by a small probe and therefore any unbalance of the detector will effectively short circuit the probe. At all times even at higher temperatures care was taken to ensure that the detector did not remain unbalanced for long.

4.5.b Probe Measurements During Discharge

After four hours electrification the electret was short circuited and the potential of each probe with respect to the cathode was measured in the manner used during electrification.

CHAPTER 5

RESULTS

5.1 Current Measurements

5.1.a Charging Current

The measured values of the charging current for temperatures from -28.0°C to 26.0°C are shown in Tables 2 to 7 and in Figures 15 to 20. The current for a given temperature is seen to decay with time towards a limiting value representing the D.C. conductivity of the material. There is no simple functional relationship between the current and time. It is not inversely proportional to time or exponential. The measured values of the current for a given time after the application of the field vary by up to three orders of magnitude in the temperature range studied, the current at a given time after electrification decreasing with temperature.

5.1.b Discharge Currents At Constant Temperature

Discharge currents were detected throughout the temperature range. The results are shown in Tables 8 to 14 and are depicted graphically in Fig. 21. The current is to a close approximation given by the well known relationship:

$$i = \frac{C}{t}$$

TABLE 2DATA FOR FIG. 15

<u>Forming Field 10kV/cm</u>		<u>Temperature + 26.0 ° C</u>	
<u>Time Since Field Applied</u>		<u>Charging Current</u>	
<u>Minutes</u>		<u>Amperes, x 10⁺⁹</u>	
1		60.0	
3		53.0	
5		48.0	
10		40.0	
15		35.0	
25		28.0	
35		24.0	
45		22.0	
65		18.0	
125		17.0	
185		16.5	
245		16.0	

TABLE 3DATA FOR FIG. 16

<u>Forming Field 10kV/cm</u>		<u>Temperature $+14^{\circ}\text{C}$</u>	
<u>Time Since Field Applied</u>		<u>Charging Current</u>	
<u>Minutes</u>		<u>Amperes, x 10^{+9}</u>	
2.5		33.0	
5.0		28.0	
10.0		18.7	
15.0		14.8	
30.0		8.8	
60.0		7.3	
120.0		6.6	
180.0		6.1	
240.0		5.5	

TABLE 4DATA FOR FIG. 17

<u>Forming Field 10kV/cm</u>		<u>Temperature $+8.5^{\circ}\text{C}$</u>	
<u>Time Since Field Applied</u>		<u>Charging Current</u>	
<u>Minutes</u>		<u>Amperes, $\times 10^{+9}$</u>	
2		23.0	
7		19.0	
12		16.2	
22		12.3	
32		9.9	
42		8.4	
52		7.5	
62		7.2	
92		6.0	
122		5.1	
182		3.9	
242		3.6	

TABLE 5DATA FOR FIG. 18

<u>Forming Field 10kV/cm</u>		<u>Temperature -3.0° C</u>	
<u>Time Since Field Applied</u>		<u>Charging Current</u>	
<u>Minutes</u>		<u>Amperes, x 10⁺⁹</u>	
1		1.09	
2		0.98	
4		0.84	
10		0.61	
14		0.49	
24		0.42	
34		0.36	
44		0.30	
54		0.26	
64		0.23	
94		0.18	
124		0.13	
184		0.10	
244		0.07	

TABLE 6DATA FOR FIG. 19

<u>Forming Field 10kV/cm</u>		<u>Temperature -11^o C</u>
<u>Time Since Field Applied</u>		<u>Charging Current</u>
<u>Minutes</u>		<u>Amperes, x 10⁺¹⁰</u>
1		3.70
3		2.82
6		2.07
9		1.65
14		1.32
19		1.11
29		0.77
49		0.60
69		0.54
129		0.42
189		0.33
249		0.24

TABLE 7DATA FOR FIG. 20Forming Field 10kV/cmTemperature -28.0° CTime Since Field AppliedCharging CurrentMinutesAmperes, x 10⁺¹⁰

1	2.45
3	1.47
6	0.82
8	0.70
13	0.37
18	0.25
28	0.15
38	0.10
48	0.08
58	0.07
128	0.03
188	0.02
248	0.02

FIG. 15

Charging current as a function of time.

FIG. 16

Charging current as a function of time.

FIG. 17

Charging current as a function of time.

FIG. 18

Charging current as a function of time.

FIG. 19

Charging current as a function of time.

FIG. 20

Charging current as a function of time.

TABLE 8DATA FOR FIG. 21Forming Field 10kV/cmTemperature $+26.0^{\circ}$ CTime Since Field RemovedDischarge CurrentMinutesAmperes, $\times 10^{+11}$

1	21.0
3	7.6
5	4.8
10	2.7
15	1.9
20	1.4
30	1.0
60	0.6
120	0.4

TABLE 9DATA FOR FIG. 21Forming Field 10kV/cmTemperature 20.0°CTime Since Field RemovedDischarge CurrentMinutesAmperes, x 10⁺¹¹

2.5	5.0
5.0	2.9
10.0	1.5
15.0	1.0
22.5	0.6
30.0	0.45
60.0	0.20
120.0	0.05

TABLE 10DATA FOR FIG. 21Forming Field 10kV/cmTemperature +15.0°CTime Since Field RemovedDischarge CurrentMinutesAmperes, x 10⁺¹

2.5	4.2
5.0	2.4
10.0	1.3
15.0	0.95
22.5	0.70
30.0	0.50
45.0	0.30
60.0	0.20
90.0	0.10
120.0	0.05

TABLE 11DATA FOR FIG. 21

<u>Forming Field 10kV/cm</u>		<u>Temperature +8.5°C</u>	
<u>Time Since Field Removed</u>		<u>Discharge Current</u>	
<u>Minutes</u>		<u>Amperes, x 10⁺¹¹</u>	
1		4.30	
2		2.07	
5		0.69	
6		0.55	
11		0.23	
16		0.17	
21		0.12	
31		0.09	
41		0.07	
71		0.05	
131		0.03	

TABLE 12DATA FOR FIG. 21Forming Field 10kV/cmTemperature -3.0° CTime Since Field RemovedDischarge CurrentMinutesAmperes, x 10⁺¹¹

1	4.5
3	1.51
6	0.77
9	0.50
12	0.37
22	0.20
32	0.13
42	0.11
52	0.093
62	0.078
92	0.060
122	0.033
182	0.018
242	0.015

TABLE 13DATA FOR FIG. 21

<u>Forming Field 10kV/cm</u>		<u>Temperature -11°C</u>	
<u>Time Since Field Removed</u>		<u>Discharge Current</u>	
<u>Minutes</u>		<u>Amperes, x 10^{*11}</u>	
1		4.0	
2		2.04	
3		1.31	
6		0.70	
12		0.32	
17		0.21	
27		0.096	
37		0.060	
47		0.048	
57		0.036	
67		0.030	
77		0.027	
137		0.015	
187		0.009	
247		0.006	

TABLE 14DATA FOR FIG. 21Forming Field 10kV/cmTemperature -28.0 °CTime Since Field RemovedDischarge CurrentMinutesAmperes, x 10⁺¹¹

2	2.64
3	2.04
5	1.20
9	0.76
19	0.41
29	0.28
39	0.21
49	0.17
59	0.13
69	0.10
99	0.06
129	0.05
189	0.02
249	0.01

FIG. 21

Discharge current as a function of $\frac{1}{\text{time}}$.

where i is the discharge current, t is the time since removal of the field and C is a constant for a given temperature. For temperatures from $+8.5^{\circ}\text{C}$ to -28.0°C the discharge curves are very nearly the same. The graph (Fig. 21) shows one line for these temperatures as the curves are too close to be clearly distinguished. The measured discharge currents were of the order of 10^{-11} amperes.

5.1.c Discharge Currents With Temperature Varied

The results for this section are shown in Tables 15 to 18 and Figures 22 to 25. When the sample is reheated the current rises to a maximum and falls again. This peak is smooth and there are no subsiding peaks. The peak is narrower for more rapid heating.

TABLE 15DATA FOR FIG. 22

Electrification Temp. +14.0° C Forming Field 10kV/cm

<u>Time Since Field Applied</u>	<u>Charging Current</u>
<u>Minutes</u>	<u>Amperes, x 10⁺⁹</u>
2.5	32.0
5.0	27.0
10.0	18.6
15.0	14.7
30.0	9.7
60.0	7.2
120.0	6.6
180.0	6.0
240.0	5.4

Discharge at -15.0° C

<u>Time Since Field Removed</u>	<u>Discharge Current</u>
<u>Minutes</u>	<u>Amperes, x 10⁺¹¹</u>
3.5	0.72
7.5	0.27
13.5	0.12
28.5	0.060
48.5	0.042
88.5	0.027
118.5	0.012

TABLE 15 Con't.

Heating Rate 1.0 °C/min.

Heating started at 120 minutes after field removal.

<u>Time Since Field Removed</u>	<u>Discharge Current</u>
<u>Minutes</u>	<u>Amperes, x 10⁺¹¹</u>
122.5	0.012
127.5	0.012
135.0	0.033
140.0	0.090
145.0	0.26
150.0	0.65
155.0	1.04
160.0	1.19
165.0	1.22
168.0	1.18
172.5	1.04
175.0	0.94
180.0	0.59
185.0	0.37
190.0	0.24
195.0	0.13
200.0	0.08
210.0	0.04
240.0	0.03

TABLE 16DATA FOR FIG. 23

Electrification Temp. 14.0 °C Forming Field 10kV/cm

<u>Time Since Field Applied</u>	<u>Charging Current</u>
<u>Minutes</u>	<u>Amperes, x 10⁺⁹</u>
2.5	33.0
5.0	28.0
10.0	18.7
15.0	14.8
30.0	8.8
60.0	7.3
120.0	6.6
180.0	6.1
240.0	5.5

Discharge at -15.0 °C

<u>Time Since Field Removed</u>	<u>Discharge Current</u>
<u>Minutes</u>	<u>Amperes, x 10⁺¹¹</u>
3.5	0.72
7.5	0.27
13.5	0.12
28.5	0.06
48.5	0.042
88.5	0.027
118.5	0.012

TABLE 16 Con't.

Heating Rate 0.5 °C/min.

Heating started at 120 minutes

<u>Time Since Field Removed</u>	<u>Discharge Current</u>
<u>Minutes</u>	<u>Amperes, x 10⁺¹¹</u>
120.0	0.012
127.5	0.012
135.0	0.015
142.5	0.024
150.0	0.042
157.5	0.069
165.0	0.102
172.5	0.177
180.0	0.255
187.5	0.320
195.5	0.370
202.5	0.420
210.0	0.470
217.5	0.500
225.0	0.530
235.0	0.500
240.0	0.450
255.0	0.320
270.0	0.180

TABLE 17DATA FOR FIG. 24Electrification Temp. 12.0° CForming Field 10kV/cmTime Since Field AppliedCharging CurrentMinutesAmperes, x 10⁻⁹

2.5	6.2
5.0	5.1
10.0	3.7
15.0	2.8
20.0	2.3
30.0	1.7
40.0	1.4
50.0	1.2
60.0	1.1
90.0	0.6
120.0	0.3
180.0	0.2
240.0	0.1

TABLE 17 Con't.

Discharge at -15.0 °C

<u>Time Since Field Removed</u>	<u>Discharge Current</u>
<u>Minutes</u>	<u>Amperes, x 10⁺"</u>
2.5	0.45
5.0	0.24
10.0	0.066
20.0	0.024
30.0	0.015
40.0	0.012
50.0	0.006

Heating Rate 2.0 °C/min.

Heating started at 50 minutes

55.0	0.006
60.0	0.015
65.0	0.066
70.0	0.23
75.0	0.59
80.0	1.02
85.0	0.84
90.0	0.42
95.0	0.21
100.0	0.06
110.0	0.01

TABLE 18DATA FOR FIG. 25

Electrification Temp. 10.0 °C Forming Field 3.3kV/cm

<u>Time Since Field Applied</u>	<u>Charging Current</u>
<u>Minutes</u>	<u>Amperes, x 10⁺⁹</u>
2.5	3.0
5.0	2.4
10.0	1.74
20.0	1.21
30.0	0.84
40.0	0.42
60.0	0.06
90.0	0.06
120.0	0.06
180.0	0.06
240.0	0.06

Discharge at -15.0 °C

<u>Time Since Field Removed</u>	<u>Discharge Current</u>
<u>Minutes</u>	<u>Amperes, x 10⁺¹¹</u>
2.5	0.34
7.5	0.135
15.0	0.066
30.0	0.036
45.0	0.021
60.0	0.015
90.0	0.012
105.0	0.009

TABLE 18 Con't.

Heating Rate 0.5°C/min.

Heating Started at 105 Minutes

<u>Time Since Field Removed</u>	<u>Discharge Current</u>
<u>Minutes</u>	<u>Amperes, x 10⁺¹¹</u>
105.0	0.009
110.0	0.010
120.0	0.015
127.5	0.024
135.0	0.048
142.5	0.066
150.0	0.084
157.5	0.110
180.0	0.170
187.5	0.200
195.0	0.190
202.5	0.180
210.0	0.160
217.5	0.110
225.0	0.040
232.0	0.010
240.0	0.001

FIG. 22

Discharge current as a function of time.

FIG. 23

Discharge current as a function of time.

FIG. 24

Discharge current as a function of time.

FIG. 25

Discharge current as a function of time.

5.2 Torque Measurements

The results of this section are shown in Tables 19 to 33 and Figures 26 to 30. The results show that the tetradecanol sample retains a macroscopic dipole moment after electrification at all temperatures studied. The results in the Tables are expressed in terms of the angle of rotation of the torsion head in minutes of arc as this was the quantity recorded in the experiment but for the graphs this quantity is converted into a macroscopic dipole moment by multiplying by the conversion factor for the balance: 0.5×10^{-3} (see Appendix C for derivation). A dipole moment corresponding to a homocharge is referred to as positive and that corresponding to a heterocharge as negative.

At -15.0°C and -7.5°C a reversal of the dipole moment takes place; this corresponds to the reversal of surface charge polarity reported in studies of other materials. At $+0.6^{\circ}\text{C}$ the early part of the curves show an increase in the dipole moment, followed by a decrease. At $+8.8^{\circ}\text{C}$ the curve for the lowest forming field shows this change of direction of the curve. Above $+8.8^{\circ}\text{C}$ there is no change in direction of the curves and the dipole moment is always positive. The largest negative dipole moment observed was equivalent to a surface charge density of 0.40 e.s.u. cm and the largest positive dipole moment observed was equivalent to a surface charge density of 0.25 e.s.u. cm .

TABLE 19DATA FOR FIG. 26Forming Field 10kV/cmTemperature -15 °CTime Since Field RemovedAngle of Rotation of Torsion HeadMinutesMinutes of Arc

2	-19
3	+138
5	+272
7	+341
9	+412
11	+443
14	+473
18	+498
20	+516
23	+480
26	+490
30	+490
33	+472
40	+452
45	+452
52	+450
59	+370
64	+412
68	+400
80	+378
91	+352
100	+346
112	+324
185	+244

TABLE 20DATA FOR FIG. 26

<u>Forming Field 5kV/cm</u>		<u>Temperature -15°C</u>	
<u>Time Since Field Removed</u>		<u>Angle of Rotation of Torsion Head</u>	
<u>Minutes</u>		<u>Minutes of Arc</u>	
3		-779	
5		-630	
9		-605	
11		-514	
13		-478	
16		-428	
20		-380	
24		-372	
27		-360	
30		-337	
45		-276	
65		-248	
80		-215	
90		-215	
100		-199	
135		-192	
160		-183	

TABLE 21DATA FOR FIG. 26

<u>Forming Field 7kV/cm</u>		<u>Temperature -15° C</u>	
<u>Time Since Field Removed</u>		<u>Angle of Rotation of Torsion Head</u>	
<u>Minutes</u>		<u>Minutes of Arc</u>	
2.5		-435	
4		-239	
6		-160	
7.5		-111	
9		-59	
11		-10	
12		+ 4	
18		+45	
21		+69	
26		+91	
35		+104	
41		+112	
46		+108	
51		+103	
61		+104	
64		+97	
84		+89	
113		+64	
124		+61	
142		+52	
219		+36	

TABLE 22DATA FOR FIG. 27

<u>Forming Field 5kV/cm</u>		<u>Temperature -7.5° C</u>	
<u>Time Since Field Removed</u>		<u>Angle of Rotation of Torsion Head</u>	
<u>Minutes</u>		<u>Minutes of Arc</u>	
4		-776	
7		-592	
10		-470	
13		-410	
20		-274	
30		-196	
41		-108	
56		-100	
65		-67	
83		-59	
98		-49	
126		-43	
255		-36	
302		-23	

TABLE 23DATA FOR FIG. 27Forming Field 7kV/cmTemperature -7.5°C

<u>Time Since Field Removed</u>	<u>Angle of Rotation of Torsion Head</u>
<u>Minutes</u>	<u>Minutes of Arc</u>
5	-605
8	-502
11	-402
16	-298
22	-180
32	-88
42	-34
52	+11
65	+27
75	+38
90	+55
104	+56
122	+55
270	+44

TABLE 24DATA FOR FIG. 28Forming Field 5kV/cmTemperature 0.6°C

<u>Time Since Field Removed</u>	<u>Angle of Rotation of Torsion Head</u>
<u>Minutes</u>	<u>Minutes of Arc</u>
4	465
6	479
9	478
14	427
20	370
24	338
29	322
37	279
60	188
70	164
80	153
98	123
100	115
128	86
142	66
156	55
161	54
169	46
284	22
320	8

TABLE 25DATA FOR FIG. 28Forming Field 7kV/cmTemperature 0.6°CTime Since Field Removed Angle of Rotation of Torsion HeadMinutesMinutes of Arc

2	488
5	506
6	501
10	465
15	431
20	406
27	355
31	333
39	292
48	245
56	211
70	158
81	132
103	85
123	56
157	28
248	10
262	6

TABLE 26DATA FOR FIG. 28Forming Field 6kV/cmTemperature 0.6°C

<u>Time Since Field Removed</u>	<u>Angle of Rotation of Torsion Head</u>
<u>Minutes</u>	<u>Minutes of Arc</u>
3	376
5	367
7	321
9	300
13	267
17	247
30	194
41	165
55	130
76	93
95	71
108	56
140	24
177	9

TABLE 27DATA FOR FIG. 28Forming Field 10kV/cmTemperature 0.6°C

<u>Time Since Field Removed</u>	<u>Angle of Rotation of Torsion Head</u>
<u>Minutes</u>	<u>Minutes of Arc</u>
2	151
3	210
5	211
7	204
9	195
14	163
23	135
29	129
41	98
59	53
73	30
92	24
110	18
126	14

TABLE 28DATA FOR FIG. 29

<u>Forming Field 1kV/cm</u>		<u>Temperature 8.8°C</u>	
<u>Time Since Field Removed</u>		<u>Angle of Rotation of Torsion Head</u>	
<u>Minutes</u>		<u>Minutes of Arc</u>	
2		21	
3		23	
5		14	
8		9	
10		7	
17		3	
30		2	

TABLE 29DATA FOR FIG. 29Forming Field 3.5kV/cmTemperature 8.8°C

<u>Time Since Field Removed</u>	<u>Angle of Rotation of Torsion Head</u>
<u>Minutes</u>	<u>Minutes of Arc</u>
1.5	300
3	242
5	175
9	113
14	85
23	50
30	40
42	25
70	16
85	9
103	7
175	5

TABLE 30DATA FOR FIG. 29

<u>Forming Field 10kV/cm</u>		<u>Temperature 8.8°C</u>	
<u>Time Since Field Removed</u>		<u>Angle of Rotation of Torsion Head</u>	
<u>Minutes</u>		<u>Minutes of Arc</u>	
2		212	
4		163	
6		119	
10		106	
16		85	
24		72	
31		57	
41		50	
61		42	
90		28	
111		26	
165		15	

TABLE 31DATA FOR FIG. 30Forming Field 5kV/cmTemperature 16.0° CTime Since Field RemovedAngle of Rotation of Torsion HeadMinutesMinutes of Arc

2	45
4	34
7	32
11	22
19	15
26	14
31	12
42	11
53	10
74	8
99	6
170	5

TABLE 32DATA FOR FIG. 30Forming Field 6kV/cmTemperature 16.0° C

<u>Time Since Field Removed</u>	<u>Angle of Rotation of Torsion Head</u>
---------------------------------	--

MinutesMinutes of Arc

3	160
5	125
9	77
17	46
23	36
30	28
52	17
61	11
66	14
80	9
107	8

TABLE 33DATA FOR FIG. 30Forming Field 10kV/cmTemperature 16.0°C

<u>Time Since Field Removed</u>	<u>Angle of Rotation of Torsion Head</u>
<u>Minutes</u>	<u>Minutes of Arc</u>
2	225
3	178
5	144
10	115
16	85
25	63
33	55
41	52
55	40
62	32
74	28
92	25
110	18
115	17
173	13

FIG. 26

Torque as a function of time.

FIG. 27

Dipole moment as a function of time.

FIG. 28

Dipole moment as a function of time

FIG. 29

Dipole moment as a function of time

FIG. 30
Dipole moment as a function of time

5.3 Probe Measurements

The results for this section are shown in Tables 34 to 43 and Figures 31 to 48. The graphs are of three types, i) A plot of the potential of each probe against time during electrification. ii) A diagram of the potential distribution during electrification. iii) A plot of the potential of each probe against time during discharge.

The results show that at temperatures of -7.5°C , $+0.5^{\circ}\text{C}$ and $+8.5^{\circ}\text{C}$ there is a non-uniform potential gradient in the electret during electrification indicating the existence of space charges. At $+16.0^{\circ}\text{C}$ the potential gradient is approximately uniform. The potential distribution changes as electrification proceeds at the lower temperatures. During discharge there was a measurable potential difference between the probes and the cathode at temperatures of -7.5°C and $+0.5^{\circ}\text{C}$. This potential persisted for times of the order of twenty minutes.

TABLE 34DATA FOR FIGS. 31, 32

<u>Forming Field 10kV/cm</u>		<u>Temperature -7.6°C</u>		
<u>Time Since Field Applied</u>		<u>Potential on Probes</u>		
<u>Minutes</u>		<u>Volts</u>		
		<u>Probe No.</u>		
		<u>1</u>	<u>2</u>	<u>3</u>
3		300		
10			1000	
120				2000
155				1800
165			370	
170		185		
200		184		
215			1200	
225				1800
240				1700
250			1300	
255		190		

TABLE 35DATA FOR FIG. 33

<u>Forming Field 10kV/cm</u>		<u>Temperature -7.5°C</u>		
<u>Time Since Field Removed</u>		<u>Potential of Probe</u>		
<u>Minutes</u>		<u>Volts</u>		
		<u>Probe No.</u>		
		<u>1</u>	<u>2</u>	<u>3</u>
0.5		0		
1.0				140
3.0				130
4.0			130	
5.0			110	
6.5		0		
7.0				30
10.0			0	
11.0				10

TABLE 36DATA FOR FIGS. 34, 35

<u>Forming Field 5kV/cm</u>		<u>Temperature -7.5°C</u>		
<u>Time Since Field Applied</u>		<u>Potential on Probes</u>		
<u>Minutes</u>		<u>Volts</u>		
		<u>Probe No.</u>		
		<u>1</u>	<u>2</u>	<u>3</u>
13				900
30			655	
40	160			900
53			740	
68	165			930
78			680	
88				810
98			490	
165				640
175	140		510	
185				
245				
250	100			
257				

TABLE 37DATA FOR FIGS. 36, 37

<u>Forming Field 5kV/cm</u>		<u>Temperature 0.5°C</u>		
<u>Time Since Field Applied</u>		<u>Potential on Probes</u>		
<u>Minutes</u>		<u>Volts</u>		
		<u>Probe No.</u>		
		<u>1</u>	<u>2</u>	<u>3</u>
10			665	
34		325		
51				1330
67		250		
79			570	
116				1250
141		280		
157			540	
168				1120
173		325		
201			535	
220				1080
240		320		

TABLE 38DATA FOR FIGS. 38, 39

<u>Forming Field 10kV/cm</u>		<u>Temperature 0.5°C</u>		
<u>Time Since Field Applied</u>		<u>Potential on Probe</u>		
<u>Minutes</u>		<u>Volts</u>		
		<u>Probe No.</u>		
		<u>1</u>	<u>2</u>	<u>3</u>
7			2150	
10				2650
12		1600		
14			2150	
17				2600
26		1400		
29			2050	
31				2600
44		1400		
47			2000	
65		1600		
72				2650
82			2150	
119			2150	
123				2550
127		1600		
185				2500
189			2050	
195		1650		
226			2050	
228		1700		
234				2500

TABLE 39DATA FOR FIGS. 40, 41

<u>Forming Field 7kV/cm</u>		<u>Temperature 0.5°C</u>		
<u>Time Since Field Applied</u>		<u>Potential on Probe</u>		
<u>Minutes</u>		<u>Volts</u>		
		<u>Probe No.</u>		
		<u>1</u>	<u>2</u>	<u>3</u>
	2		820	
	10			1500
	20	595		
	26		925	
	33			1370
	42	395		
	110		810	
	115			1200
	124	445		
	140	470		
	147		840	
	155			1200
	190	520		
	192		960	
	195			1250
	230	500		
	235		900	
	241			1200

TABLE 40DATA FOR FIG. 42

<u>Forming Field 7kV/cm</u>		<u>Temperature 0.5°C</u>		
<u>Time Since Field Removed</u>		<u>Potential on Probes</u>		
<u>Minutes</u>		<u>Volts</u>		
		<u>Probe No.</u>		
		<u>1</u>	<u>2</u>	<u>3</u>
1.0				685
1.5				600
2.0			400	
3.0			380	
3.5	105			
4.0	100			
5.0				250
6.0				230
7.0				210
9.0				205
10.5			180	
11.5			155	
12.0			145	
14.0	89			
15.0	85			
16.0	71			
17.0				105
18.0				105
19.0				95
20.0				90
21.5			75	
27.0	65			
28.0	63			
29.0				74
30.0				80
31.0				74
32.0			68	
33.0			63	
34.0			63	

TABLE 41DATA FOR FIGS. 43, 44

<u>Forming Field 10kV/cm</u>		<u>Temperature 8.5°C</u>		
<u>Time Since Field Applied</u>		<u>Potential on Probe</u>		
<u>Minutes</u>		<u>Volts</u>		
		<u>Probe No.</u>		
		<u>1</u>	<u>2</u>	<u>3</u>
25			1800	
37		710		
41				2800
45			1550	
50		660		
54				2800
75		625		
80			1800	
84				2800
94		525		
105			1600	
108				2800
143		525		
150			1500	
157				2550
185		565		
190			1550	
193				2650
212		565		
230			1540	
241				2650

No detectable potentials after field removed

TABLE 42DATA FOR FIGS. 45, 46

<u>Forming Field 5kV/cm</u>		<u>Temperature 8.5°C</u>		
<u>Time Since Field Applied</u>		<u>Potential on Probes</u>		
<u>Minutes</u>		<u>Volts</u>		
		<u>Probe No.</u>		
		<u>1</u>	<u>2</u>	<u>3</u>
3		305		
8			660	
25				860
29		205		
34			645	
41				690
60		155		
65			575	
70				820
100		200		
109			550	
115				940
136		310		
142			520	
147				960
186		300		
190			500	
194				960
224		300		
229			550	
234				960

No potential detected after field removed.

TABLE 43DATA FOR FIGS. 47, 48

<u>Forming Field 10kV/cm</u>		<u>Temperature 15.0°C</u>		
<u>Time Since Field Applied</u>		<u>Potential on Probes</u>		
<u>Minutes</u>		<u>Volts</u>		
		<u>Probe No.</u>		
		<u>1</u>	<u>2</u>	<u>3</u>
2		700		
5			1800	
8				2700
26		845		
29			2000	
31				2650
41		830		
44			2000	
46				2600
88		830		
92			1950	
95				2600
190				2650
193		830		
196			1950	
230		830		
233			2000	
236				2650

No potential detected after field removed.

FIG. 31

Probe potential as a function of time during electrification.

FIG. 32

Potential distribution during electrification.

FIG. 33

Probe potential against time during discharge.

FIG. 34

Probe potential as a function of time during electrification.

FIG. 35

Potential distribution during electrification.

FIG. 36

Probe potential as a function of time during electrification.

FIG. 37.
Potential distribution during electrification.

FIG. 38

Probe potential as a function of time during electrification.

FIG. 39

Potential distribution during electrification.

FIG. 40

Probe potential as a function of time during electrification.

FIG. 41

Potential distribution during electrification.

FIG. 42

Probe potential as a function of time during discharge

FIG. 43

Probe potential as a function of time during electrification.

FIG. 44

Potential distribution during electrification.

FIG. 45

Probe potential as a function of time during electrification.

FIG. 46

Potential distribution during electrification.

FIG. 47

Probe potential as a function of time during electrification.

FIG. 48

Potential distribution during electrification.

5.4 Reliability of Experimental Results

The results of the current measurements were reproducible to within $\pm 15\%$. The largest source of error lay in the value of the forming field. The thickness of the sample was measured to within $\pm 3\%$ with vernier callipers and the applied voltage was measured to $\pm 10\%$ with the voltmeter of the power supply. These errors are additive giving an expected error of $\pm 13\%$. This indicates that there is no other source of error unaccounted for.

The results of the dipole moment measurements were reproducible to within $\pm 20\%$. From the sensitivity of the balance (Appendix C) it would be expected that the results should be reproducible to within $\pm 2\%$. The discrepancy arises from the disturbance produced by removal of the forming electrodes.

When the forming electrodes are removed from the surface of the sample there may be a loss of charge from the sample due to discharge between the sample and the electrode. Because of this loss of charge the results of the dipole moment measurements will be treated as evidence of the dipole moment changes taking place within the sample and not as quantitative measurements of the undisturbed initial surface charge.

The reliability of the probe measurements depends upon the certainty of the position of the probes and of the potential of the probes. The position

of the probes was measured to within $\pm 0.1\text{mm}$ with vernier callipers. The uncertainty of the potential of the probes depends upon the sensitivity of the null detector. Although the detector used could be adjusted to respond to an unbalance of ± 2 volts it was found to be more convenient to use it with the sensitivity reduced to ± 10 volts. These limits of experimental error are shown on the appropriate figures. All probe measurements were repeated to check the reproducibility of the results. Owing to the time required to balance the null detector it was not possible to measure the probe potentials at the same elapsed time in all cases, but the character of the potential distribution within the sample was reproduced. With the apparatus used it was not possible to measure the potential of the three probes simultaneously but an equivalent simultaneous measurement was derived. The potentials of each of the three probes were plotted against elapsed time, as in Figures 31, 34, 36, 38, 40, 43, 45 and 47, and the potential of each probe at specific elapsed times was interpolated from these graphs. The selected elapsed times were chosen to be near the times at which the potentials were measured, or during periods when the potentials seemed to be varying slowly. To indicate the reliability of the data the derived potentials plotted in Figures 32, 35, 37, 39, 41, 44, 46 and 48 have been shown with a spread of ± 20 volts

at positions of the probes measured to within $\pm 0.1\text{mm}$.

CHAPTER 6

DISCUSSIONS OF RESULTS AND CONCLUSIONS

The first conclusion to be drawn is that 1-tetradecanol shows the electret effect in the temperature range studied. The reasons for choosing 1-tetradecanol as a material for study are given in Chapter 2.4. This work is the first extensive study of the electret properties of a pure organic compound. The fact that electret behaviour is observed in such a material indicates that the electret effect arises from normal dielectric behaviour of a molecule in a polycrystalline state and is not a property restricted to mixtures of substances.

It is clear that existing theories of electrets must be modified to explain the behaviour of 1-tetradecanol.

The two-charge theory has been accepted by all recent workers (Chapter 2.2). An electret may exhibit either a heterocharge, or a homocharge, or a heterocharge followed by a homocharge. The two observed polarities of surface charge can be explained by assuming that in the electret there are two charge distributions of opposite polarity, one a surface charge of the same polarity as the adjacent forming electrode,

and the other an internal polarization which produces net surface charges of opposite polarity to the adjacent forming electrode. When the surface charge predominates, the electret exhibits a heterocharge. In 1936, Thiesen, Winkel and Hermann proposed that the surface charge was produced by conduction across the dielectric-electrode interface and all recent workers have agreed with this; however, the nature of the internal polarization has been a matter of dispute.

Gemant (1935), Thiesen, Winkel and Hermann (1936), and Antemnen (1955) proposed that the internal polarization was due to space charges.

Gross (1949) attributed the internal polarization to a uniform volume effect but did not exclude the existence, in addition to this, of space charges.

In 1953 Gemant revised his original theory, which had attributed the surface charge to the piezoelectric effect. He now proposed that it arose from conduction across the dielectric-electrode interface and that the internal polarization consisted of space charges and a uniform component due to dipole orientation. Gerson and Rohrbaugh (1955) considered that although the internal polarization might have components due to dipole alignment and space charges, neither of these were important, and they suggested that some electron-trap mechanism might be responsible. In 1962 Gross and Demoraes rejected the existence of

space charges but offered only a tentative explanation of the internal polarization in terms of a distorted double well. Perlman and Meunier (1964) rejected the existence of space charges but offered no mechanism as an alternative. All recent workers have attributed the charging and discharging currents to the build up and decay of some form of internal polarization.

Our opinion is that the electret effect in 1-tetradecanol is due to the superposition of an internal polarization and a true surface charge. The internal polarization is due to the accumulation of space charges near the electrodes, and the surface charge is due to conduction across the dielectric-electrode interface. The discharge current arises from the decay of the surface charge.

This brief summary of opinions shows that no two groups agree on all points and therefore, the experimental evidence on which the conclusions are based will be examined briefly.

Thiesen, Winkel and Hermann (1936) attempted to find the internal charge distribution by measuring the surface charge remaining on an electret after successive layers were removed from the surface by planing. Such a severe mechanical treatment of the surface cannot be expected to leave the surface charge undisturbed; therefore, the results are of doubtful value.

Gemant (1935) and Antennen (1953) measured the internal potential differences within an electret by probe techniques and found that the potential gradient was not uniform, indicating the existence of space charges near the electrodes.

Gerson and Rohrbaugh (1955) measured the surface charge of an electret and the discharge current and the dielectric constant of natural and electrified carnauba wax. They found no significant difference in the dielectric constants of natural and electrified wax and therefore, concluded that dipole alignment did not play an important part in the electret mechanism. An electron-trap mechanism was postulated to explain their results.

In 1962 Gross and Demoraes published the results of a series of experiments designed to determine whether the internal polarization is uniformly distributed. The experiments involved the total discharging of sections of different thicknesses obtained from different regions within the electret. The total charge liberated was found to be almost independent of the thickness of the section and its original position in the electret. They therefore concluded that the charge arose from the decay of a uniform volume polarization. Such a sectioning experiment is of very doubtful value. As in the work of Thiesen, Winkel & Hermann (1936) by machining away unwanted wax and such drastic physical treatment cannot be expected to leave the

original charge distributions undisturbed. Gross and Demoraes concluded that there were no space charges within the carnauba wax electrets but it is quite possible that any space charge would be destroyed or masked by the machining.

The work of Perlman and Meunier (1964) throws no new light upon the nature of the internal polarization. These workers derived an integral equation expressing the initial surface charge of an electret in terms of a polarization function, the conductivity of the wax and the dielectric constant of the wax. The assumptions made in deriving the equation are i) the polarization response at a given time can be expressed in terms of the field and an empirical polarization function, ii) the true surface charge decays only by ohmic conduction. They considered the equation only held if there was no space charge accumulation within the wax. The values of surface charge predicted are found to agree well with experimental results. They therefore concluded that there was no space charge accumulation. However, this is false. The polarization function in the equation contains no restrictions upon the nature of the polarization. The surface charge measurements (by lifted electrode techniques) made to determine the polarization function, give no information about the nature of the polarization; therefore, a space charge mechanism is not excluded by these results. The remainder of the paper

is a good demonstration that the surface charge decays by ohmic conduction but their conclusion on the nature of the internal polarization is invalid.

The evidence may be summarized by saying that probe measurements have always shown the existence of space charges but no experiments have shown that dipole alignment occurs to any detectable degree. The conflict appears to have arisen because of a prejudicial feeling on the part of some workers that space charges should not exist rather than because experimental results indicate that they do not exist. The chief objection to the existence of space charges is the feeling that the charges should quickly move to annihilate each other. However, the supporters of the uniform volume polarization theory have not firmly proposed any mechanism to account for such a polarization.

In this investigation, measurements of the macroscopic dipole moment replaced the surface charge measurement of other workers. On the basis of the two-charge theory, the macroscopic dipole moment of an electret will be the vector sum of the net dipole moment of the internal polarization and the net dipole moment of the real surface charge. If the real surface charge predominates, the macroscopic dipole moment will correspond to the existence of a homocharge, and if the internal polarization predominates, the macroscopic dipole moment will correspond to the existence of a heterocharge (Fig. 50). In the experimental results

a dipole moment corresponding to the existence of a homocharge is taken as positive. A measurement of the macroscopic dipole moment is a measurement of the combined effects of the two charge distributions. The problem is to examine the behaviour and distribution of either kind of charge in the presence of the other; even if this can be done only on a qualitative basis, the electret problem will be clarified. Fortunately, there are two functional relationships of charge with time, one of which appears to be associated with the surface charge and the other with the internal polarization. Both relationships are temperature sensitive and this variation with temperature can be used to separate the effects. At -15.0°C and -7.5°C for a forming field of 5kV/cm the internal polarization always predominates. For forming fields of 7kV/cm and 10kV/cm the internal polarization initially predominates, but it decays more rapidly than the surface charge, and the observed dipole moment changes from negative to positive. At temperatures of 0.5°C and 8.5°C , the surface charge always predominates but the rapidly decaying internal polarization reduces the size of the early readings. (See illustration on page 14Q)

At 16.0°C there is no indication from the measurements of dipole moment of the existence of an internal polarization. Figures 26 and 27 show a different behaviour for electrets produced with different forming fields. The change in apparent ratio of the two charge distribution shows that the mechanism resulting in the accumulation of surface charge is not linear with applied potential. A non-linear conduction mechanism associated with a surface potential barrier could result in the observed response. This behaviour is similar to the results obtained by other workers with carnauba wax.

The results of the probe measurements are in agreement with the dipole moment measurements. At -7.5°C , $+0.5^{\circ}\text{C}$, and $+8.5^{\circ}\text{C}$, the potential gradient in the electret is non-uniform, showing the existence of space charges near the electrodes of opposite sign to

the adjacent electrode, but at $+16^{\circ}\text{C}$ the potential gradient is uniform (Figs. 31 to 48). The temperature at which these space charges are detected are those at which the dipole moment measurements indicate the existence of an internal polarization; i.e. in the turnover regions; therefore, I conclude that the internal polarization is due to space charges.

Further examination of the curves yields some information on the nature of the charge carriers producing these space charges. Fig. 32 and Fig. 35 show that at -7.5°C for forming fields of 10kV/cm and 5kV/cm there is a negative space charge at the anode and no space charge accumulation at the cathode. The space charge becomes more strongly concentrated at the anode as the electrification proceeds. At $+0.5^{\circ}\text{C}$ for forming fields of 5kV/cm , 7kV/cm and 10kV/cm (Figs. 37, 39 and 41) there is a negative space charge near the anode and a positive space charge near the cathode. With 5kV/cm the space charge accumulation is largest at the anode, at 7kV/cm the curve is almost symmetrical and at 10kV/cm the space charge accumulation is largest at the cathode; again the space charges increase as electrification proceeds. At $+7.5^{\circ}\text{C}$ with a forming field of 5kV/cm the potential distribution shows the accumulation of space charges near both electrodes (Fig. 46), but the potential on the probes varied considerably during electrification (Fig. 45). With

a forming field of 10kV/cm at this temperature, the space charges are absent (Fig. 44). At +15°C there is no evidence of the accumulation of space charges (Fig. 48).

It has been suggested (Meakins and Hammar 1953) that proton transfer may take place along hydrogen bonded chains of hydroxyl groups in solid alcohols. If this were the mechanism responsible for the space charge accumulation in the experiments, one would expect an accumulation of positive charges near the cathode while the negative ions would remain scattered throughout the volume. This is not observed; therefore it seems unlikely that proton transfer plays an important part in the process.

If the charge carriers arise from ionic impurities, application of a field would cause negative electrons to move more readily than the larger positive ions. As the temperature of the sample is increased the mobility of the ions will increase. This behaviour will account for the results of the probe measurements. At -7.5°C the mobility of the positive ions is very low and they remain approximately uniformly scattered throughout the volume while the electrons move to form a negative space charge near the anode. At +0.5°C the mobility of the charge carriers is increased and some positive ions move to form a positive space charge near the cathode. For higher forming fields the positive ions will move more rapidly and the space charge

near the cathode will be larger. It seems that with a forming field of 10kV/cm the negative space charge near the anode decreases. This could be the result of the electrons discharging at the anode under the influence of the higher field. At +8.5°C the space charges accumulate under the lower field (5kV/cm) but with a field of 10kV/cm the charge carriers is such that the charge carriers pass to the electrodes and the space charges do not develop. The mechanism by which charge carriers are prevented from moving to the electrodes is not fully understood, but the existence of some barrier which hinders the discharging of ions at the electrodes and allows space charges to accumulate would account for the observed results. This barrier is more easily overcome as the temperature increases.

The measurements of the potential of the probes after the removal of the forming field were made as a further check on the existence of space charges. At -7.5°C there was no potential difference measured between the cathode and the nearest probe. This supports the previous statement that there was no space charge accumulation near the cathode at -7.5°C. At -7.5°C a potential difference was measured between the probes remote from the cathode and the cathode, and at +0.5°C a potential difference was measured between all probes and the cathode after the forming

field had been removed. This shows that there was a space charge accumulation at these temperatures.

On these points the results are in agreement with the two-charge theory, and the internal polarization is a space charge effect.

When the charging and discharging currents are taken into account a contradiction arises between these results and the normally accepted two-charge theory. Our measurements show that a discharge current is present at all the temperatures studied. From -28.0°C to $+8.5^{\circ}\text{C}$ the graphs of discharge current as a function of time for different temperatures are identical. Above $+8.5^{\circ}\text{C}$ the discharge current, at a given time since removal of the forming field, increases with increasing temperature. In this region above $+8.5^{\circ}\text{C}$ no volume polarization was detected by dipole moment and probe measurements and therefore the discharge must be attributed to a surface charge.

A solution can be found by considering Maxwell's (1873) approach to polarization in a medium consisting of layers of dielectrics with different conductivities. The surface of tetradecanol is not perfectly regular; therefore, there is a region between the main body of the sample and the electrodes that has conduction and dielectric properties different from the sample itself. The two surface regions can therefore, be considered as one dielectric and the main

body of the sample as the second. Maxwell's treatment of this case predicts that the application of a field to the dielectric will produce a current which decays with time to a steady conduction value as charges accumulate at the interface between the dielectrics. If the plates are later short circuited a current will flow in the opposite direction (Appendix D). In the case of tetradecanol the outer layer will contain adsorbed gas and surface contamination. The charge carriers may be ions from these impurities. The charges will reside on the surface of the main body of the sample shown below. A fuller discussion is given in Appendix D.

This is just what happens in the case of tetradecanol electrets. If the two dielectrics have the necessary relationships between their dielectric properties (as outlined in Appendix D), the polarization produced will take the form of an accumulation of charge on the surface of the main sample of the same sign as the adjacent forming electrode (Fig. 50).

One piece of evidence is found in the results of other workers that supports the assumption that the discharge current is a surface effect. Gerson and Rohrbaugh (1955) found that when iron filings are sprinkled on the surface of an electret and the electrodes are replaced, the discharge current increases considerably. If the discharge is due in part to a decay of charges in the surface layer, then conducting filings would be expected to release more charge as they are pressed into the surface.

The discussion so far has not included the measurements of discharge current at variable temperature (page 72). These measurements were made to check for the existence of "trapped" charges that might be liberated at a particular temperature. The curves obtained for different conditions are all smooth and therefore give no evidence of charges trapped at discrete levels.

There is a discrepancy between the observed macroscopic dipole moment and the total charge flowing

FIG. 50

during electrification. If this current produces an accumulation of surface charge it might be thought that the maximum observed dipole moment would correspond to a charge, equal to the integral of the charging current over the period of electrification, distributed over the surface of the sample. However, a consideration of the experimental conditions will show that this is not to be expected. In the dipole moment measurements, after electrification the electrodes were removed from the sample. As the electrodes leave the surface of the sample a discharge may take place between the sample and the electrode. This discharge has been found by other workers (Wiseman and Feaster 1957) to limit the surface charge density for an electret, in air at atmospheric pressure, to approximately 1 esu/cm^2 . This discharge effect will limit the surface charge in the experiment. The maximum observed charge density in the dipole moment experiments was of the order of 0.5 esu/cm^2 . After this initial disturbance the dipole moment measurements do not disturb the sample and therefore are a valid indication of the dipole changes taking place in the sample, but owing to the initial disturbance they cannot be considered as a quantitative measurement of the initial conditions.

On the basis of these results, I conclude that the electret behaviour of tetradecanol is due to the interaction of a real surface charge and a space

charge within the sample. The surface charge arises from conduction across the dielectric-electrode interface. The space charges arise from the motion of ionic impurities in the applied field. The observed currents are the result of the build-up and decay of the surface charge and at lower temperatures the build-ups and decay of the space charges contribute to the net current.

The contribution that this work has made to the knowledge of electrets can be summarized as follows:

This is the first detailed investigation of the electret properties of a pure organic substance through the temperature range in which at different temperatures, the samples show all the aspects of electret behaviour, i.e. only a heterocharge, heterocharge changing to homocharge, and only a homocharge.

The measurement of macroscopic dipole moment by means of the torsion balance was developed for this work. The method gives consistent results and is sufficiently sensitive to allow small samples to be used. The fact that after the removal of the forming electrodes the sample is not disturbed by the measuring system makes this method superior to the lifted electrode technique used by other workers.

The fact that discharge currents were measured in the temperature region in which no internal polarization was detected shows that a study of the internal

polarization of electrets cannot be based solely on discharge current measurements.

Finally, as the substance used was a pure material, easily obtainable, and the thermal treatment of the samples was very simple, this investigation provides the first set of results which could be repeated by other workers with expectations of agreement.

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APPENDIX A

The Internal Field of a Short Circuited Electret

A short circuited electret forms a three layer capacitor as shown below

The regions are of thickness d_1 d_2 d_3

The dielectric constants are κ_1 κ_2 κ_3

The fields are E_1 E_2 E_3

The displacements are D_1 D_2 D_3

and σ is the true surface charge on the interfaces

The outer plates are short circuited

$$\therefore E_1 d_1 + E_2 d_2 + E_3 d_3 = 0 \quad (1)$$

$$D_2 - D_1 = \sigma$$

$$D_3 - D_2 = \sigma$$

$$D_1 = D_2 - \sigma$$

$$D_3 = D_2 - \sigma$$

$$E = \frac{D}{\epsilon_0 \kappa}$$

$$\therefore E_1 = \frac{1}{\epsilon_o \kappa_1} (\epsilon_o \kappa_2 E_2 - \sigma)$$

$$E_3 = \frac{1}{\epsilon_o \kappa_3} (\epsilon_o \kappa_2 E_2 - \sigma)$$

Substituting in (1)

$$\frac{d_1}{\epsilon_o \kappa_1} (\epsilon_o \kappa_2 E_2 - \sigma) + E_2 d_2 + \frac{d_3}{\epsilon_o \kappa_3} (\epsilon_o \kappa_2 E_2 - \sigma) = 0$$

$$\therefore E = \frac{\frac{\sigma}{\epsilon_o} \left(\frac{d_1}{\kappa_1} + \frac{d_3}{\kappa_3} \right)}{\frac{\kappa_2 d_1}{\kappa_1} + \frac{\kappa_2 d_3}{\kappa_3} + d_2}$$

Therefore the internal field in a short circuited electret is given by

$$E = \frac{\frac{\sigma}{\epsilon_o} \left(\frac{d_1}{\kappa_1} + \frac{d_3}{\kappa_3} \right)}{d_1 \frac{\kappa_2}{\kappa_1} + d_2 + d_3 \frac{\kappa_2}{\kappa_3}}$$

If the shielding plates are close fitting

$$d_1 \rightarrow 0 \quad \text{and} \quad d_3 \rightarrow 0$$

$$\therefore E \rightarrow 0.$$

Appendix B

Analysis of Carmauba Wax

General composition given in Biochemists' Handbook (1)

Alcohols	$C_{24} - C_{34}$
Glycols	$C_{27} - C_{31}$
Hydrocarbons	$C_{18} - C_{30}$
+ Some Acids and Hydroxy Acids	

Analysis by Sturke (2)

A crystalline paraffinoid hydrocarbon M.P. $50^{\circ}C+$

Ceryl Alcohol $C_{27} H_{55} OH$

Myricyl Alcohol

Adihydric Alcohol $C_{23} H_{40}(CH_2 OH)_2$

An Acid $C_{23} H_{47} COOH$

Cerotic Acid

σ An Acid $CH_2 OH C_{19} H_{38} COOH$

1) Biochemists Handbook, published by E & F.N. Spon Ltd., 988, (1961).

2) F. Sturke Annalen 223-283.

Appendix C

Calculation of the Sensitivity of the Torsion Balance

With the optical system used a movement of ± 2 divisions of the torsion head is detectable. This corresponds to a rotation of the suspension of $\pm 2'$ arc. Therefore the smallest detectable dipole moment is that which, in the field of the balance, produces a torque equal to that produced by a twist of the suspension of $2'$.

$$\tau = \mu \times E = \kappa \theta$$

For the balance used $E = 0.13 \text{ esu cm}^{-1}$

$$\kappa = 0.09 \text{ dyne cm radian}^{-1}$$

$$\mu = \frac{\kappa \theta}{E}$$

Minimum detectable dipole moment per unit volume

$$= \frac{\mu}{V} = \frac{\kappa \theta}{E V}$$

$$V = 0.3 \times \pi \times (0.625)^2$$

$$\frac{\mu}{V} = \frac{0.09}{0.13} \times \frac{\pi}{180} \times \frac{2}{60} \times \frac{1}{0.3 \times \pi \times (0.625)^2}$$

$$= 1.067 \times 10^{-3} \text{ esu cm}^{-3}$$

The torsion balance can detect a change in the dipole moment per unit volume of $\pm 1 \text{ esu cm}^{-3}$ and a rotation of the torsion head of one division corresponds to a dipole moment per unit volume of 0.5 esu cm^{-3} .

Appendix D

Charge Accumulation in an Inhomogeneous Dielectric

The electret can be considered as a three layer capacitor as shown below.

If a potential difference V is applied to the plates the internal fields are given by

$$E_1 = \frac{V - \frac{d_2}{K_2} \frac{\sigma}{\epsilon_0}}{d_1 + \frac{K_1}{K_2} d_2 + \frac{K_1}{K_3} d_3}$$

$$E_2 = \frac{V + \left(\frac{d_1}{K_1} + \frac{d_3}{K_3} \right) \frac{\sigma}{\epsilon_0}}{\frac{K_2}{K_1} d_1 + d_2 + \frac{K_2}{K_3} d_3}$$

and if $K_1 = K_3$

$$E_3 = E_1$$

The current through a medium is given by

$$G E$$

where G is the electrical conductance and E is the electric field.

Therefore the current through medium 1 and 3 is

$$i_1 = G_1 E_1$$

and the current through medium 2 is

$$i_2 = G_2 E_2$$

in general $i_1 \neq i_2$

Therefore there is an accumulation of charge at the interface between media 1 and 2 and between media 2 and 3, given by

$$\Delta \sigma_{12} = (G_1 E_1 - G_2 E_2) \Delta t$$

$$\Delta \sigma_{23} = (G_2 E_2 - G_1 E_1) \Delta t$$

If $G_1 E_1 > G_2 E_2$ this charge accumulation is positive at the interface near the anode and negative at the interface near the cathode, i.e. a homocharge.

This accumulation of charge reduces E_1 and increases E_2 until

$$G_1 E_1 = G_2 E_2$$

and a steady state of conduction is reached.

If the forming field is removed and the electrodes short circuited the internal fields are given by

$$E_1 = E_3 = \frac{-\frac{d_2}{K} \frac{\sigma}{\epsilon_0}}{d_1 + \frac{K_1}{K_2} d_2 + \frac{K_1}{K_3} d_3}$$

$$E_2 = \frac{+ \left(\frac{d_1}{K_1} + \frac{d_3}{K_3} \right) \frac{\sigma}{\epsilon_0}}{\frac{K_2}{K_1} d_1 + d_2 + \frac{K_2}{K_3} d_3}$$

The fields E_1 and E_3 cause a current in the exterior shorting link in the opposite direction to the charging current. The current flow reduces the surface charges which create the field and therefore the current decays to zero.