THE ALUMINIUM ANODE FILM DIELECTRIC.

By M. Subramaniam.

SYNOPSIS.

Some of the properties of aluminium anode film condensers have been studied and some observations made of which previous records have not been found. By means of a polarising P. D. it has been shown that both the plates forming such a condenser when used in alternating current circuits behave as anodes; neither film breaks down unless the applied alternating crest P. D. exceeds the film-formation voltage. Measurements of voltage, current and power-factor confirm the observations, made by other experimenters, that the capacity depends upon the voltage at which the film is formed.

It is found that the leakage-resistance of the film is inversely proportional to the applied volts for a given formation-voltage, and directly proportional to the formation-voltage. The leakage-resistance was found to be nearly independent of frequency, within the range of the tests, and consequently its effect on the power-factor of the condenser diminishes with the increase of frequency. With a given electrolyte and temperature the film, if subjected to a voltage exceeding a critical value, collapses, the breakdown being accompanied by flashes of light and crackling sounds, the pitch of which corresponds to the frequency of the supply voltage and appears to be an octave higher. Ondographe records showing the above phenomena are given.

INTRODUCTION.

The property of asymmetrical conductivity is possessed by many electrolytic cells, the resistance to the flow of current from certain metals to the electrolyte being very great; the metals aluminium, tantalum, tungsten, bismuth and magnesium have been found to possess the property to a marked extent. An aluminium electrode immersed in a solution of ammonium borate gives relatively high conductivity when the aluminium is the cathode but when the applied voltage is reversed, making the metal an anode, the conductivity rapidly falls, the initial current dying away practically to zero in a time which depends largely upon its area, after which the anode film withstands the full potential difference applied (Fig. 1) within certain limits, The asymmetrical conductivity is due to an exceedingly thin film[1] formed on the surface of the aluminium electrode by electrochemical oxidation. The anode becomes coated with a thin gelatinous precipitate, full of minute punctures, which E. Wilson, using an aluminium anode in dilute sulphuric acid, found to be a basic sulphate of aluminium. In the experiments described below a solution of ammonium borate was used and the precipitate analysed by Mr. Raghavendra Char was found to be a basic borate of aluminium. Probably a coating of aluminium hydroxide first forms on the anode, afterwards reacting with the electrolyte.

The most commonly accepted theory regarding the nature of the film is that due to Schulze[2] who suggested that the valve action is due to a thin film of occluded gas in the oxide-covered metal. The gas is believed to be oxygen and impermeable to all ions excepting those of hydrogen. This conclusion is based on the observation, made by several experimenters, that the thickness of the visible film formed on an aluminium anode at a particular voltage, measured directly by the method of interference colours, or estimated by the increase in weight of the anode, differs widely with the electrolyte used. For instance, at 100 volts the thickness has been found to vary from 20×10^{-6} cm. and 170×10^{-6} cm., whereas the thickness of the dielectric film calculated from capacity measurements assuming unit permitivity is almost independent of the electrolyte, varying only between 0.95×10^{-6} cm. and $1{\cdot}1 \times 10^{-6}$ cm., at the above formation-voltage, viz., 100.

The film is observed to build up quickly when a polarising P. D. is applied until its 'thickness' or insulation is sufficient to withstand the applied volts. The time for the formation of the film depends on the area of the plate in addition to the current density and the impressed voltage, requiring from a few seconds to several hours for complete formation. The thickness of the film is proportional to the applied polarising formation-voltage, and for this reason the capacity formed by the dielectric film is very much greater for low values of formation-voltage.

The commonly used type of aluminium anode electrolytic rectifier generally shows the capacity effect of this thin film in its current wave form. Three components of current make up the resultant current, as shown in Fig. 2, through such a rectifier. The components are :—

(*a*) The unidirectional current I_{DC} which is in phase with the P. D. and flows during the first half of a cycle.

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[1] See Bibliography Nos. 12, 14, 16, 18 and 20. Literature on the thickness of the film has been summarised by Bairsto and Mercer (No. 20).

[2] *Trans. Far. Soc.*, 1913, 9, 266,

(*b*) A leading capacity current I_C which flows during the second half of a cycle.

(*c*) A leakage current I_L which is in phase with the P. D. and flows during the second half of a cycle.

The usual form of electrolytic condenser consists of two aluminium electrodes covered with the extremely thin dielectric film, and as a result it possesses a very high value of capacity per sq. cm. The capacity is inversely proportional to the formation-voltage as is shown by the measurements given in Table I for various values of formation-voltage. The capacity was calculated from the observed alternating current at twenty-five cycles per second, and power measured by the three ammeter method. This method of measuring the power was found to be suitable in the absence of an electrostatic voltmeter.

TABLE I.

Formation-voltage (Battery positive terminal to anode)	Microfarads per sq. cm. of film	Capacity × Voltage (Col. 1 × Col. 2)
5·0	1·40	7·0
17·4	0·56	9·7
30·0	0·30	9·0
48·0	0·15	7·2
80·0	0·10	8·0
170·0	0·044	7·7
196·0	0·043	8·4

The above results are in close agreement with those published by G. E. Bairsto and R. Mercer[1] and confirm the interesting fact that the product of the formation-voltage and the capacity is practically a constant.

The constancy of the capacity may be seen in Fig. 11 which shows the linear relation between the current and alternating P. D. for values of crest P. D. less than the formation voltage, viz., 105 volts in this instance.

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[1] *Trans. Far. Soc.*, 1911, 7, 1.

THE ACTION OF AN ELECTROLYTIC CONDENSER CARRYING ALTERNATING CURRENT.

If an ordinary aluminium plate condenser, which has already been provided with a dielectric film by means of a D.C. formation-voltage, is connected to a suitable alternating voltage source as shown in Fig. 3 the following observations are typical :—

(*a*) The P. D. across the condenser which consists of two films in series is that of the source as shown in Fig. 4 by the sine wave V_1 (dotted graph).

(*b*) The P. D. between each plate and the electrolyte takes the form of a displaced sine wave V_2 or V_3 of such amplitude that $V_1 = V_2 + V_3$ at all instants.

It will be observed that this voltage distribution differs from that found across a pair of ordinary condensers of equal capacity and having, for instance, mica as the dielectric. In such a case the voltage across each condenser would be the same at all instants without the displacement found in the electrolytic type. It is to be concluded that the electrolyte becomes negatively charged to an extent sufficient to keep both plates at a higher potential than the liquid at all instants. The effect of this negative charge at usual alternating frequencies is to maintain a polarising P. D. across each film, and consequently both electrodes behave as anodes. Attention has been drawn to this fact by Zimmerman[1] who describes an interesting hydraulic analogue.

The following experiments throw considerable light on the behaviour of this type of condenser :—

Experiment No. 1 : Polarised Electrolytic Condenser.

The electrolyte was kept at a predetermined potential below that of either plate by means of a polarising battery as shown in Fig. 5 and a sinusoidal alternating voltage at 25 cycles was impressed on the condenser. There was no direct current once the film had been formed, provided the alternating crest voltage was sufficiently low to keep the plates at a higher potential than the electrolyte throughout the cycle. The alternating voltage in one experiment was observed (Fig. 6) to give a leading current of about 2 amperes (Fig. 7) in the circuit. Under these conditions there is no doubt about the existence of a negative charge in the electrolyte at these frequencies. Alteration of the D. C. voltage, or its complete removal, causes no sensible change in the alternating current voltmeter, ammeter, or wattmeter readings. From this experiment it is to be concluded that both the

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[1] *Trans. Amer. Elec. Chem. Soc.*, 1914, 5, 147.

plates behave as anodes throughout the cycle and a negative charge exists in the electrolyte which at these frequencies is not entirely lost through the leakage-resistance paths across the films. Ondographe records of these effects, for example Fig. 7, show that the current and voltage wave-forms are not changed by altering the polarising D. C. voltage.

Experiment No. 2: The Negative Charge.

It may be demonstrated that a negative charge exists in the electrolyte by suddenly cutting off the alternating supply voltage, and short-circuiting (discharging) the two plates by an external path. If now a voltmeter is connected between *either plate* and the electrolyte, a current will flow from the metal to the electrolyte. If left for some time the electrolyte becomes discharged through the film leakage path.

Experiment No. 3: Single Film Condensers.

The capacity of a single film was tested by means of a pulsating unidirectional voltage.

This was applied between one aluminium electrode and a lead, or other, cathode the circuits being as shown in Fig. 8. A unidirectional pressure of 39 volts on which an alternating pressure of about 25 volts (r. m. s.) was superimposed gave the Ondographe records shown in Figs. 9 and 10[1] of the current and voltages. The r. m. s. alternating component of the unidirectional pulsating pressure across the condenser was 13·5 volts, the remainder of the 25 volts being absorbed in a rheostat. The sinusoidal current was 1·8 amperes and the power-factor 0·87. Consequently the capacity was 1,700 m. fds.[2] which is twice the capacity of two identical sets of aluminium plates for which as nearly as possible the same conditions of formation were used, viz., 890 m. fds. These observations show that in an electrolytic condenser with two aluminium electrodes the dielectric films are constant and are effectively in series, neither film behaving at any instant as a good conductor.

CONSTANCY OF CAPACITY FOR ALTERNATING CURRENTS.

The relation between capacity current and applied voltage for a particular electrolytic condenser when working at terminal pressures below that of the formation-voltage are plotted in Fig. 11, from the observations given in Table II.

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[1] The alternating voltage record was obtained by connecting a D. C. voltage in the recorder circuit to neutralise the polarising voltage in the cell circuit.

[2] $C = \frac{I}{\omega V \sin\phi} = \frac{1{\cdot}8}{2\pi \times 25 \times 13\frac{1}{2}} \times 0{\cdot}5 = 0{\cdot}001697$ farad.

TABLE II.

Solution (*A*) vide *Appendix.*

Alternating pressure in volts (r. m. s.) less than formation-voltage	Alternating current in amperes (leading)
60	1·05
57	1·00
86	1·50
114	2·00
137	2·50

LEAKAGE-RESISTANCE.

The leakage-resistance of the dielectric film, although high, is the cause of losses in a condenser carrying an alternating current. The following observations relating to leakage in a double film condenser were made :—

1. At a given frequency and film formation-voltage the leakage-resistance was found to vary inversely with the applied volts as is shown in Table III and Fig. 12 for the particular condenser tested.

TABLE III.

Solution B and formation-voltage 150.

Terminal pressure in volts. (1)	Leakage-resistance on ohms (2)	Col. (1) × Col. (2)
50·0	850	42,500
60·0	715	42,900
85·0	550	46,750
100·0	470	47,000
120·0	400	48,000
130·0	380	49,400

2. The leakage-resistance was found to be proportional to the formation-voltage. Table IV gives data obtained in the course of these experiments at 25 cycles per second.

TABLE IV.

Formation-voltage	Resistance per sq. cm. of film for one Electrode[1]
5·0 volts.	0·016 megohm
17·4 ,,	0·042 ,,
30·0 ,,	0·080 ,,
48·0 ,,	0·165 ,,
80·0 ,,	0·242 ,,
170·0 ,,	0·546 ,,
196·0 ,,	0·563 ,,

The fact that the leakage-resistance is directly proportional to the formation-voltage indicates that the thickness or density of the complex film builds up a sufficient thickness of dielectric to withstand the P. D. applied.

The harmful effects, i.e., the energy losses due to the leakage resistance, if it behaves as a high resistance shunt across a perfect condenser, should diminish at higher frequencies.

It was found that the effect of the leakage on the power-factor diminished with increase of frequency. This was investigated for frequencies up to 300 cycles per second with the results shown in Tables V and VI and Fig. 13 (*a*) which gives the graph (plotted from Table VI) for the equivalent series resistance, obtained by wattmeter measurements of the losses at different frequencies.

The equivalent series resistance, for which the formula $R_S = \frac{R_L}{1 \times \omega^2 R_L^2 C^2}$ was used is shown in Fig. 13 (*b*) calculated on the assumption of constant capacity and leakage-resistance. The close agreement between the two curves shows the constancy of the capacity and the leakage-resistance at frequencies up to 300 cycles per second.

[1] $R_L = \frac{V}{I \cos\phi}$ = resistance in parallel with capacity.

TABLE V.

Condenser No. I (b).

Frequency (cycles per second)	Equivalent series resistance (Ohms)
26·66	8·35
32·00	6·30
34·66	5·70
40·66	4·70
44·66	4·15
50·00	3·55

TABLE VI.

Condenser No. I (c).

Frequency (cycles per second)	Equivalent series resistance (Ohms)
25	7·3
35	6·0
43	4·0
47	3·5
50	3·0
150	1·55
300	0·50

BREAKDOWN OF THE DIELECTRIC FILM.

An electrolytic condenser of the type considered is found to retain its properties unless the dielectric is subjected to (*a*) mechanical injury by scratching, over-heating, destructive action of the electrolyte, or (*b*) a voltage exceeding the formation-voltage. For instance, on the application of an alternating P. D. the crest value of which exceeds the formation-voltage, the film breaks down and a large conduction current flows. On the persistent application of this over-voltage the current slowly diminishes, while a fresh film is forming capable of withstanding the higher P. D.

The effect of over-voltages on the current wave-form is shown in Fig. 14. It will be noticed that at a particular point in each half-cycle there is a rush of current corresponding to the collapse of the film which in the next half cycle seems to re-form.

The critical voltage at which breakdown occurs is found to depend both on the metal and the electrolyte. This is about thirty volts for aluminium anodes in dilute sulphuric acid, whereas in dilute ammonium borate (solution C) [1] it is as high as 600 volts. In the solution A used for most experiments it is about 200–250 volts. When the applied P. D. exceeds the critical value the film apparently breaks at weak points with a phosphorescent glow, which on increasing the pressure becomes disruptive, emitting flashes of light and sounds, the pitch depending upon the frequency of the A. C. supply and roughly appearing an octave higher.

The effect of impressing a voltage higher than the critical voltage on the film is indicated by Fig. 15 where it will be noted that the P. D. and the current are practically in phase, showing that the capacity effect has ceased to exist.

The periodic breakdown of the dielectric appears similar to that used in the Wehnelt interrupter and, as it is a matter of some interest, experiments are now being carried out at high frequencies, such as 100 kilo-cycles per second. On account of the high critical voltage of over 1,000 said to have been observed for the metal tantalum it is hoped that condensers of this type may be studied.

The writer wishes to thank Professor Catterson-Smith for suggesting this investigation and for his encouragement and help during its progress.

APPENDIX I.

Composition of the Ammonium Borate.

Solution A.—1	Kgm.	Boric Acid.
4	litres	Concentrated Ammonia.
12	,,	Distilled Water.
Solution B.—1	Kgm.	Boric Acid.
4	litres	Concentrated Ammonia.
24	,,	Distilled Water.
Solution C.—1	Kgm.	Boric Acid.
4	litres	Concentrated Ammonia.
36	,,	Distilled Water.

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[1] For concentrations of these solutions, see Appendix I.

APPENDIX II.

Variation of Capacity with Time.

TABLE VII.

Condenser No. 3 (a).

Time in days	Capacity micro-farads	Capacity of double film mic.-fds. per sq. cm.
0	2,800	0·133
1	3,100	0·145
2	3,400	0·162
3	3,500	0·166
4	3,700	0·176
5	3,750	0·178
7	3,825	0·180
8	3,900	0·185

Area of one electrode 21,000 sq. cm.

Current 10·5 amperes at 20 to 16 volts, 25 cycles per second.

At the end of the above period the current was accidentally cut off for some hours and when switched on again it was found that the capacity had fallen to about 3,500 M. fds. It slowly increased again during a further run of eight days.

The above observations show that the capacity is approximately constant for such purposes as do not require it to remain closer than five or ten per cent., for a few hours, and where very large currents at low frequencies are to be handled.

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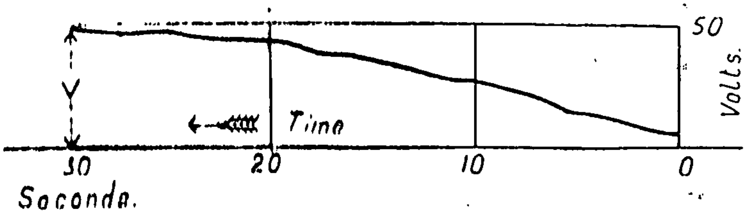

Fig 1_Voltage across the aluminium anode during formation.

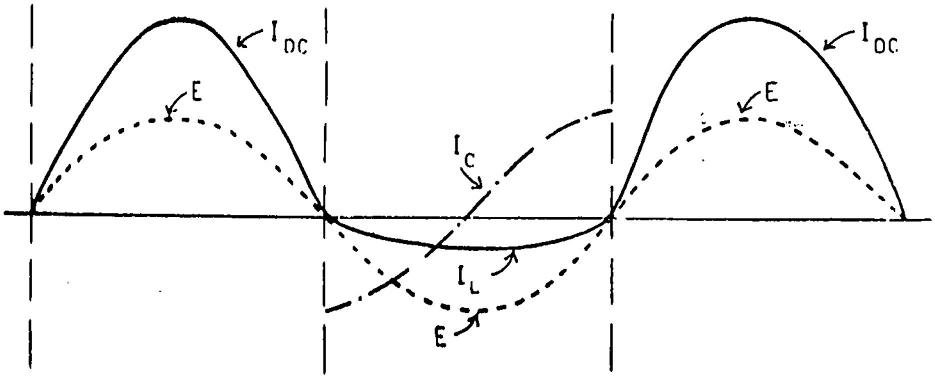

Fig 2_Components of current flowing through rectifier.

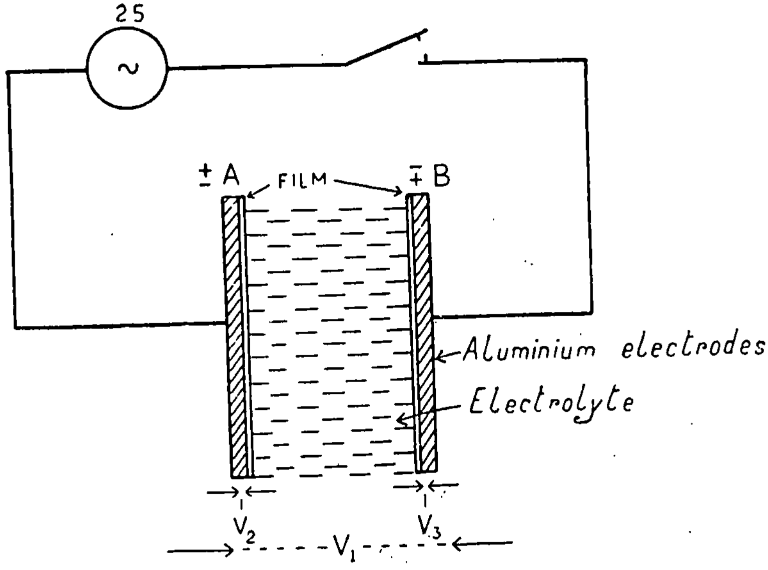

Fig 3

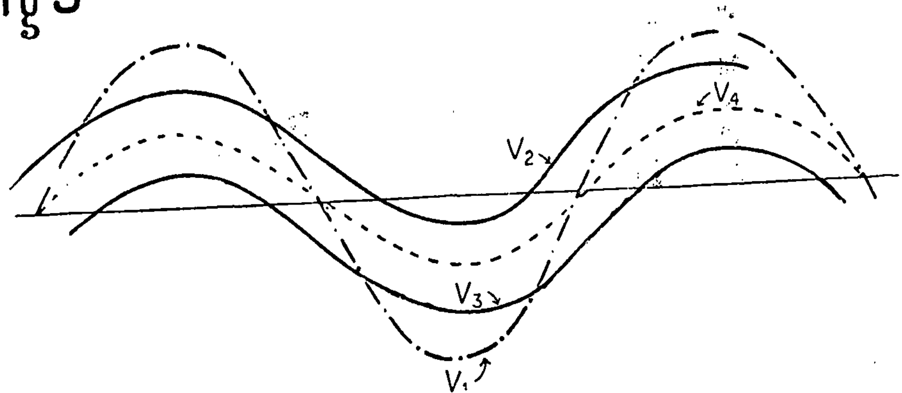

Fig 4 _ P.D. Components across films.

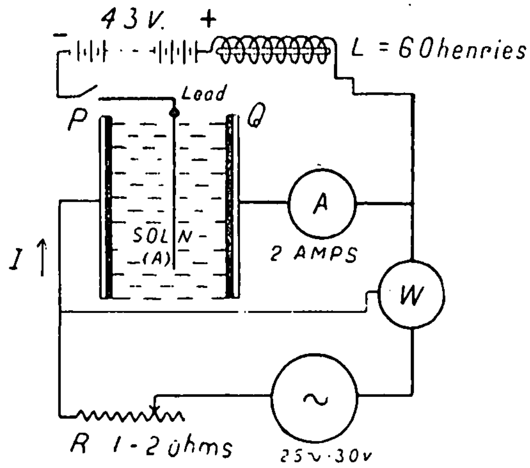

Fig 5_ Test circuit.

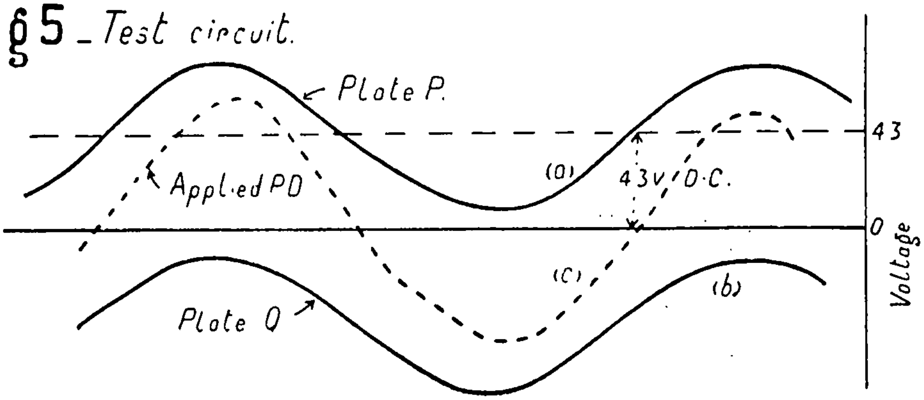

Fig 6_ Wave form of P.D. between plate & electrolyte.

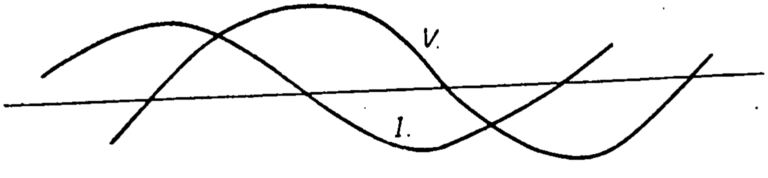

Fig 7_ Capacity current flowing in circuit

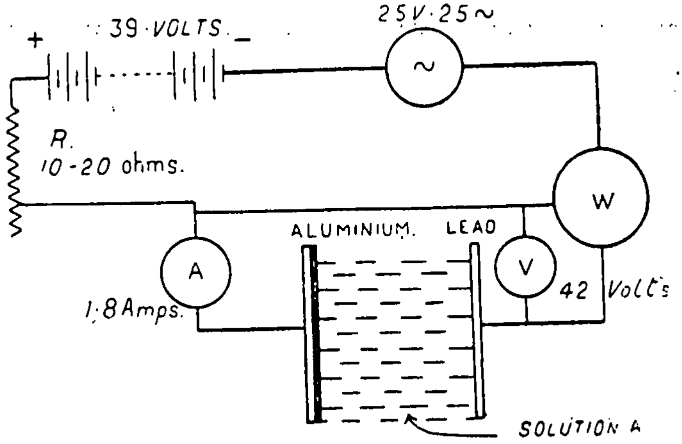

Fig 8 _ Single film test circuit.

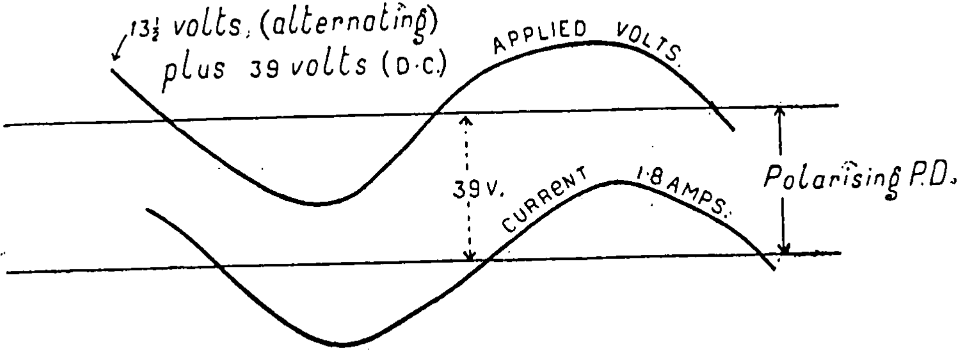

Fig 9 _ Single film capacity current.

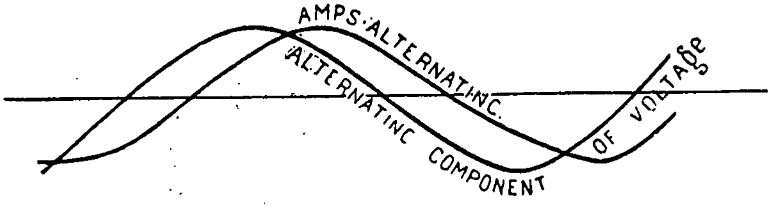

Fig 10 _ Alternating P.D. and current with single film.

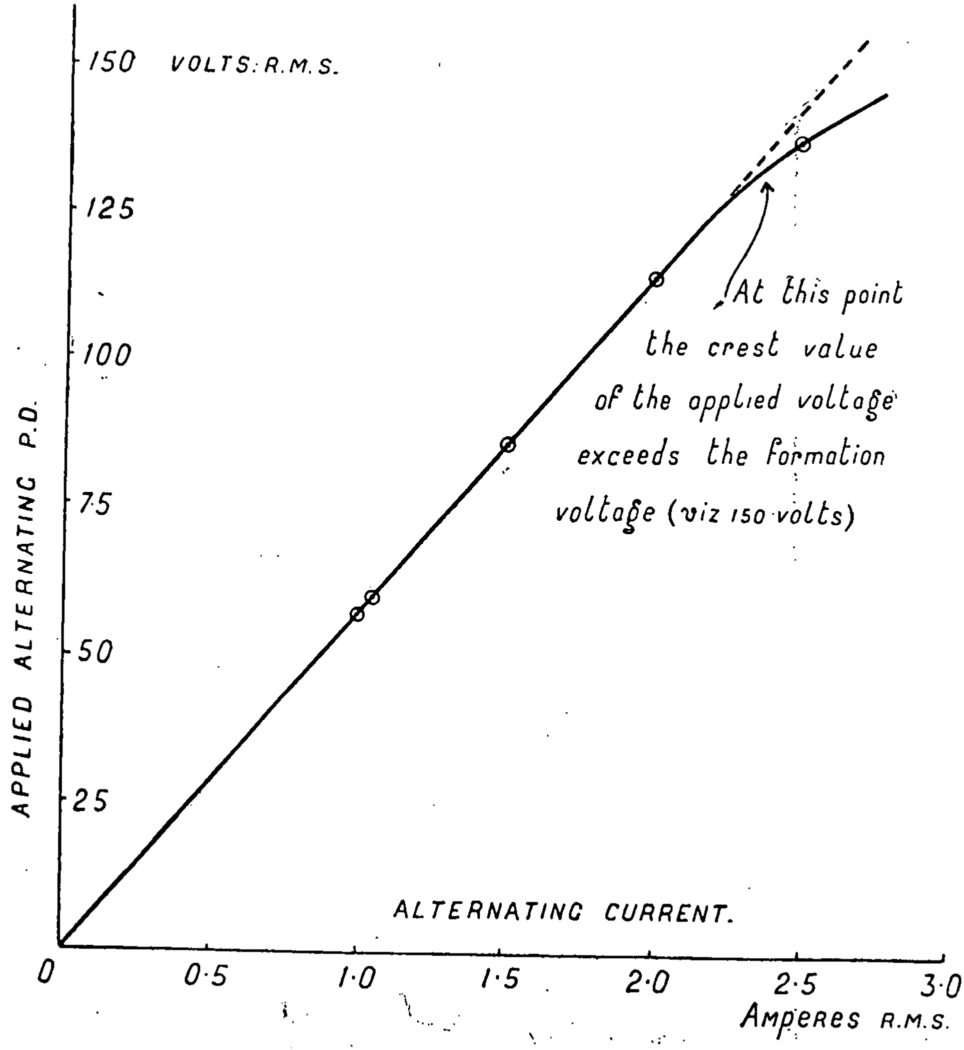

Fig 11_Constancy of film capacity

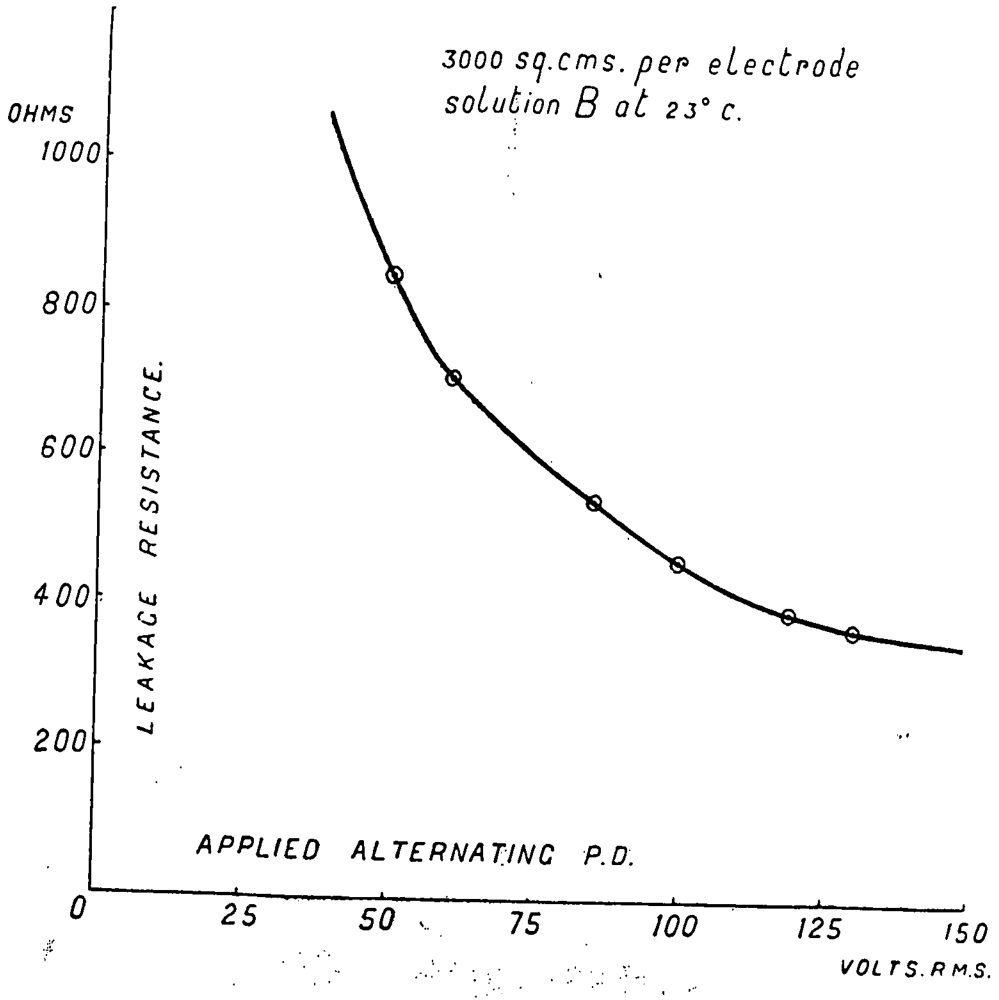

Fig 12 – *Film leakage resistance.*

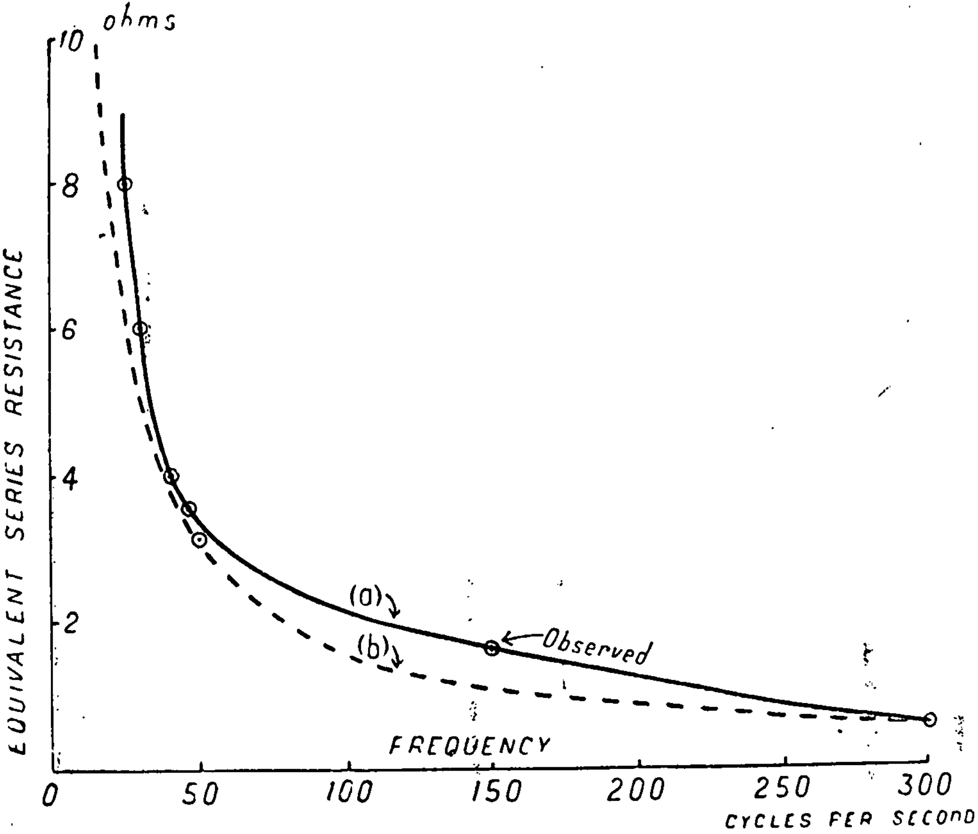

Fig13 _ Equivalent (series) resistance.

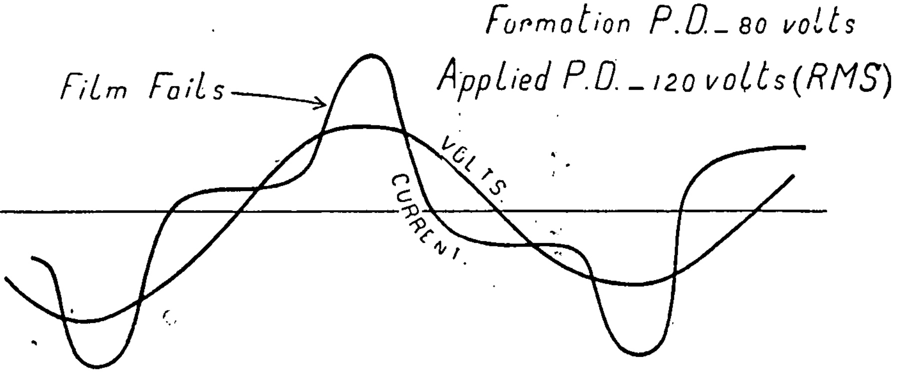

Fig 14_ Current wave form with failing film.

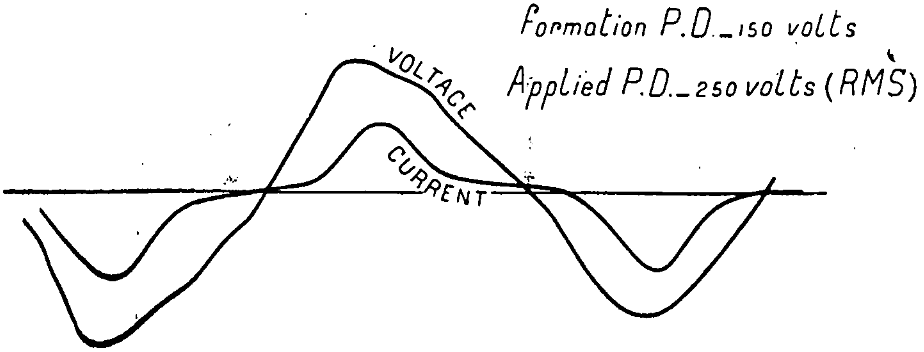

Fig 15_ Current wave form with film injured.

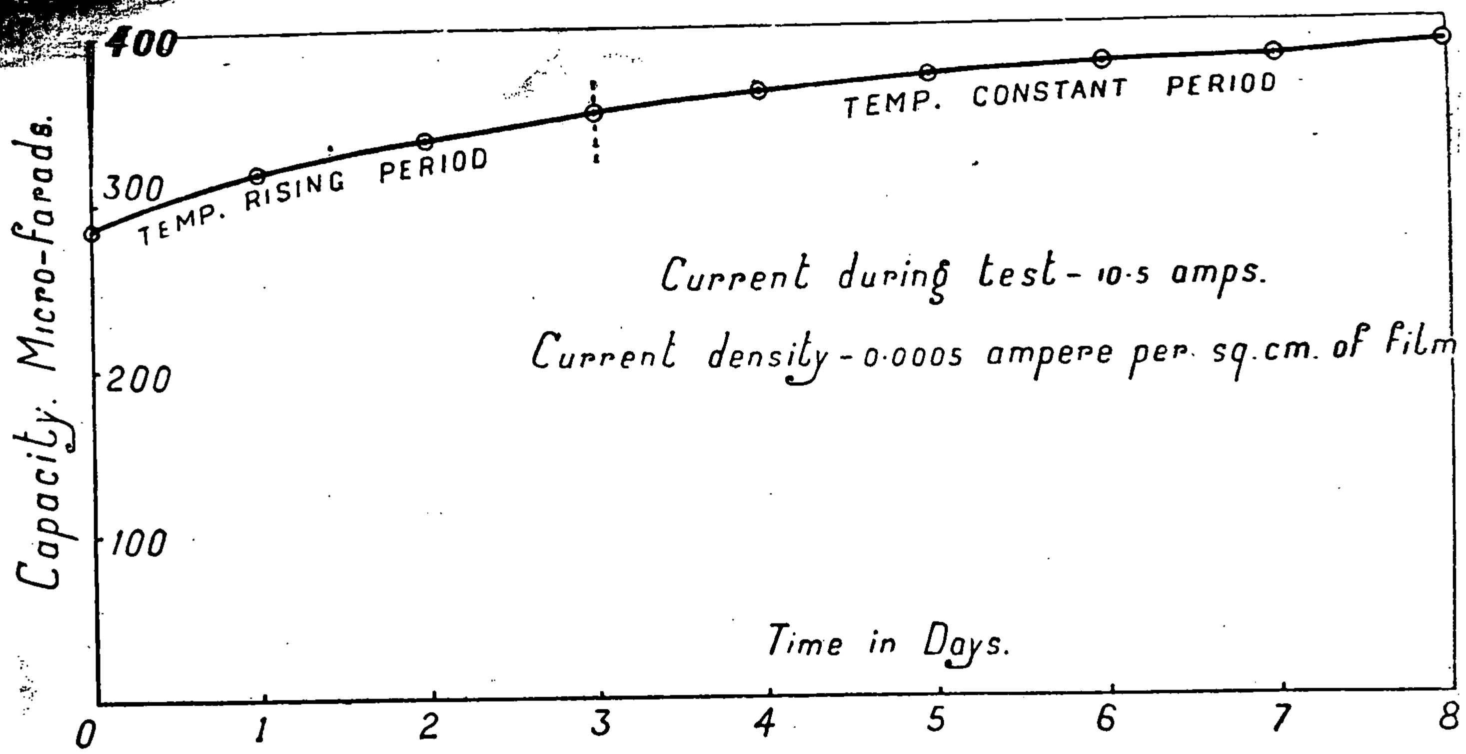

Fig 16 _ Slow change in capacity with time and temperature.