The Conditions of Formation and Stability of Films at the Electrodes in Dielectrics

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The conditions for formation and destruction of films at the electrodes in dielectrics were studied with respect to their dependence on the type of heat treatment and on the action of the electric field. A connection between the change of electrical conductance produced by impurities and the change of properties of the electrode films was discovered and investigated.

1. GENERAL REMARKS

CLARIFICATION of the condition for formation and destruction of films at the electrodes in self-forming dielectrics is of considerable interest; for occurrences at the electrodes in dielectrics and semi-conductors have a bearing on the possibility of application of technically important devices (electrolytic condensers and rectifiers, high-temperature insulation, etc.).

Researches conducted earlier[1] on the electrical conductivity of quartz and of alkali-halide crystals showed that phenomena connected with the formation and destruction of a film at the anode lead to an extremely complex variation of the current with time. In the present work these researches are extended to a series of other dielectrics: porcelain, Eternit (an asbestos cement), mica and asbestos. Besides the previously used method of successive changes of the direction of the electric field, a new method was applied, which enables one to examine in succession the separate important features of the process of formation of the dielectric.

In the study of the variation of current with time, two similar specimens were clamped in an iron frame; a second electrode was placed between them. Thus the two specimens were connected in parallel; this eliminated the necessity for using insulation. The frame was placed in a tubular electric furnace. The constancy of the temperature was carefully controlled; a compensation scheme of thermocouple connection was used for this purpose. For photographic recording of the variation of current with time, the apparatus used was a string electrometer, shunted with a wire resistance, and a rotating drum with a photographic film. During the photographing, the commutation of the voltage occurred only in the circuit of the dielectric under study. In the photographs, therefore, the curves for currents in both

[1] Ia. N. Pershits, J. Exper. Theoret. Phys. USSR 17, 251 (1947)

directions were obtained on one side of the zero position; this facilitated their comparison.

The object under study was subjected to prolonged electrolysis (30-60 min), and then the variation of current with time was recorded in the "permeable" and the "shut-off" directions.

In Figs. 1 and 2 are shown curves of the variation with time of the "permeable" and "shut-off" current in fused quartz. From Fig. 1 it is evident that in the specimen of fused quartz (temperature 550° C, $E = 120$ V/cm), subjected to prolonged electrolysis, after a change of direction of the field there develops a "permeable" current that increases abruptly and passes through a maximum (coefficient of unipolarity $K = 10$). Such dependence of the "permeable" current on time occurs in all the dielectrics studied. At the same time, as we shall see later, even in a single specimen the character of the current in the "permeable" direction depends on the previous treatment; specifically, on the action of the electric field and on the type of heat treatment.

The most characteristic features, for all the dielectrics, are the curves of variation of current with time after a repeated change of direction of the field ("shut-off" current). For different dielectrics these curves may differ in the rate of fall of current, but the character of the variation is quite similar for different dielectrics. Comparison of the curves drawn in Figs. 2a and 2b shows that the rate of decrease of current in the "shut-off" direction depends on the duration of the current in the "permeable" direction. This rule is so general that it leads us to surmise the presence of an electrode film in the dielectric even when none can be observed by probe measurements of the potential distribution.

It has already been established by probe measurements[1] that the dependence shown in Figs. 1 and 2 is connected with the destruction and restoration of a film at the anode, produced by electrolysis of the dielectric. In the present work, as a result of a
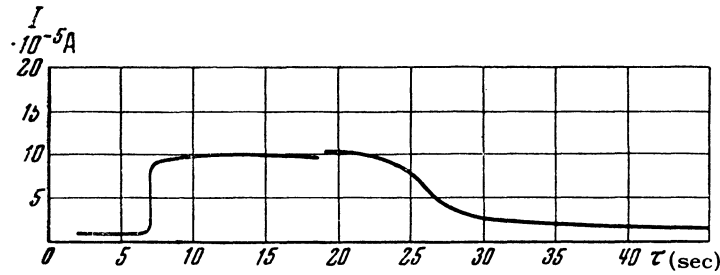
Fig. 1. Variation of current with time for "permeable" and "shut-off" currents. Rising curve (at left), "permeable" current": falling curve (at right), "shut-off" current.
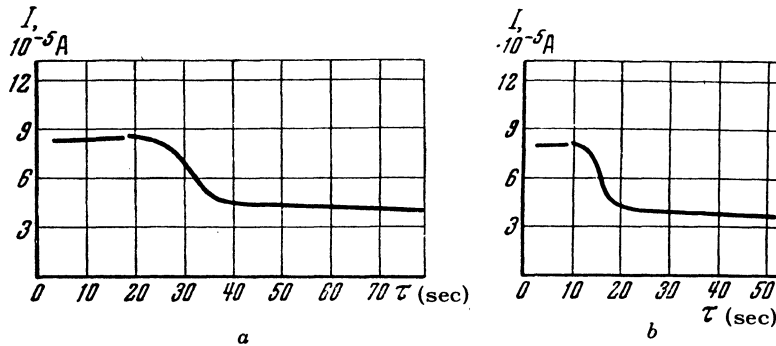

Fig. 2. Dependence of current in the "shut-off" direction on duration of current in the "permeable" direction. Duration of "permeable" current: a, 14 sec; b, 7 sec.

study of different dielectrics, we arrived at the following conclusions, the basis of which we will give below:

1) In the electrolysis it is possible for two high-resistance films to be formed at the electrodes: a cathodic and an anodic. The cathodic film is stable; the anodic is unstable and completely determines the observed unipolar phenomena.

2) The degree of stability of the anodic film and its resistance depend on the conditions of formation of the film, and specifically on the character of the previous heat treatment and the time of action of the electric field.

3) Certain conditions (heating, electrolysis), which contribute to an increase of resistance of the electrode film, produce a simultaneous increase of conductivity of the specimen itself.

4) The magnitude of the coefficient of unipolarity for a given dielectric depends on the conditions of heat treatment and the action of the electric field.

2. CATHODIC AND ANODIC HIGH-RESISTANCE FILMS

Simultaneous formation of high-resistance films on the cathode and the anode was observed in E-

ternit. We shall describe one of the experiments. On specimens of Eternit ($17 \times 10 \times 4$ mm) there were deposited on one side (17×10 mm) continuous graphite electrodes, and on the opposite side pairs of similar graphite electrodes, separated by a thin strip of the pure dielectric. Two specimens were clamped in an iron frame in such a way that both continuous electrodes butted against the frame, whose holder served to connect these electrodes to one of the terminals of the current source. The small graphite electrodes were face to face; between them were placed iron plates, which served to connect the specimens to the other terminal of the current source. In Fig. 3 is shown the wiring diagram of the specimens. Shown in black in the diagram are the plates that cover the graphite electrodes deposited on the Eternit specimens. The terminal C is connected to the continuous electrode, terminals A and B to the small electrodes. Hereafter these same letters will represent the corresponding electrodes. By means of a switch it was possible to connect electrodes AC or BC to the current source. The frame was placed in a tubular furnace and heated to a temperature of 580° C.
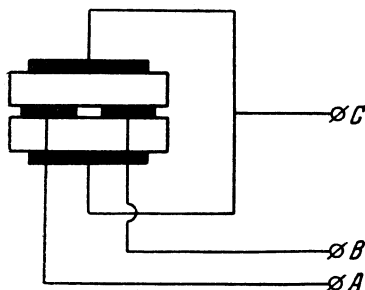
Fig. 3. Wiring diagram of specimens with auxiliary electrode *(B)*.

Fig. 4. Change of current in Eternit during and after formation of a cathodic film.

With equal areas of electrodes A and B, the initial currents existing at the instant of application of a field between electrodes A and C or B and C, were also equal (for $E = 225$ V/cm, I_A $= I_B = 4 \times 10^{-5}$ A). Initially the electric field was applied in such a direction that electrode A was the anode, electrode C the cathode; the auxiliary electrode B remained free. Eleven minutes after the beginning of electrolysis, the current had diminished to 1.6×10^{-5} A. At this time the "permeable" current was equal to 3.2×10^{-5} A. On the replacement of electrode A by electrode B, the current was also equal to 3.2×10^{-5} A (Fig. 4, point M). As a result of further electrolysis, the current between electrodes A and C for the "shut-off" direction became equal to 1.2×10^{-5} A, and for the "permeable" 2.4×10^{-5} A; but upon replacement of A by electrode B the value 2.4×10^{-5} A was again obtained for the current. Subsequent formation of the specimen between electrodes B and C led to a corresponding decrease of the current, but the "permeable" current in this case was equal to the current passing between electrodes B and C at the instant of application of the field (2.4×10^{-5} A). The process described is shown in Fig. 4.

In These experiments, two circumstances are noteworthy: a) passage of current through the specimen between electrodes A and C has an effect on the conductance of the specimen between electrodes B and C; b) at any instant of time the initial value of the current passing through electrode B is equal to the value of the "permeable" current passing through electrode A. The decrease of conductance of the specimen between electrodes B and C, when current flows between electrodes A (+) and C (−), shows that the electrolysis is accompanied either by an increase of resistance near the cathode, i.e., by creation of a cathodic film, or by decrease of the volume conductivity. The latter hypothesis is easily excluded by means of a similar control ex-
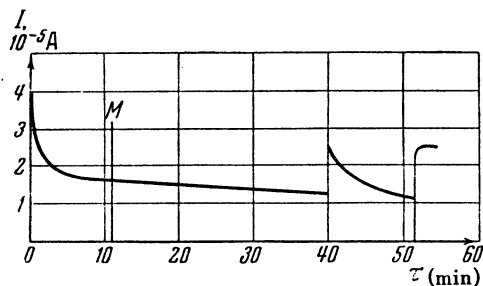
periment in which electrode C serves as anode. In this case electrolysis between electrodes A (−) and C (+) also produce a decrease of conductance between B (−) and C (+) in consequence of the creation of an anodic film on electrode C; but now after change of the direction of the field between electrodes A and C ("permeable" current), the current between electrodes B and C is equal to the value that was measured upon first application of the field, i.e., before formation. From this it is also clear that the anodic film is easily destroyed by an electric field in the "permeable" direction.

Concerning the cathodic film it is so far possible only to conclude that it either is not destroyed at all, or is incompletely destroyed, since both in this and in the other case the "permeable" current is less than the current that passes through the unformed specimen. However, it is not hard to show that only on the anode does there form a film on which the electric field has an effect, and that the cathodic film is comparatively stable. For this purpose, after passage of "permeable" current between electrodes A (−) and C (+) we pass current in the "shut-off" direction between B (+) and C (−). The characteristic variation with time of the "shut-off" current is not observed in this case. But if we apply to the electrodes a difference of potential as in the control experiment mentioned above, then replacement of electrode A by electrode B after passage of current in the "permeable" direction produces in the "shut-off" direction a decrease in current according to the characteristic curve, dependent on the duration of current in the "permeable" direction.

Experiments conducted on porcelain showed that after electrolysis of brief duration ($\sim$ 10 min, t = 340° C), the initial value of "permeable" current was appreciably less than the initial value of current passing through the specimen at the instant of application of the field. However, investiga-

tions conducted by the method described above disclosed that in porcelain no high-resistance film forms on the cathode. Thus in one of the experiments ($t = 250°$ C, $E = 180$ V/cm) the initial values of the currents for electrodes A and B were equal to 2.4×10^{-5} A. During 42 minutes of electrolysis the current between electrodes A $(+)$ and C $(-)$ decreased to 1×10^{-5} A, and the "permeable" current between these electrodes was equal to 1.5 $\times 10^{-5}$ A; but the current between electrodes B and C upon switching on of electrode B did not decrease as compared with the initial value of the currents.

Observation of the character of the currents upon change of electrodes, by the method indicated above, showed that in porcelain all the changes connected with change of direction of the field occur only at the anode.

3. STABILITY AND RESISTANCE OF ELECTRODE FILMS

In the study of electrode films, one is impressed by the diverse character of the curves of "permeable" current. From photographs presented in Ref. 1 and and from Figs. 1 and 2 of the present article, it is evident that even in a single dielectric (quartz) these curves may be different. Furthermore it appeared that for all dielectrics, the course of the variation of the "permeable" current with time is determined by the conditions of preparation of the specimen. A change of direction of the field after prolonged electrolysis always gives a "permeable" current that rises more or less, and subsequent reversals give a smaller rise and then a constant current. This effect is very noticeable in the photographs in Ref. 1 (Fig. 8, quartz). It is more marked in Eternit and particularly in porcelain. In Fig. 5 are shown three curves of "permeable" current for Eternit specimens. The first curve was obtained after prolonged electrolysis, the second and third after the subsequent brief electrolysis (2-3 min) necessary for restoration of the anodic film destroyed by current in the "permeable" direction. Comparison of the curves shows that in conse-- quence of the reversals there is a change of character of the curves: upon subsequent reversals, the values of "permeable" current very appreciably exceed the "permeable" current that passed after the first change of direction of the field.

Detailed study of the dependence of "permeable" current on the preceding preparation showed that the character of the curves is determined by the degree of stability of the anodic film. Special experiments with use of an auxiliary electrode showed
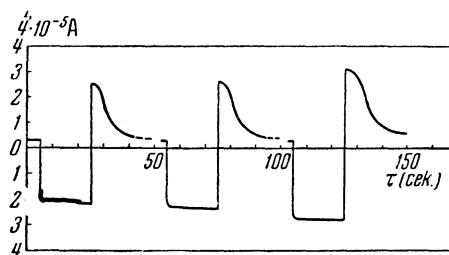

Fig. 5.

that passage of current in the "permeable" direction is always accompanied by growth of the film on the new anode ["permeable" current between $C(+)$ and A $(-)$ is accompanied by decrease of conductance between C and B]. But this film, originating during the short time of passage of current in the "permeable" direction, is comparatively unstable (in Eternit), and after a change of direction of the field it disappears practically instantaneously.

If, despite the increase of resistance of the new anodic film, an increasing or even constant "permeable" current is observed, sometimes over an extended time (1-2 min), this means that the passage of "permeable" current is in this case connected with a destruction of relatively stable components of the anodic film. This disappearance of a tight film on one electrode and growth of a not very stable one on the other causes a peculiar unipolar effect, which in different dielectrics has a different relative magnitude. From Fig. 1 (quartz) and Fig. 5 (Eternit) it is clear that the fall of the current in the "shut-off" direction after reversal of the field starts from a value larger than the maximum current in the "permeable" direction. This effect is particularly pronounced in those dielectrics in which short-duration electrolysis does not cause formation of stable components of film at an electrode (for example, in Eternit). In this case the high resistance on the new anode exists only for current of one direction; and since passage of current is accompanied by a diminution of resistance at the other electrode, upon change of direction of the field to the "shut-off" direction the resistance of the specimen as a whole is less than the resistance for "permeable" current. Venderovich and Lapkin [2], measuring the distribution of potential in porcelain, found that the poorly conducting film gradually disappears on change of direction of the field. The authors cited used specimens that had undergone prolonged electrolysis.

[2] A. M. Venderovich and B. Lapkin, J. Exper. Theoret. Phys. USSR 9, 46 (1939)

In this case there forms on the anode in porcelain a comparatively stable film; however, an appreciable part of the film, as our experiments have shown, is always very unstable even in porcelain.

To solve the problem of the formation of a stable component an of its relation to the unstable, we again used and auxiliary electrode.

The specimens were formed initially at temperature 320° C; the following values of current were obtained: in the "shut-off" direction, $I_A = 2 \times 10^{-5}$ A; in the "permeable", $I_C = 8 \times 10^{-5}$A; between the common electrode C and the auxiliary electrode B, $I_B = 16 \times 10^{-5}$ A. Under these conditions there formed a relatively stable electrode film. Then the temperature was raised to 420° C for a few minutes, and as the result of brief electrolysis the following currents were measured: $I_A = 5.2 \times 10^{-5}$ A; I_C increasing from 24×10^{-5} A to 40×10^{-5} A; $I_B = 40 \times 10^{-5}$ A. That is, as a result of comparatively rapid annealing at a higher temperature, the anodic film became not very stable. Further observations were made after 1 hour (Fig. 6 a) and after 2 hours (Fig. 6 b) in an applied field ($E = 180$ V/cm). It was found that in both cases $I_B = 56 \times 10^{-5}$A. The large difference between the currents passing through electrode A in the "permeable" direction and through electrode B shows clearly that in this case the tight component is large; furthermore it increases in proportion to the passage of current.

It is very interesting that the current passing through the auxiliary electrode not only did not decrease, but actually increased a little (from 40×10^{-5} A to 56×10^{-5} A).

This at once shows that the decrease of current upon prolonged electrolysis in the "shut-off" and "permeable" directions is connected with the growth and enlargement of a stable electrode film, and not with any volumetric effect.

The stability of the electrode film and its resistance are much influenced by the heat treatment of the specimen. The character of the curves of "permeable" current, and also the values of the currents in the two directions at a given temperature, depend on the previous heat treatment.

In all cases a cooling of the specimen, especially of one previously annealed at a higher temperature than that of the measurements (580° C for E-ternit), produces an appreciable increase of stability of the film at the anode and an increase of resistance of the specimen for currents in the "shut-off" and "permeable" directions. As a result of such treatment, there is also an increase of resistance of a specimen that has no electrode film. The procedure of cooling and subsequent heating of the specimen produces quite the same change in character of the "permeable " current curves as does prolonged electrolysis.

To study this phenomenon, the frame with the specimens was quickly withdrawn from the hot furnace, and then reinserted after partial or complete cooling. The cooling was done both in an applied field and without a field. The reheating was usually done with the field off. The electrolysis after the new heating was continued for only a few minutes; for such duration of the electrolysis, without preliminary cooling, the effect of the tight film was not noticeable. The procedure in these measurements was briefly as follows: After prolonged electrolysis, the stability of the film is decreased by a series of successive changes of direction of the field; then follow the cooling and the reheating.

In order to determine the effect of cooling on the magnitude of the electrical conductance, the specimens were subjected to electrolysis of such duration that a practically stationary current was obtained, i.e., such in each case that in the interval of time necessary for the repeated electrolysis, no noticeable change of current occurred. By use of the auxiliary electrode, it was possible to compare the change of resistance of the films and of the specimen itself.

In Table 1 are presented the data on specimens of Eternit with various preliminary treatments; for all specimens, the highest temperature used in the heating was 720°C.

It is evident from the table that the cooling-heating cycle was accompanied by an appreciable decrease of the electrical conductance with respect to currents in the "shut-off" and "permeable" directions, and also a decrease of conductivity of the specimen itself without regard to films at the electrodes. There is no doubt that, in Eternit, the resistance of the electrode film changes very greatly as a result of cooling and subsequent heating.

A diminution of conductance of electrode films and of the specimens themselves, after annealing at a high temperature, cooling and reheating, was observed also in other dielectrics (porcelain, asbestos, mica, rock salt).

4. FORMATION OF ELECTRODE FILMS AND INCREASE OF CONDUCTANCE OF DIELECTRICS
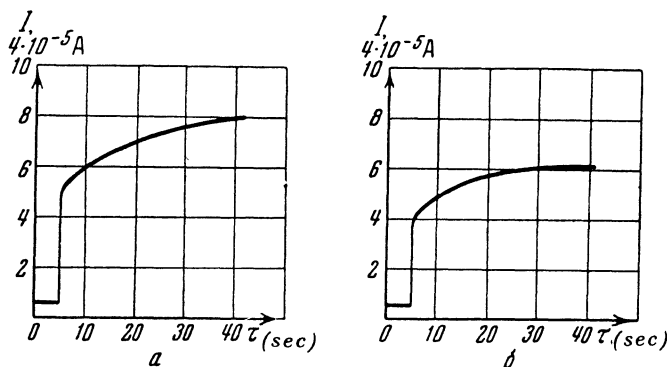
Fig. 6. Change of "permeable" current
as result of the action of an electric
field.

Table 1

Temperature of Measurement 0°C	Before Cooling 1 × 10⁵ A			After Cooling 1 × 10⁵ A			%			Remarks
	I_A	I_C	I_B	$I_A{}'$	$I_C{}'$	$I_B{}'$	$\dfrac{I_A{}'}{I_A}$	$\dfrac{I_C{}'}{I_C}$	$\dfrac{I_B{}'}{I_B}$	
580	3.2	12	13.2	2.4	10	12	75	83	90	Partial Cooling
580	2.8	11.2	14.4	2	8.8	12	71	79	83	
580	4	14	(a)	3	11.2	---	75	80	---	
580	1.6	8.8	(a)	1.2	8	---	75	91	---	
580	1.6	9.2	(a)	1	8	---	62	87	---	Complete Cooling
580	1.6	8.8	(a)	1	7.6	---	62	86	---	
580	1.2	10.8	(a)	0.8	8.8	---	67	81	---	
720	9.2	56	64	7.6	48	56	82	86	88	Partial Cooling

(a) Without the additional electrode

The electrolysis of a self-forming dielectric, pre-
viously annealed at an elevated temperature, is ac-
companied by two processes, which have opposite
effects on its electrical conductance: a) an increase
of the conductivity of the specimen; b) a rise in
the resistance of the electrode film. The increase
of conductivity is usually masked by the marked
rise in resistance of the electrode film; but the
observations and special experiments confirm that
the conductivity of the annealed specimen in-
creases upon subsequent action of the electric
field.

In Eternit, as a result of annealing at an ele-
vated temperature and of subsequent electrolysis,
the "permeable" current is often no smaller than
the initial current, passing at the instant of ap-
plication of the field; with short-duration electroly-
sis (1-2 min), the "permeable" current may even
exceed the initial current.

Special control experiments showed that even at
high temperatures a cathodic film is formed; there-
fore it may be hypothesized that the increase of
"permeable" current under such treatment is the
result of an increase of conductivity of the specimen
itself. This hypothesis was confirmed by special
experiments. In one of the experiments, porcelain
was annealed a long time at temperature 420° C.
The specimen had an auxiliary electrode. At the
instant of application of the field ($E = 180$ V/cm),
the current between electrodes A - C and B - C was
equal to 1.6×10^{-3}A. After a two-minute electroly-
sis, the "permeable" current was equal to 2
$\times 10^{-3}$ A, and in a few seconds it rose to 2.4
$\times 10^{-3}$ A; the current between the control electrode
B and the common cathode C was equal to 3
$\times 10^{-3}$ A (until now no current had passed between
B and C) : i.e., as a result of electrolysis of the
annealed specimen, the electrical conductance in-

creased almost twofold.

An increase of conductivity of the specimen, with simultaneous creation of a high-resistance film, fully explains why, in many dielectrics, the creation of electrode films may not be accompanied by a decrease of the current passing through the specimen. In connection with this, a phenomenon observed in asbestos is interesting. Specimens with a supplementary electrode were heated to 780° C. A brief switching in showed that a current of 2×10^{-5} A existed in each of the electrodes A and B. Twenty-six minutes after the start of electrolysis, the current strength between electrodes A and C was still equal to 2×10^{-5} A; but instantaneous switching in of control electrode B clearly showed that creation of an electrode film was occurring on electrode A, since at this time the current between B and C had risen to 4×10^{-5} A. As a result of electrolysis of longer duration, the current in the "shut-off" and "permeable" directions decreased (after 75 min, $I_A = 0.8 \times 10^{-5}$A, $I_C = 1.2 \times 10^{-5}$A), but the current through the control electrode remained equal to 4×10^{-5}A.

Observations of the same sort showed that in alkali-halide crystals (rock salt), the creation of films at the electrodes can even be accompanied by an increase of the current passing through the specimen.

5. ON THE COEFFICIENT OF UNIPOLARITY

The opposite influence of the two factors mentioned—i.e., the increase of conductivity of the specimen and the rise in resistance of the electrode film—and also the phenomenon of fixation of the electrode film under the action of the field, and the increase of resistance of the film and of the specimen itself upon lowering of the temperature, make up the very complicated picture that is observed on passage of current in dielectrics at high temperatures, and that gives the "history" of the specimen.

From the discussion above it is clear that the coefficient of unipolarity at a given temperature and at constant field must depend on the previous history of the specimen. For Eternit ($17 \times 10 \times 4$ mm), at temperature 580° C and field $E = 225$ V/cm, as a result of prolonged electrolysis (30-60 min) we have $K \approx 2$. With increase of electrolysis time, the currents in the "permeable" and "shut-off" directions decrease, but this does not lead to a noticeable change in the coefficient of unipolarity. With increase of the temperature

to 720° C and annealing at this temperature for one to two hours, after subsequent electrolysis at temperature 580° C it was found that $K \approx 4$. With the same heating, accompanied by electrolysis and subsequent lowering of the temperature to 580° C (with field applied), the value $K \approx 10$ was obtained. In porcelain ($16 \times 10 \times 5$ mm), annealing at a high temperature, with simultaneous action of the field ($E = 180$ V/cm), produced an even greater change in the coefficient of unipolarity. With increase of temperature from 300 to 420° C, with subsequent lowering of temperature to 300° C after prolonged electrolysis, the coefficient of unipolarity changed from $K = 4$ to $K = 23$.

The observed increase of the coefficient of unipolarity, measured at a single temperature, is due to a decrease of current in the "shut-off" direction and an increase of current in the "permeable" direction. If a specimen, initially subjected only to heat treatment at an elevated temperature (720°C) and to electrolysis at a reduced temperature (580°C), is then subjected to the action of field and heating, the rise in the coefficient of unipolarity (at $t = 580$°C) in this case is invariably accompanied by a decrease of current in the "shut-off" direction.

CONCLUSION

The phenomena connected with the formation and destruction of electrode films can be explained in the following way: impurities, present in the dielectric or diffusing into the specimen at the high temperature[3,4], exist in it in the form of colloidal particles[5,6], and partly in a dissociated state; the possible concentration of impurity ions depends on temperature.

At an elevated temperature, the ions migrate to the electrodes and, by giving up their charges, become transformed to neutral particles. Since, upon passage of current and lowering of temperature, the concentration of impurity ions near the electrode may exceed the equilibrium concentration possible at the given temperature, a coagulation occurs, and this leads to an increase in the stability of the electrode film and an increase of its resistance. In

[3] B. M. Gokhberg and A. V. Ioffe, Zh. R. F.-Kh. O. 62, 433 (1930); J. Exper. Theoret. Phys. USSR 1, 264 (1931); 3, 303 (1933)

[4] B. M. Gokhberg, J. Exper. Theoret. Phys. USSR 7, 1031, 1044 (1937)

[5] R. Mattai, Z. Phys. 68, 85 (1931)

[6] A. Edner, Z. Phys. 73, 623 (1932)

the same way it is possible to explain the decrease of electrical conductivity observed on lowering of the temperature, and dependent on impurities that result from annealing of the dielectric at an elevated temperature.

Upon change of the direction of the electric field, free ions leave the anode; this disturbs the equilibrium in the film. As a result, additional ionization occurs, which may continue until the anodic film is completely destroyed. A similar process of destruction of a colloidal film is observed visually in the formation of a colored film on the boundary of two dielectrics (one of which must be an alkali-halide crystal[7]).

Simultaneously with the destruction of the more stable film on one electrode, a not very stable film is formed on the other. The motion of the ions emitted by the anodic film progresses in the form of a cloud, in which the concentration of impurity ions is increased as compared with the concentration in the whole volume of the dielectric. Upon a new change of direction of the field, there again occurs an immobilization of ions at the boundary, which leads to a growth of the electrode film.

The observed changes of the coefficient of unipolarity can be explained in the following way: a) annealing at the more elevated temperature increases the number of impurity ions free to participate in the creation of an electrode film; b) the electric field, by transporting ions to the electrode, increases the number of ions that become immobilized in the electrode film.

Several authors[2], on the basis of the researches of Warburg and Tegetmeier[8], are inclined to ascribe the creation of electrode films at the anode in all cases to the migration of cations, which leave the anode and thus create a high-resistance film. From this point of view it is hardly possible to explain the effect of annealing and of the electric field; therefore it seems to us more probably that the anodic film, in the dielectrics studied, is created as the result of the migration of anions. The role of electronic conduction is also not excluded in these phenomena. The electronic component of conductivity may have a large value in the neighborhood of the electrode film, where a very strong electric field is created.

[7] Ia. N. Pershits, J. Exper. Theoret. Phys. USSR 24, 347 (1953)

[8] E. Warburg and F. Tegetmeier, Wied. Ann. 32, 447 (1887); 35, 445 (1888)

Translated by W. F. Brown, Jr.
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