

## The Mechanism of the Formation of Anode Layers in Molded Dielectrics

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It is established that the mechanism of formation of electrode-attached layers is identical in dielectrics with various structures. By means of a comparative study of the electrode-attached effects in various dielectrics, it is shown that the mechanism of formation suggested by Warburg<sup>1,2</sup> is unsatisfactory.

**I** DURING the electrolysis of many dielectrics, there appears a gradual decrease of current, associated with the formation of an electrode-attached (anode) layer of high resistance. Molded dielectrics possess unipolar conductivity: the flow of current in the "easy" direction is considerably greater than the flow of current in the "hard" direction, coinciding with the direction of the molding current. It has been shown<sup>3,4</sup> that for the dielectrics investigated (fused quartz, porcelain, eternit, mica, asbestos, alkali-haloid crystals) there appear the peculiarly typical curves of the time dependence of the "hard" current following the transient passage of the "easy" current (reference 4, Figs. 1,2). For all the dielectrics investigated, the curves of "hard" current have a point of inflection; moreover, the rate of decrease of the current in the "hard" direction is shown to depend on the duration of the current in the "easy" direction. Conformance with this behavior always indicates the presence of an unstable electrode-attached layer of high resistance in the dielectric.

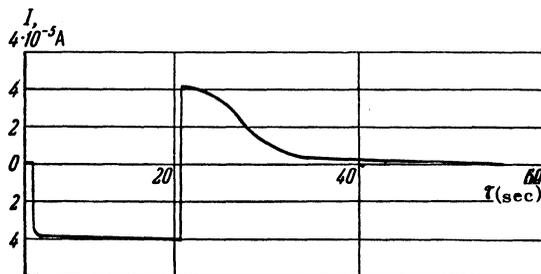


FIG. 1. Time dependence of current for molded glass

In the present work, glass was investigated. As is well-known, a molded layer is also created in glass as a result of electrolysis. The study of the character of the "easy" and "hard" currents in glass was conducted with a view to the establishment of a common mechanism of formation of the electrode-attached layer in glass and in dielectrics investigated previously. During the investigation of glass, it was discovered that the state of the surface of the dielectric has a considerable influence on the effects associated with the formation and destruction of electrode-attached layers.

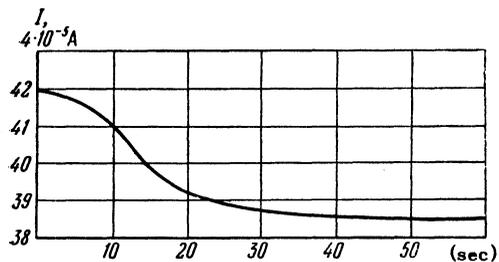


FIG. 2. Variation of the current in the "hard" direction for rock salt.

If the casting of the glass is carried out with the use of the usual metal electrodes at a comparatively high temperature (250 - 400°C), then at the change in the direction of the field, the destruction of the electrode-attached (anode) layer of high resistance at one electrode and the formation of a layer at the other electrode take place extremely rapidly, as disclosed by the corresponding change in the current. In this connection, it is important as to whether the metal electrodes are placed on the usual smooth surface of the glass, or, on a surface worked with sandpaper (made opaque). Under identical experimental conditions, the decrease of current following the change of direction of the field in a cast sample takes place more slowly in the second case than in the first, which indicates the influence of the state of the surface of the dielectric on the conditions for the formation of the electrode-attached layer. Using graphite

<sup>1</sup> E. Warburg, Wied. Ann. 21, 622(1884)

<sup>2</sup> E. Warburg and F. Tegetmeier, Wied. Ann. 32, 442 (1887); 35, 445 (1888)

<sup>3</sup> Ia. N. Pershits, J. Exper. Theoret. Phys. USSR 17, 251 (1947)

<sup>4</sup> Ia. N. Pershits, J. Exper. Theoret. Phys. USSR 28, 181 (1955); Soviet Phys. 1, 110 (1955)

electrodes, it was found possible, even for glass, to obtain curves fully coinciding with those presented in reference 4, Figs. 1,2,5. These curves differ from those obtained for glass with metal electrodes, in that here it is found that the "easy" current passes through a maximum, i.e., following the change in direction of the field, the "easy" current increases during a certain period of time. In one of the experiments, the sample of glass ( $6\text{cm}^2 \times 0.4\text{ cm}$ ), furnished with graphite electrodes, was subjected to electrolysis at a temperature of  $250^\circ\text{C}$ . The casting was performed during the course of one hour. The change in the direction of the field following the protracted electrolysis gave the usual picture (as, for example, in porcelain and eternit) of the increase of the "easy" current, and subsequent to the switching a smaller growth and then a constant current. A similar change of the "easy" current was described earlier for eternit (reference 4, Fig. 5). In Fig. 1, a curve is presented showing the time dependence of the flow of current in the "easy" and "hard" directions for the present sample of glass at a temperature of  $210^\circ\text{C}$ . This curve differs from the curves obtained, for example, for quartz, only by the considerably large coefficient of unipolarity. In the present case, the coefficient of unipolarity is  $K \sim 200$ .

It has been noted<sup>4</sup> that the heat treatment of the sample has considerable influence on the stability of the electrode-attached layer. A decrease in the temperature of the cast sample leads to an increase of the stability of the electrode-attached layer, which is manifested in the character of the curves of the "easy" current. Cooling the sample, with a subsequent warming up to the temperature at which the casting was performed, stimulates a substantial increase of the stability of the electrode-attached layer and an increase of the resistance of the sample for current in the "easy" and "hard" directions. The procedure of cooling and subsequent heating of the dielectric leads to the same change in the character of the time dependence of the current, as does a protracted electrolysis.

The influence of cooling on glass was investigated in the same way as for the other dielectrics<sup>4</sup>. A frame with the sample cast at a high temperature was removed from the furnace, and, after complete cooling, was again placed in the furnace and heated to the previous temperature. For these investigations, use was made of a special arrangement in the form of a sled, with which the frame with the dielectric was moved. This device guaranteed the rigorously identical position of the dielectric in the furnace during the two successive measurements of the current. The constancy of the temperature was

carefully controlled with the use of a thermocouple, included in a compensating system. Furthermore, during the series of observations, an electronic temperature regulator was used, which helped to maintain a constant temperature in the furnace and automatically effected the locking of the dielectric bonds at the given temperature.

In one of the experiments, the sample of glass was cast for a long time at a temperature of  $250^\circ\text{C}$ . After cooling, it was again introduced into the furnace and was subjected to an extremely short electrolysis at a temperature of  $250^\circ\text{C}$ , after which the direction of the field was changed. The "easy" current (increasing), recorded at the instant the field was switched, comprised only 60% of the current obtained in the same direction before the cooling of the sample ( $0.65 \times 10^{-3}\text{ A}$  and  $0.36 \times 10^{-3}\text{ A}$ ). Figure 1 refers to a sample subjected to such a procedure and then cooled down to  $210^\circ\text{C}$ .

Comparing the character of the time and temperature dependence of the current in glass and in other dielectrics<sup>4</sup> previously investigated, we see that they are completely identical. This allows us to think that in all of the dielectrics investigated, we have to do with one and the same mechanism of formation and destruction of electrode-attached layers.

At the present time, the generally accepted mechanism of formation is that proposed by Warburg<sup>1,2</sup>. It is assumed that the molded layer in solid dielectrics represents simply a region with a deficiency of mobile positive ions<sup>5,6</sup>; but this is completely incapable of accounting for the processes taking place in the layer under the action of an electric field and heat. A study of the conditions of formation of electrode-attached layers in dielectrics has shown<sup>4</sup> that these processes must be taken into account in the explanation of the molding effects.

It should be noted that the shortcomings of the mechanism of formation suggested by Warburg also follow from the experiments of Kosman and Sozina<sup>7</sup>, who investigated polarization effects in cast glass. It was established by them that there is a nonlinear dependence in glass of the effective thickness of the polarized layer on the amount of electricity that has flowed past. Kosman and Sozina showed that the thickness of the layer

<sup>5</sup> A. Venderovich and B. Lapkin, Zh. Tekhn. Fiz. 9, 46 (1939)

<sup>6</sup> Ia. M. Ksendzov, Zh. Tekhn. Fiz. 18, 3 (1948)

<sup>7</sup> M. S. Kosman and N. N. Sozina, J. Exper. Theoret. Phys. USSR 17, 340 (1947)

that is formed does not increase proportionately to the amount of electricity gone by, but that in a sizable formation the accumulation of the electrode-attached layer, in general, practically ceased. In order to bring these results into conformance with the classical mechanism of formation proposed by Warburg, Kosman and Sozina put forward the hypothesis that there exists in glass a substantial electronic composition of the current. However, it is necessary to keep in mind that the limitation of the thickness of the layer that is formed also takes place in dielectrics for which there is no basis for the assumption of electronic conductance, as for example, in alkali-haloid crystals.

In alkali-haloid crystals, the currents in the "hard" and "easy" directions generally differ by only 5-10%. Figure 2 shows the diminishing part of the curve of the current in the "hard" direction, obtained following a protracted electrolysis (10 hours) of natural rock salt (using iron electrodes) at a temperature of 600°C. In the "easy" direction the current continued for 20 seconds, and during this time remained unchanged. As is evident in the figure, the coefficient of unipolarity in this case is  $K = 1.1$ . This leaves no doubt that the mechanism of formation of electrode-attached layers in alkali-haloid crystals is the same as in the other dielectrics investigated. Since the effects associated with the formation and destruction of electrode-attached layers are more graphically displayed by large differences of "hard" and "easy" currents, we strove to obtain the largest possible coefficient of unipolarity. By gradually decreasing the temperature of the molded crystal of rock salt, and from time to time switching the field, it was possible to observe the increase of the coefficient of unipolarity from  $K = 1.1$  to  $K = 1.43$  (at  $T = 350^\circ\text{C}$ ).

Under these circumstances, however, in order to maintain the relatively large value of  $K$ , it was necessary to make sure that the temperature did not change during the course of the experiment. If the temperature fell to a lower value than that at which the measurement was made (350°C), then, even at the given temperature (350°C) the coefficient of unipolarity was reduced, and its value could be restored only by a repetition of the casting at a higher temperature, and a new lowering of the temperature to 350°C. This extremely complex temperature dependence of the coefficient of unipolarity was not observed in the other dielectrics investigated. We presume that this is connected with the special conditions of penetration and binding of the admixtures in alkali-haloid crystals. Since in the majority of dielectrics the casting effects are associated with always having

admixture in the dielectric, it may be conjectured that in alkali-haloid crystals the basic role is played by admixtures diffusing in the sample at the high temperature. This question must be subjected to special study in the future. A further increase of the coefficient of unipolarity to  $K \sim 2$  in the same crystal was obtained by means of a decrease of the difference of potential applied to the sample. The increase of the coefficient of unipolarity at reduced field intensities is explained in that for molded crystals, Ohm's law is obeyed for current in the "easy" direction, but is not obeyed for current in the "hard" direction.

The investigation of cast samples of rock salt indicated that in them as in other dielectrics, there is a sharp increase of the "easy" current following the change in direction of the electric field. Hence, it follows that the electrode-attached layer in rock salt, for instance, and in glass, has little stability and is easily destroyed by a field in the opposite direction. But if the limitation of the growth of the thickness of the layer in glass could be explained by the layer having a very large resistance, so that in the course of time the current would become negligibly small, such an explanation would not be possible in the present case. It is evident from the experiments that for the complete formation of the layer in rock salt it is sufficient to conduct the electrolysis for one hour. If in reality an anode layer of high resistance would be created by the simple uncompensated departure of cations of the admixtures, then we would obtain as a result of an extremely protracted electrolysis, a layer of such thickness that it could not remain in the same way with little stability, as in glass, and with a change of the direction of the field, there would be observed a gradual, and not an abrupt change of current. At the same time, it is of course not possible to explain the limitation of the growth of the layer in alkali-haloid crystals, as was proposed in reference 7 for glass, by electronic conduction.

If there had been electronic conduction in alkali-haloid crystals, or if it had appeared as a result of electrolysis, it would have provoked a coloring of the crystal, since the movement of electrons in alkali-haloid crystals is accompanied by the formation of  $F$ -centers.

2. A time dependence of current completely analogous to that which is observed in solid dielectrics at high temperatures has been successfully disclosed also at low temperatures (10-15°C) at which, in such objects, it hardly has meaning to speak of electronic conductivity. At room temperature, the molding effects accompanied by the formation of an anode layer of little stability are easily detected in eternit, which is a hydro-

philic dielectric; in a humid atmosphere, it may possess considerable conductivity, which disappears after warming. In eternit the curves of the time dependence of current at low temperatures are completely the same as those at high temperatures<sup>4</sup>, and besides, a considerable coefficient of unipolarity is observed (at  $T = 10^\circ\text{C}$ ,  $K \sim 50$ ). The possibility of observing molding effects at low temperatures renders their investigation exceptionally easy.

Using a plate of eternit supplied with clamps to serve as electrodes, the effects observed in glass and other dielectrics at high temperatures were successfully reproduced with the clarity of a demonstration experiment. Here, it is particularly easy to ascertain the role of the anode layer. If one of the electrodes on the border of the dielectric is moistened with a liquid electrolyte, the character of the curves is changed, so that at once the role of the anode in the process of the formation of the layer is disclosed.

Effects, quite analogous to those studied in other dielectrics, are also observed during the electrolysis of skin. The tissues of a living organism represent an extremely complex electrolytic conductor, consisting of liquid and semi-liquid media. The greatest resistance is possessed by dry skin, especially the horny layer. When metal electrodes are used, complicated processes take place in the tissues at the points of contact, associated with the electrolysis of tissue fluid and the subsequent formation of secondary chemical unions. As a result of these processes, oxygen is isolated at the anode and hydrogen at the cathode.

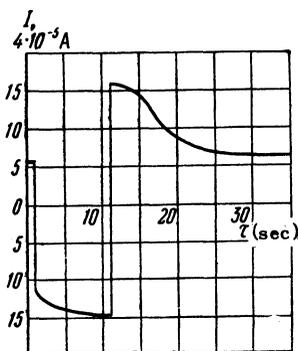


FIG3. Time dependence of current for formed skin (dry anode).

Here, as our observations have shown, an electrode-attached layer arises at the anode, quite the same as in other dielectrics, as for example, in glass and in alkali-haloid crystals. This circumstance, it appears, introduces interest in

that relation, which will permit a deeper understanding of the electro-physiological tissue electro-conductivity studied, especially if it is taken into account that analogous effects could take place on the borders of cells, and also on the surfaces separating different tissues.

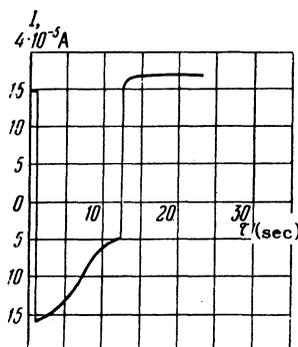


FIG. 4. Time dependence of current for skin (moist anode).

To study this effect, circular metallic electrodes ( $d = 3 \text{ mm}$ ) were placed on the ends of fingers ( $V = 75 \text{ V}$ ). As was to be expected, the character of the effects taking place were essentially dependent on the state of the electrodes (dry or moist). During the passage of current, as is well-known, the resistance of skin decreases; therefore, when using dry electrodes, the current gradually increases. Here, however, an electrode-attached layer of high resistance is created at the anode. This layer is easily disclosed by means of successive changes of the direction of the electric field. The formation of an anode layer follows from the character of the curve of current in the "hard" direction, which appears quite the same as for other dielectrics. In conformance with this, in considering the dependence on the state of the electrodes, it is necessary to distinguish two cases: a) during the initial imposition of the field, the border of the anode is dry skin, and the border of the cathode is moist skin; b) during the initial imposition of the field, the border of the anode is moist skin, and the border of the cathode is dry skin. In the first case, in spite of the increase of the conductivity of the skin during the imposition of the field, a drop in the current is observed as a consequence of the rapid formation of an electrode-attached layer. With the change of direction of the field, an increasing current is observed, and with a repeated change of the direction we obtain the usual characteristic curve (Fig. 3). In the second case, when the anode is moist, the formation of a layer of high resistance

at the anode does not take place (as for example, also in eternit) and during the imposition of the field, a considerable increase of current is disclosed. At the change of direction of the field the current is diminished as a consequence of the formation of a layer at the new anode (dry), and with a repeated change of direction of the field, the current is almost constant. This is fully understandable, because the layer formed at the dry anode is destroyed, and no layer is created at the moist electrode (Fig. 4).

It should be noted that during the conditions of formation of the anode layer, the observed dependence of the curve of diminishing current in the "hard" direction from the time of the passage of current in the "easy" direction is completely the same as described for other dielectrics<sup>3,4</sup>. The corresponding curves, obtained with the aid of a cathode ray oscillograph, are presented in Fig. 5.

Thus, there is a basis for the assertion that in all of the cases we have to do with the identical physical process.

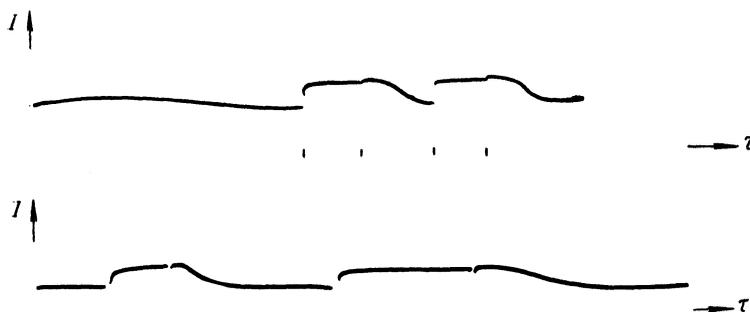


FIG. 5. Dependence of the "hard" current from the time of the passage of the "easy" current during the electrolysis of skin. The increasing curves represent the "easy" current, and the decreasing curves represent the "hard" current.

### CONCLUSION

As a result of investigations conducted with various dielectrics we come to the following conclusions: 1) the character of the electrode-attached effects is the same for all the dielectrics investigated, and it is possible also for all molded dielectrics; 2) these effects cannot be explained by a simple uncompensated motion of cations. It appears that to a considerable degree, the effects are conditioned by processes in which anions are involved.

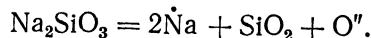
Taking into account the extraordinary generality of the effects in the different dielectrics, it may be conjectured that in the formation of the layer a particular role is played by oxygen produced at the anode during electrolysis. This is all the more probable since for many dielectrics, and in the first place for glass, the production of hydrogen is associated with the transfer of cations<sup>8,9,10</sup>. In

<sup>8</sup> M. LeBlanc and F. Kerschbaum, *Z. Phys. Chem.* **72**, 468 (1910)

<sup>9</sup> G. Schulze, *Ann. Physik* **37**, 435 (1912)

<sup>10</sup> P. P. Kobeko and I. V. Kurchatov, *Dokl. Akad. Nauk USSR* **1**, 187 (1928)

glass for example, the reaction assumed at the anode is



The question of the character of the changes taking place in the electrode-attached layer under the action of a field and of temperature requires still further investigations. The experimental and theoretical data of the majority of authors<sup>11,12,13</sup> leads to the conclusion that in glass there exists purely ionic conductivity. It would be important to establish whether the purely cationic conductivity is maintained in the electrode-attached layer in glass, or whether the anions possess a certain mobility in the layer. The clarification of this question is necessary for the theoretical investigation of the disclosed time dependence of the current.

As concerns the role of electronic conductivity, it is impossible to deny that it takes place in the actual electrode-attached layer, because very

<sup>11</sup> H. Schiller, *Ann. Physik* **83**, 137 (1927)

<sup>12</sup> A. M. Venderovich and V. I. Chernykh, *Tr. Sib. FTI* **24**, 156 (1947)

<sup>13</sup> V. A. Presnov, *Tr. Sib. FTI* **30**, 175 (1950)

strong fields are created therein. To assume that electronic conduction must exist in the whole volume of the molded dielectric<sup>7</sup> does not have satisfactory grounds in our opinion, because such

an assumption is found to be in contradiction with experimental data.

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## Investigation of the Isotope Effect in the Uranium Spectrum

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The isotope shift in the spectrum of uranium has been measured for 346 lines among the components of the isotopes  $U^{238}$  and  $U^{235}$ . The regularities obtained in the isotope shift have been employed for the extension of the classification of the uranium spectrum and for the establishment of the isotope shift in several terms of U I and U II.

Starting from the shift of the terms  $5f^4 7s^6 I_{9/2}$  and  $5f^3 7s^2 4 I_{9/2}$ , it is found that the lowest electron configuration for U II is  $5f^4 7s$ .

THE isotope effect in the spectrum of uranium was first discovered by Anderson and White<sup>1</sup> and was later studied by a number of other investigators<sup>2-4</sup>, including ourselves. As the problem of the present research, which was carried out in 1951, a much more complete investigation was conducted of the isotope shift in the lines of uranium, with the aim of establishing the dependence of the isotope shift on the electron configuration and the determination of the shift in the terms. It was also desirable to establish the presence of even-odd shift, which had not yet been observed in the uranium spectrum at that time. The results of these investigations are given below.

### 1. EXPERIMENTAL PART

Three spectrographs were used for the investigation of the isotope shift in the spectrum of uranium. The spectral region 2300-2700 Å was obtained with the help of a large Hilger quartz spectrograph whose dispersion in this region

ranged from 2.3 to 3.1 Å/mm. The interval 3900-4400 Å was spectrographed by means of a Zeiss three prism glass spectrometer with an auto-collimating chamber  $f = 1300$  mm. The dispersion of this apparatus in the given region varied from 1.3 to 2.6 Å/mm. The intervals 2700-3900 Å and 4400-6600 Å were obtained with a Baird diffraction spectrograph with a concave grating of radius of curvature 3 m, with 600 lines/mm. Some parts of these intervals were spectrographed in second order (dispersion 2.6 Å/mm) and some in third order (dispersion 1.8 Å/mm).

An arc of variable current between graphite electrodes was used as an excitation source. The arc was fed by a generator DG-1. The current strength was 5 A.

In the investigations we used samples of enriched uranium which represented a mixture of two isotopes,  $U^{238}$  and  $U^{235}$ , and also samples of a three isotope mixture,  $U^{238}$ ,  $U^{235}$ ,  $U^{233}$ , or  $U^{238}$ ,  $U^{235}$ ,  $U^{234}$ . In addition to the spectra of these samples, we recorded the spectra of natural uranium and of iron. For a survey of the spectra of uranium from mixed oxides, we prepared aqueous solutions of uranium nitrate from a calculation of 0.06 cm<sup>3</sup> of distilled water per milligram of salt. This sample, in the form of an aqueous solution, was applied on the tips of the upper and lower graphite electrodes (length 50 mm, diameter, 5 mm) and dried out on the slab. For the survey of each spectrum we used 2 milligrams of material, the time of

<sup>1</sup> D. E. Anderson and H. E. White, Phys. Rev. 71, 911 (1947)

<sup>2</sup> L. E. Burkhart, G. L. Stukenbrocker and S. Adams, Phys. Rev. 75, 83 (1949)

<sup>3</sup> J. K. McNally, J. Opt. Soc. Am. 39, 271 (1949)

<sup>4</sup> D. D. Smith, G. L. Stukenbrocker and J. K. McNally, Phys. Rev. 84, 383 (1951)