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# ON THE RESIDUAL VOLTAGE WITH ELECTROLYTIC CAPACITORS

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### Summary

After an electrolytic capacitor, e.g., $Al/Al_2O_3$/electrolyte, has been charged and discharged, a voltage is found to be developing anew across the capacitor plates. This is called the residual voltage, and it is found to be proportional to the product of the field strength in the oxide layer and the thickness of this layer. It is assumed that $Al^{3+}$ ions in the lattice have moved to adjacent positions, considering the fact that there is a large number of vacancies in the $Al_2O_3$ lattice. A simple computation shows that for an average shift of an $Al^{3+}$ ion over a distance of 2 Å, 0·1 % of the available $Al^{3+}$ ions have been displaced.

### Résumé

Après charge et décharge d'un condensateur électrolytique, par exemple le système $Al/Al_2O_3$/électrolyte, il se produit une tension résiduelle entre les bornes du condensateur. On a trouvé que cette tension est proportionelle au produit de l'intensité du champ électrique dans la couche par l'épaisseur de la couche. On admet que des ions $Al^{3+}$ sont déplacés vers des positions adjacentes en raison du fait qu'il existe un grand nombre de sites non occupés dans le réseau $Al_2O_3$. Après le déchargement du condensateur, les ions retournent par diffusion vers leurs sites primitifs, et une tension résiduelle se produit. Un calcul simple permet de constater que pour un écart moyen de 2 Å, 0,1% des ions présents se sont déplacés.

### Zusammenfassung

Nach Ladung und Entladung eines elektrolytischen Kondensators, z.B. das System $Al/Al_2O_3$/Elektrolyt, entsteht eine neue Spannung zwischen den Elektroden, d.h. zwischen Anode und dem Elektrolyten. Diese Spannung wird Restspannung genannt, und es zeigt sich daß sie dem Produkt aus Feldstärke in der Oxydschicht und ihrer Dicke proportional ist. Es wird die Annahme gemacht, daß $Al^{3+}$-Ionen im Gitter nach benachbarten leeren Gitterstellen verschoben werden, weil sich eine große Zahl unbesetzter Stellen im Gitter befindet. Eine einfache Rechnung lehrt, daß, bei einer mittleren Verschiebung der $Al^{3+}$-Ionen über 2 Å, 0,1% der anwesenden Ionen verschoben sind. Nach der Entladung können die verschobenen Ionen wieder nach ihren ursprünglichen Stellen zurückkehren, und eine Restspannung entwickelt sich.

## 1. Introduction

It has been long known that capacitors with certain dielectrics, e.g. glass, after being initially charged and then discharged, are able to produce several more short-circuiting currents $^{1}$).

This phenomenon is usually explained, according to Maxwell and Wagner, by the assumption that the dielectric is stratified, and consists e.g. of two layers of different conductivities and sometimes also of different dielectric constants. When an electric tension is applied across such a capacitor, the major part of the voltage is across the more poorly conducting layer of the dielectric. A space charge will be present on the boundary layer between the two strata. When the capacitor is discharged, the charge will disappear from the plates. After the initial discharge the space charge on the boundary layer will pass through the dielectric to the plates, thus opening the possibility of a new discharge.

The explanation proposed by us differs from the classical one. This article mainly concerns the study of the residual voltage with electrolytic systems, e.g. $Al/Al_2O_3$/electrolyte. The fact that residual voltages occur here has been earlier established by Charlesby [2]). It is known that there are several metals, such as Zr, Ta, Ti, Nb, which, when covered with an electrolytically applied oxide layer, constitute a rectifying system, which may form a capacitor if the metal is the positive pole. As soon as the metal forms the negative pole, a considerable current flows through the system.

In this article the phenomenon of the residual voltage with electrolytic capacitors will be examined more closely. We measured the residual voltage of Al capacitors as a function of the applied voltage at constant skin thickness. We also determined the residual voltage at a constant field strength in the skin for an increasing thickness of the oxide layer. We shall also indicate how the residual voltage, after the capacitor has been short-circuited, is built up as a function of time, and how it is dependent upon the temperature. Finally, an attempt is made to explain the occurrence of the residual voltage with the aid of the known structure of $Al_2O_3$. A solution of boric acid and borax in a mixture of glycol and water was used as the electrolyte. The capacitors were specially built to prevent the residual voltage from leaking away.

## 2. Experimental part

When we used the system $Al/Al_2O_3$/electrolyte as a capacitor, Al was as a rule the positive pole, since then the leakage current was very slight. With this polarity, voltage was applied to the system in the reverse direction. If Al is made to form the negative pole, the system lies in the forward direction. At voltages below 6 V, however, the system may also be used as a capacitor with Al as negative pole, because then the forward current is still very small. If higher voltages are to be applied, Al is always used as the positive pole.

The experiment for determining the residual voltage was in fact very simple. A direct voltage was applied to the capacitor in order to charge it. Then the system was discharged and immediately afterwards connected to an electrostatic voltmeter or to a voltmeter with extremely high internal resistance.

The duration of the short-circuit could be fixed, since this was temporarily established by a pendulum touching a mercury surface. The contact between pendulum and mercury, during a few hundredths of a second, determined the duration of the short-circuit. This time was measured with the aid of an oscilloscope.

The duration of the short-circuit should be short with respect to the period in which the residual voltage is developed, since otherwise too low a value for the latter was measured. The residual voltage has the same sign as the voltage originally applied.

## *The residual voltage as a function of time*

Figure 1 shows the residual voltage as a function of the time elapsed after the short-circuit. The capacitor, therefore, was first charged, in this case up to 100 V (Al+), then the voltage source was disconnected and the capacitor short-circuited and directly afterwards connected to a voltmeter of very high resistance. The measurements were carried out at 20 and 80 °C. Since the temperature range extended only from 0 to 100 °C (aqueous solution), and the leakage increases considerably above room temperature, the measurements were not found sufficiently accurate to measure the residual voltage as a function of the temperature. Consequently we only know that the residual voltage increases at higher temperatures.

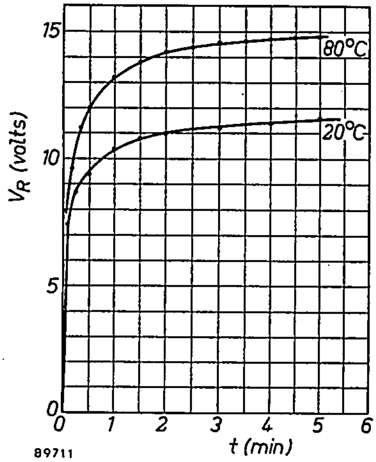

Fig. 1. The residual voltage ($V_R$) as a function of time ($t$) for two different temperatures.

### *The residual voltage as a function of the field strength in the oxide layer at a constant layer thickness*

For a given skin thickness ($3{\cdot}5.10^{-5}$ cm) the residual voltage was measured as a function of the charging voltage at several values of the latter. The maximum residual voltage was measured. The result is shown in fig. 2. It was found that $V_R$ is proportional to the charging voltage $V_S$, or, since the layer thickness is constant, to the field strength $F$.

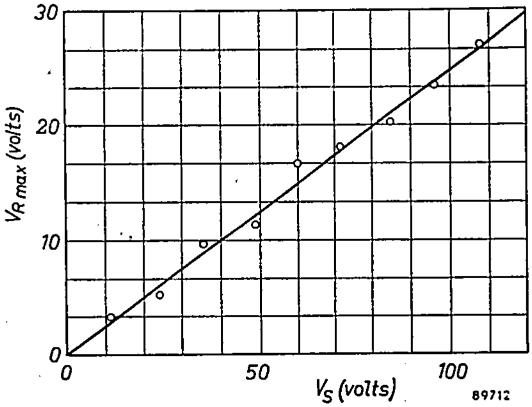

Fig. 2. The maximum residual voltages ($V_{R\,\max}$) as a function of the applied charging voltage ($V_S$) at a constant thickness of the oxide layer.

### *The residual voltage at varying layer thickness, the field strength in the layer being kept constant*

The residual voltage was measured for capacitors with varying layer thickness. The voltage up to which the capacitor was charged was always made proportional to the layer thickness, so that during charging the field strength in the various skins was always the same. It was found that at constant field strength the residual voltage was proportional to the layer thickness (fig. 3). In connection with the foregoing we may put therefore $V_R \propto Fd$.

### *The residual voltage after successive discharges*

First of all a voltage of 100 V was applied to a capacitor with a layer thickness of $2.10^{-5}$ cm, for the purpose of reducing the leakage current to a low value. After that the capacitor was short-circuited for some time to carry off the residual voltage thus produced. This could never be completely achieved; even after a prolonged period there always remained a low residual voltage of some tenths of a volt. There always remained a "memory", particularly of a previous (Al+) arrangement.

In our experiments we made sure that the ultimate residual voltage was very small.

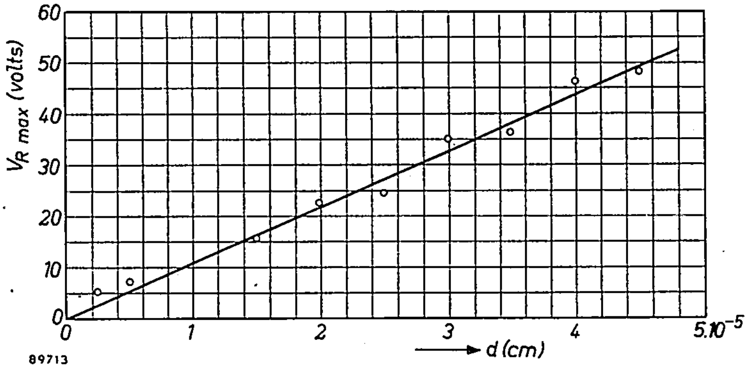

Fig. 3. The maximum residual voltage ($V_{R\,\text{max}}$) as a function of the thickness of the layer ($d$) at constant field strength in the oxide layer.

In the actual experiment a tension of 6 V (Al+) was applied to the oxide layer. This low value was selected in view of the fact that we intended to repeat a similar experiment with Al as negative pole, and since this is in the forward direction, the voltage should be so low that no perceptible forward current will occur. After the tension of 6 V had been applied for some time, it was disconnected and the capacitor was short-circuited for a very brief period. Then, after a minute during which no voltage was applied, to provide some opportunity for the residual voltage to develop, the capacitor was discharged across a ballistic galvanometer and the discharge current measured. The same measurement was repeated at minute intervals. A similar experiment was carried out with Al as the negative pole. This, as we have mentioned earlier, is in the forward direction, but the forward current is only very small, so that the system still functions as a capacitor.

Figure 4 shows the discharge current as a function of the discharges repeated at regular intervals. We notice that for Al— there is a tendency after a few discharges to produce again a current in the reverse direction, just as if Al had been the positive pole during charging. This might be a "memory" of a previous Al+ arrangement, or perhaps the structure of the oxide layer is such that there is preferential direction of the ions. When we add the discharge current in fig. 4 (Al+) we find that in this diagram an amount of electricity of $2.10^{-7}$ coulombs/cm$^2$ has been discharged. It is apparent, however, that after 20 discharges the residual charge is by no means exhausted and will undoubtedly be able to produce an amount of electricity several times greater than has already been discharged. As the layer thickness was $2.10^{-5}$ cm, the charge per $cm^3$ is at least $10^{-2}$ coulomb or $10^{17}$ elementary charges per $cm^3$. In this experiment the residual voltage amounted to about 1 V.

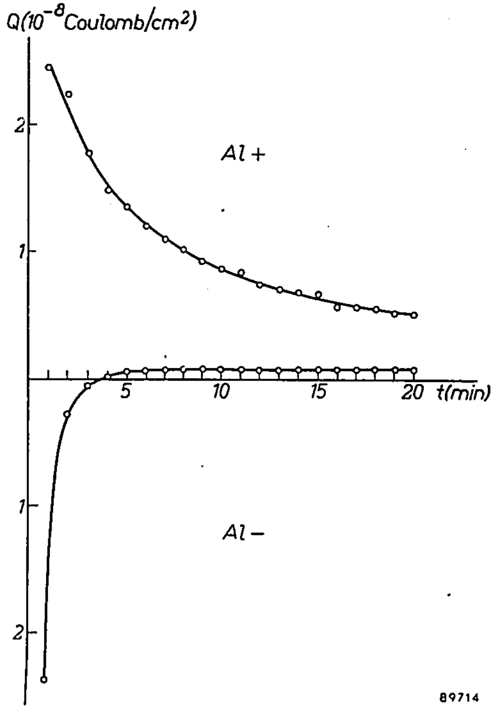

Fig. 4. Measurement of the residual current by repeatedly discharging the capacitor across a ballistic galvanometer, with intervals of one minute.

## 3. Conclusions

### *The structure of the oxide layer*

X-ray photographs show that the oxide layer formed at room temperature is amorphous. During oxidation at 100 °C, as well as the amorphous oxide also $\gamma'$-$Al_2O_3$ 3) is formed. We may assume that the oxide skin consists mainly of a lattice of the cubic close-packed oxygen ions. The lattice is not strictly cubic, nor regular.

In the interstices of the oxygen-ion lattice the $Al^{3+}$ ions are statistically distributed. According to Verwey 4) a unit cell consists of 32 $O^{2-}$ ions, in which there are 96 sites, 32 of which are octahedral sites and 64 are tetrahedral sites. The octahedral sites contain 70% of the $Al^{3+}$ ions, whilst only 30% of these is contained in the tetrahedral sites. In the unit cell of 32 $O^{2-}$ ions there are on the average $21\frac{1}{3}$ $Al^{3+}$ ions, whereas there are 96 available vacant sites. It will thus readily be understood that an external field may cause a change in the distribution of the ions among the sites. We assume that under the influence of the external field ions are displaced towards adjacent sites and that, after the field has been removed, they return by diffusion to their original positions. It will also be clear that, as is shown in fig. 1, at higher temperature the migration towards adjacent holes is facilitated, so that the residual voltage becomes greater.

### *The relation of residual voltage to field strength and layer thickness*

As we have demonstrated above, there is every reason to assume that owing to the electric field $Al^{3+}$ ions can be displaced towards adjacent sites. Owing to this charge shift, electrostatic influence will produce a charge on the capacitor plates, and this charge remains bound as long as any ions in the dielectric are displaced, even when the capacitor is short-circuited. Directly after the disappearance of the field, when the charges shifted in the dielectric return to their original positions, the charge formerly bound to the plates is released. A potential difference develops across the plates, rapidly at first and then gradually more slowly (fig. 1).

Let us assume that there are per $cm^2$ $N$ shifted charges, each of a value $3e$ ($Al^{3+}$), and let the shift amount to $x$ whilst the distance of the capacitor plates is $d$, then the charge induced on the plates amounts to

$$Q = \frac{3Nex}{d},$$

and as $Q = CV_R$, where $C$ is the capacity, we have $V_R \propto Nex$.

Now we find from our experiments that $V_R$ is proportional to $Fd$. The quantity $Nx$, therefore, is also proportional to $Fd$, where $N$ is proportional to $d$ and $x$ to $F$.

In our experiment $d$ was $2.10^{-5}$ cm (fig. 4). For the shifted charge we found at least $10^{17}$ elementary charges per $cm^3$ per volt of residual voltage. From this it follows that in our capacitor ($d = 2.10^{-5}$ cm) the shifted charge is at least $2.10^{12}$ $e/cm^2$.

Consequently we find

$$3\,Nex/d = 2.10^{12}e, \text{ and } Nx = 10^7 \text{ for } F = 5.10^4 \text{ V/cm}.$$

If we assume $x$ to be $2.10^{-8}$ cm, then we find $N = 5.10^{14}$. Now there are per $cm^3$ approximately $2.10^{22}$ $Al^{3+}$ ions, and our layer, having a thickness of

$2.10^{-5}$ cm, contains $4.10^{17}$ ions. Therefore, when we assume a shift of 2 Å, we find that 0·1% of the $Al^{3+}$ ions have participated in the shift.

If we assume that for the same field $x$ always has the same value, then, with increasing thickness, $N$ will increase proportionately, and the total charge induced on the plates will remain the same. The potential due to the release of this charge is porportional to the thickness, since the charge is the same but the capacitance change is inversely proportional to the thickness, so that the potential increases in proportion to the thickness.

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