



LB-944

STUDIES OF THE INTERFACE LAYER

IN OXIDE CATHODES

**RADIO CORPORATION OF AMERICA
RCA LABORATORIES DIVISION
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Approved



Studies of the Interface Layer in Oxide Cathodes

Introduction

This bulletin presents new data on interface effects in commercial tubes and points up the complex nature of interface layers. Considerable stress has been placed on the latter because of its bearing on practical interface measurements. Certain precautions to be observed in making interface-resistance measurements have been suggested in the hope that the observation of these precautions may enable various workers in the field to obtain consistent and comparable results. Finally, the bulletin reports some exploratory experiments to determine the possible physical mechanisms which may lead to the observed complex behavior of a $2\text{BaO}\cdot\text{SiO}_2$ layer in contact with a metal and BaO or BaO + SrO. These experiments have not been carried to the point where they yield definitive results. They have been included so that the results may be available to others.

General Discussion

In the course of RCA studies of the oxide cathode, it has been necessary to separate out the various mechanisms which contribute to the overall behavior of the diodes in which the cathodes have been studied.^{1, 2} One of the separable effects is the high-speed ten-volt effect³, which is an anode effect, yet is easily confused with certain cathode effects. A second separable effect is that due to an insulating layer which may form at the interface between the base metal and the oxide of a cathode. No major effort has been devoted to either of these effects. They have been pursued until they were sufficiently understood so that their presence was easily recognized and their

contribution to diode behavior could be separated out from the effects due to the oxide of the cathode. In the case of the interface layer, a simple circuit for measurement of the layer impedance was devised, the impedances of a substantial number of tubes were measured, and life test data to determine the rate of growth of interface impedance are still being accumulated. In quite another connection, some of the electrical properties of barium-orthosilicate ($2\text{BaO}\cdot\text{SiO}_2$) were measured.²

In view of the practical importance of the interface layer and the widespread interest in it, it seems worthwhile to report on the information accumulated. It has also been noted that some of the various methods used to measure interface impedance do not yield like results when applied to the same tubes. Study at RCA Laboratories of the electrical properties of $2\text{BaO}\cdot\text{SiO}_2$ suggests an explanation of the observed discrepancies and points to the precautions which must be taken if the various measurements are to yield consistent and coherent results.

¹R. M. Matheson and L. S. Nergaard, "Decay and Recovery of the Pulsed Emission of Oxide-Coated Cathodes", *JAP*, Vol. 23, No. 8, pp. 869-875, August, 1952.

²L. S. Nergaard, "Studies of the Oxide Cathode", *RCA REVIEW*, Vol. 13, No. 4, pp. 464-545, December, 1952.

³LB-833, *High-Speed Ten-Volt Effect*.

A Brief Review of Interface Literature

The presence of and, to some extent, the importance of interface layers was first recognized by Wehnelt in about 1905. Somewhat later Arnold⁴ observed a platinate interface layer on the platinum-iridium filaments he was using. In 1940, Rooksby⁵ published the results of his X-ray studies of interface compounds. He identified a number of compounds including $2\text{BaO} \cdot \text{SiO}_2$, which has been the subject of much further study. In 1946, Fineman and Eisenstein⁶ reported silicate interface layers in oxide-coated cathodes and described interface resistance measurements under pulse conditions. In 1949, Eisenstein^{7, 8} published an extensive paper on barium-orthosilicate interface layers. His paper describes the effect of such layers on cathode sparking and on cathode resistance. It also shows the rate at which the thickness of the layer increases on a cathode with 5 per cent silicon in the nickel base metal, and gives extensive data on the conductivity of $2\text{BaO} \cdot \text{SiO}_2$ and its temperature dependence.

About 1949, it became apparent that tubes in computer and time-division-multiplex service were failing at an early stage of life. It further appeared that the tubes that failed had been operating under very low-duty conditions. The failures were soon correlated with the silicon content of the base metals used in the cathodes of these tubes, hence with $2\text{BaO} \cdot \text{SiO}_2$ interface layers. At the 1950 Conference on Physical Electronics, a number of papers on the interface problem was presented.

In 1951, Waymouth⁹ and Eisenstein¹⁰ published further studies of interface layers and their effects on the performance of tubes in practical circuits. In the same year Bounds and Briggs¹¹ published a paper on the nickel alloys used for oxide cathodes and described the effect of the alloying materials on cathode performance.¹²

Some Electrical Properties of Barium Orthosilicate

A considerable number of interface materials is known; tungstites, platينات, silicates, and titanates, for example. Of these, $2\text{BaO} \cdot \text{SiO}_2$ has the lowest conductivity and is therefore of most practical concern. These compounds are formed by residues of the reducing agents used to free the base-metal nickel from oxide, or by small amounts of specific reducing agents added to the base metal in controlled amounts to achieve easy activation and long life of the cathode^{11, 13}. The reducing agents diffuse out of the base metal and react with BaO to form the various interface compounds. For example, silicon diffuses out of the nickel and reacts with BaO to form silica and "excess" barium according

⁹J. F. Waymouth, Jr., "Deterioration of Oxide Coated Cathodes Under Low Duty-Factor Operation", *JAP*, Vol. 22, No. 1, pp. 80-86, January, 1951.

¹⁰A. Eisenstein, "The Leaky Condenser Oxide Cathode Interface", *JAP*, Vol. 22, No. 2, pp. 138-148, Feb., 1951.

¹¹A. M. Bounds and T. H. Briggs, "Nickel Alloys for Oxide-Coated Cathodes", *Proc. IRE*, Vol. 39, No. 7, pp. 788-799, July, 1951.

¹²In the past few years, interface problems have received attention at a number of conferences, for example, at the Conference on Electron Tubes for Computers at Atlantic City, N.J., Dec. 11-12, 1950 and at the technical session on "Recent Developments in Electron Emitters" of the AIEE General Winter meeting in New York, Jan. 21-25, 1952. Recent papers seem chiefly concerned with measurement methods and accumulated life-test data to which reference will be made in a later section.

¹³H. E. Kern and R. T. Lynch, "Initial Emission and Life of a Planar-Type Diode as Related to the Effective Reducing Agent Content of the Cathode Nickel", *Phys. Rev.*, Vol. 82, No. 4, p. 574, May 15, 1951.

⁴H. D. Arnold, "Phenomena in Oxide-Coated Filament Electron Tubes", *Phys. Rev.*, Vol. 16, No. 1, pp. 70-82, July, 1920.

⁵H. P. Rooksby, "Applications of X-ray Technique to Industrial Laboratory Problems," *J. Royal Soc. Arts*, Vol. 88, pp. 308-336, 1940.

⁶A. Fineman and A. Eisenstein, "Studies of the Interface of Oxide Coated Cathodes", *JAP*, Vol. 17, No. 8, pp. 663-668, August, 1946.

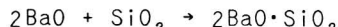
⁷A. Eisenstein, "Some Properties of the Ba_2SiO_4 Oxide Cathode Interface", *JAP*, Vol. 20, No. 8, pp. 776-790, August, 1949.

⁸The chemical formula for barium orthosilicate is written $2\text{BaO} \cdot \text{SiO}_2$ by some authorities, Ba_2SiO_4 by others.

to the equation



The silica reacts with BaO to form the silicate:



The complete reaction has two effects, (1) it produces excess barium which is desirable because it makes the cathode more active; (2) it produces an insulating material which impairs the performance of the cathode.

The rate at which the interface layer forms is determined by the concentration of the reducing agent in the base metal, its diffusion through the base metal, the rate of the reaction between the reducing agent and the oxide, and perhaps by the rate at which one of the reactants can diffuse through the layer already formed. Eisenstein found that the silicate layer, formed on a cathode having 5 per cent silicon in the nickel base, reached a thickness of about 2×10^{-3} cm when operated at 1125 degrees K for 100 hours.⁷ Just how the apparent resistance of the layer depends on its thickness is not completely resolved. However, the experiments next considered suggest that the apparent resistance does not show a simple linear increase with thickness.

A sample of $2\text{BaO} \cdot \text{SiO}_2$ was prepared by firing barium oxide and silica in ortho proportions at 1630 degrees K until the reaction was complete. The sample was a cylinder, $3/8$ inch in diameter and $1/2$ inch long. This cylinder was provided with platinum electrodes on its ends and a platinum "probe" ring about $1/16$ inch from one end of the sample, as shown in Fig. 1. These electrodes were painted and then fired on.

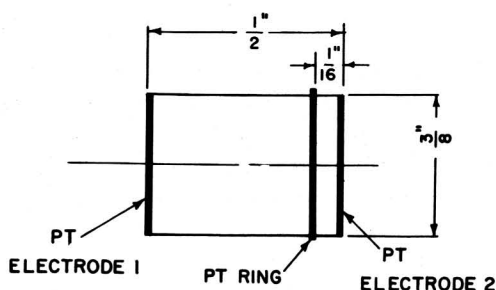


Fig. 1 - A cylindrical sample of $2\text{BaO} \cdot \text{SiO}_2$ (Sample XXV-51) with platinum electrodes for resistance measurements.

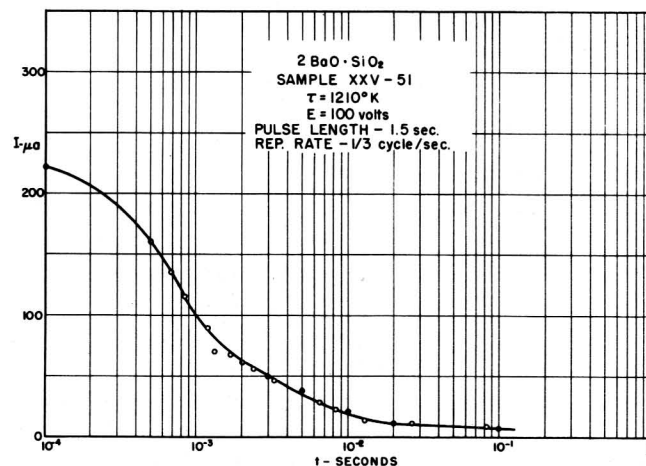


Fig. 2 - The decay of current with time in Sample XXV-51 of $2\text{BaO} \cdot \text{SiO}_2$ on application of a "unit-function" voltage.

The first measurement made on the barium-orthosilicate cylinder was a measurement of the current decay under constant-voltage conditions. Such a decay curve is shown in Fig. 2. It was obtained with the sample at 1210 degrees K, with 100 volts applied across the sample in 1.5 sec. pulses at a repetition rate of $1/3$ cycle per second. The initial current is 220 microamperes and the current decays to about 7 microamperes in 0.1 second. The decay is not exponential, but accords with the Sproull decay formula¹⁴ up to about 4×10^{-2} second. Beyond 4×10^{-2} second there is a very slow downward drift not found in the Sproull formula. The Sproull formula was originally derived on the assumption that current decay in the oxide cathode results from the electrolytic transport of barium from the emitting surface. The observation of Sproull decay in the present experiment suggested that a similar mechanism might be operating and that if some constituent of the silicate were transported electrolytically, the voltage distribution along the sample would not be linear. Accordingly, the voltage drops from Electrode 1 to the platinum ring and from the platinum ring to Electrode 2 in Fig. 1, with current flowing from end to end in the sample, were measured. Electrode 2, which is closest to the ring, was positive. It was found that at higher temperatures the major fraction of the voltage drop occurred near the

¹⁴R. L. Sproull, "An Investigation of Short-Time Thermionic Emission from Oxide Coated Cathodes", *Phys. Rev.*, Vol. 67, Nos. 5 and 6, pp. 168-178, March 1 and 15, 1945.

positive end. For example, at about 600 degrees K only 5 volts out of 46 volts appeared between Electrode 1 and the platinum ring. It appears that there is a depletion of some constituent at the positive end of the sample which raises the resistivity near the end. The behavior is similar to that observed earlier in a "Pyrex" glass sample at elevated temperatures.² The thickness of the depletion layer in the glass sample was measured and was found to be about 10^{-6} centimeter. The resistances of the silicate between Electrode 1 and the ring, the "bulk resistance", and between the ring and Electrode 2, the "depletion layer resistance", were measured as a function of temperature from 700 degrees K to 1100 degrees K. The bulk material shows an activation energy of about 0.80 ev., the depletion layer an activation energy of about 1.2 ev.

It now seems clear that the resistance of a $2\text{BaO} \cdot \text{SiO}_2$ layer is not proportional to the thickness of the layer. Hence the thickness of a layer is not a simple measure of the resistance the layer will display.

In studies of the oxide cathode, it was found that the peak pulse current which may be drawn from an oxide cathode is a decreasing function of duty. Because the $2\text{BaO} \cdot \text{SiO}_2$ sample, like the oxide cathode, displays Sproull decay, it was thought that the silicate sample might display a similar behavior with duty. Fig. 3 shows data to explore this possibility. The silicate sample was operated at 1210 degrees K, with 100-volt pulses applied at a repetition rate of 100 cycles per second. The duty was varied by varying pulse length. The initial current (I_1 in Fig. 3), disregarding the initial spike, showed no marked change with duty (the initial spike and narrow part of the inverse spike were traced to stray capacitance in the measuring circuit). The final pulse current shows a marked dependence on duty.

Because an oxide cathode and the $2\text{BaO} \cdot \text{SiO}_2$ sample both show Sproull decay and exhibit depletion layers, it is of interest to inquire why they differ in their behavior with respect to duty. An examination of the conditions of measurement for the two cases shows that the measurements were not made in the same way. The measurements on oxide cathodes were made in diodes. Hence, any polarization voltage developed in the cathode by current flow is

impressed across the cathode-anode space in such a direction that no conduction current can flow through the external circuit during the off period. In the case of the silicate sample, the circuit was such that a depolarizing current could flow through the external circuit. The negative transient subsequent to the pulse may be such a depolarizing current. It has a height which is linear with the total charge passed through the sample during the pulse, a behavior one associates with depolarization. Hence, it is possible that both would behave similarly under similar conditions of measurement and that the peak pulse current of the silicate sample would be a function of duty if no conduction current could flow through the external circuit between pulses. Unfortunately, the silicate sample was fractured and such a measurement cannot now be made.

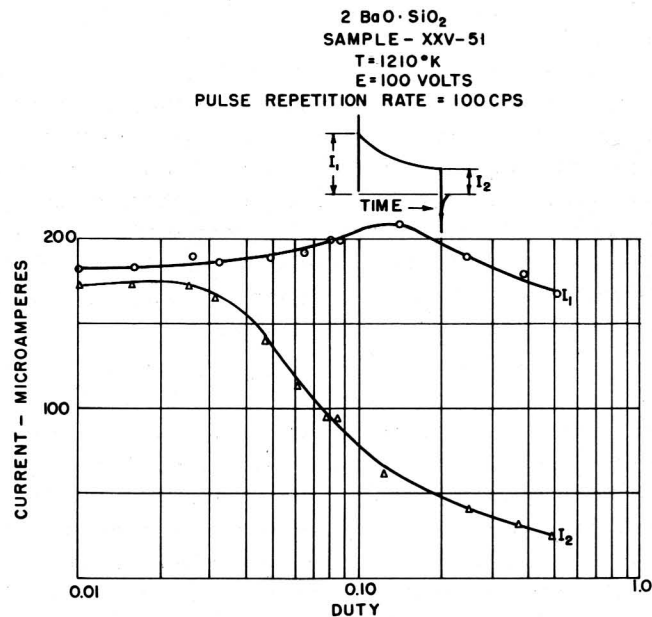


Fig. 3 - The initial and final pulse currents in Sample XXV-51 of $2\text{BaO} \cdot \text{SiO}_2$ as a function of duty.

It is tempting to assume that $2\text{BaO} \cdot \text{SiO}_2$ is an impurity semiconductor and that the observed decay and voltage distributions result from an electrolysis of donors away from the positive boundary. If this assumption is made and if it is further assumed that the donors are similar to those in BaO, then the results of the foregoing experiments and the results of the experiments now to be described can be accounted for in a simple and coherent manner.

Studies of the Interface Layer in Oxide Cathodes

In the experiments described above, the measured resistances were very high, much higher than those observed in cathodes. It is believed that this occurs because the electrodes in the present tests were of platinum whereas the positive electrode in a cathode is BaO or (BaSr)O. Explicitly, and in terms of the model above, it is believed that donors can diffuse and electrolyze from the oxide into the silicate. Such diffusion and electrolysis can produce two effects:

- (1) It can inhibit the formation of a depletion layer so that the apparent resistance of the interface layer is greatly reduced.
- (2) It can increase the donor density in the interface layer so that the bulk resistance is reduced.

The following observations bear on these consequences of the electrolytic model and are interpreted in terms of the model.

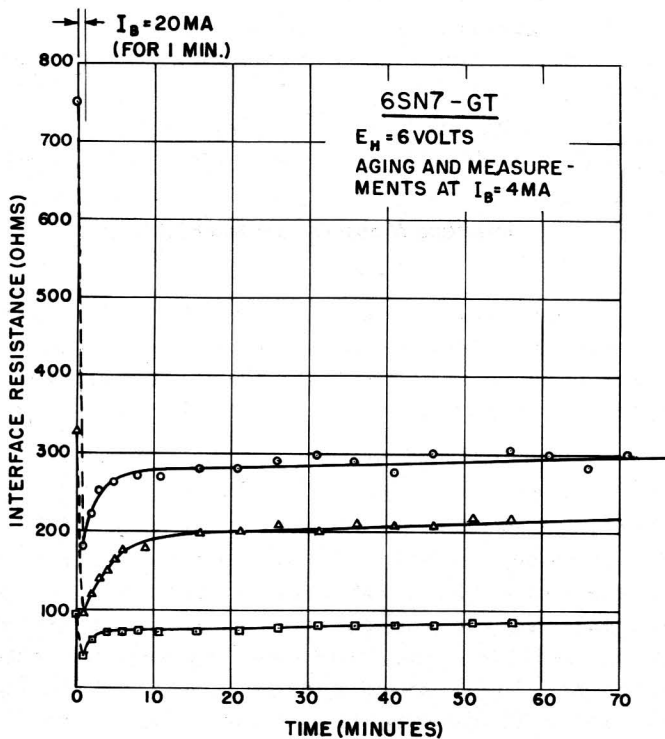


Fig. 4 - The reduction of interface resistance as a function of time after passing excess current through the interface.

It is observed that tubes which have aged without plate current show a much higher interface resistance than tubes which have aged in presence of substantial plate current. This observation suggests that the equilibrium

distribution of donors between the oxide and the silicate is such that the silicate is relatively inactive. It is also observed that tubes which have aged without plate current show a marked decrease of interface resistance when current is drawn for even moderate periods of time. The decrease of resistance is not permanent and the resistance increases as the cathode is aged without current. An example of this behavior is shown in Fig. 4. These data pertain to three 6SN7-GT tubes which had interface resistances of 750, 330 and 93 ohms, respectively, measured at an anode current of 4 ma. After the interface resistances had been measured each of the tubes was operated at an anode current of 20 ma for one minute after which the current was restored to 4 ma and the interface resistance was measured as a function of time. The initial readings were obtained within 15 seconds after restoring the anode current to 4 ma. The reduction in resistance immediately after drawing excess current, and the reduction in resistance after the first hour of aging at 4 ma are plotted versus the initial interface resistance in Fig. 5. The

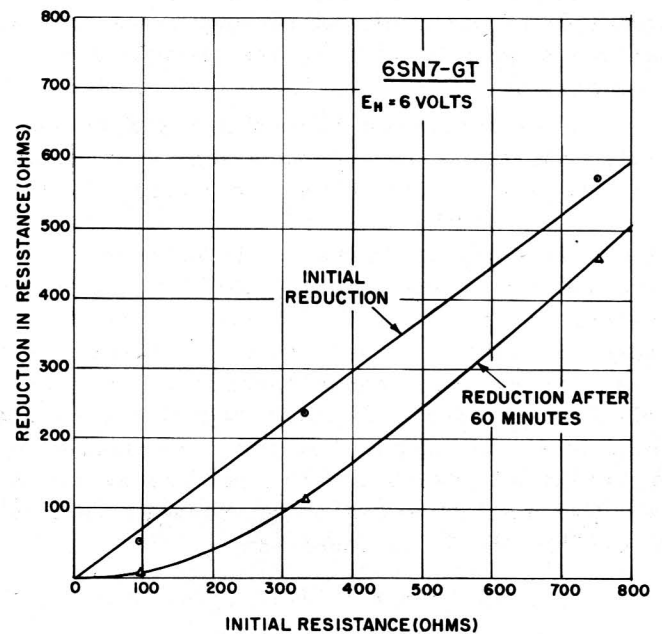


Fig. 5 - The initial reduction in interface resistance and reduction in resistance after aging for an hour at 4.0 ma plate current as a function of the resistance before passing excess current.

initial reduction in resistance is proportional to the initial resistance, approximately. The reduction after an hour of aging is proportional to the square of the initial resistance,

approximately. The curves in Fig. 4 show a slow upward trend after the initial rise. The data were extended for another seven hours for the uppermost curve. The resistance remained at about 300 ohms over this period. It appears that drawing excess current produces an activation of the interface layer which persists for at least a few hours. This behavior can be interpreted in terms of an electrolysis of donors into the interface layer by the excess current and a loss of donors by back diffusion when the current is small.

Whatever the details of the physical mechanism which leads to the behaviors described above, certain precautions to be observed in making measurements of interface resistance are indicated:

1. Measurements should be made at average currents comparable to those used in the aging processes if the measurements are not to change the quantities being measured.

2. If measurements are to be made at a specified current, adequate time for the realization of equilibrium must be provided.

3. Because the apparent resistance is a function of duty, all measurements must be made at the same duty if they are to show a simple correlation.

When interface layers are subjected to pulse operation, one or more short-time decays are observed. The time constants of these decays are of the order of 0.5–2 microseconds. These time constants appear to be more or less independent of the actual interface resistance. Hence, it is difficult to account for them in terms of simple capacitances. It seems likely that the apparent capacitances are associated with an electronic or ionic blocking layer. It may be noted in passing that the dielectric constant of $2\text{BaO}\cdot\text{SiO}_2$ was measured by the immersion method using an acetone–benzene dielectric. The value found was

$$\epsilon = 12.4$$

The time effects described above may be represented approximately by the simple equivalent circuit shown in Fig. 6. In the figure, the diode represents the emitting surface, the interelectrode space and the anode of the actual diode. The electrical network represents the internal behavior of the cathode. R_0 , R_1 , and C_1 , in combination, have a time constant of

the order of 10^{-9} second, hence the combination represents the polarization mechanism which yields the slow decay. In the representation of practical tubes, R_1 is usually of the order of 5–10 times R_0 . R_0 , R_1 , and C_2 in combination have a time constant of the order of 1 microsecond, hence represent the short time-constant mechanism which is characteristic of interface layers. The circuit element which distinguishes the effect of an interface layer from other cathode effects is C_2 . More detailed equivalent circuits are discussed elsewhere.¹⁵

The above equivalent circuit uses linear circuit parameters. This is an approximation as is apparent in the form of the current-decay. If the decay effects are due to a depletion layer the apparent resistance and capacitance are not linear. If the interface layer is thin and of low conductivity, and no depletion effects are apparent, the layer will act as a rectifying blocking layer with an exponential current-voltage characteristic. In neither case can the apparent circuit parameters be matched by linear circuit elements over an extended current range.

Interface-Measurement Methods

A variety of methods has been used to measure interface resistance in tubes. Some of these methods will be described briefly. Their apparent relative merits will be outlined.

a. Simple Pulse Methods

In the simplest version of the pulse method, a constant-voltage pulse of about 10 microseconds duration is applied to the anode of the diode whose interface resistance is to be measured and the current decay is observed on an oscilloscope. The leading edge of the pulse should be steep enough so that there is no substantial decay during the time of application of the pulse, and the oscilloscope should have a bandwidth adequate to display the pulse accurately. The initial and final currents are determined from the oscilloscope display. If the current decay is small enough so that the diode impedance does not change appreciably

¹⁵LB-945, *A Bridge for the Measurement of Cathode Impedance*.

with the change in current during decay, the decay may be regarded as due to the gradual insertion of the interface resistance in series with the cathode return. Hence, the interface resistance is

$$R_i = E \left(\frac{1}{I_\infty} - \frac{1}{I_0} \right)$$

in which E is the applied voltage, I_0 is the initial current and I_∞ is the final current. If the decay is substantial, the change in diode impedance must be taken into account.

An alternative is to use a constant-current pulse and to display the voltage across the diode on an oscilloscope. In this case, the voltage rises from an initial value V_0 to a final value V_∞ . Because the diode resistance remains constant, the interface resistance is simply

$$R_i = \frac{V_\infty - V_0}{I}$$

in which I is the pulse current.

In the case of multielectrode tubes, the tubes are usually diode connected, i.e., all of the grids and anode are tied together. The alternative is to connect a multielectrode tube in its normal amplifier connection, drive the control grid with a constant-voltage pulse and observe the voltage pulse across the plate load. Because the interface resistance appears in the cathode circuit, it degenerates the transconductance of the tube. If g_{m0} is the transconductance of the tube in the absence of interface resistance and R_i is the interface resistance, the apparent transconductance is

$$g_m = \frac{g_{m0}}{1 + g_{m0} R_i}$$

This is the transconductance which is observed after pulse decay is complete or at frequencies low enough so that the interface resistance is not shunted out by the apparent interface capacitance. In a high- μ tetrode or pentode, the voltage across the plate load at the beginning of a constant voltage pulse is

$$V_0 \approx g_{m0} R_p V_g$$

and after decay is complete is

$$V_\infty \approx g_{m0} R_p V_g$$

where R_p is the plate-load resistance and V_g is the pulse voltage applied to the grid. Hence, the interface resistance is

$$R_i = \frac{1}{g_{m0}} \left(\frac{V_0}{V_\infty} - 1 \right)$$

The amplifier connection has the advantage of yielding a certain amount of voltage gain. This is offset in part by the necessity of determining g_{m0} .

It should be noted that the foregoing method is exact only for triodes. In tetrodes, pentodes and other tubes having additional positive electrodes the cathode current is not equal to the plate current and the feedback voltage developed across a cathode resistance is not proportional to the plate current. If a triode connection cannot be used, corrections must be made to account for these additional currents.

In any of these pulse methods, the apparent capacitance may be computed from the measured resistances and the time-constant of decay.

All of these methods suffer from a lack of accuracy, particularly when the interface resistance is very low. All of these methods have been used during the course of this study.

b. The Wagner Method

H. M. Wagner has modified the simple pulse methods described above so that he achieves a considerable advantage in accuracy.¹⁶ He drives the diode-connected "unknown" tube with a constant-voltage pulse and views the current decay on an oscilloscope. He then inserts a "substitution resistor" in series with the tube and adjusts this resistor until the leading edge of the displayed pulse coincides with the previous position of the final current after decay. If the current decay is small so that the diode resistance does not change appreciably, the inserted resistance is equal to the interface resistance. To increase the sensitivity, he divides off a fraction of the driving voltage and applies this voltage and the voltage across the tube-current-measuring resistor to a

¹⁶H. M. Wagner, "Cathode Interface Impedance and Its Measurement", presented at the National Electronics Conference, Chicago, Ill., 1952.

difference amplifier which drives the oscilloscope. Thus the oscilloscope displays only the amplified decay characteristic. By this means he achieves a sensitivity adequate to measure an interface resistance as low as one ohm.

Again, the apparent capacitance is determined from the time-constant of decay and the interface resistance.

This measurement method is one of the simpler and more accurate methods which has been used in the Laboratories.

A modification of this method in which the "unknown" tube is triode connected, the grid is driven with a square-wave voltage, and the current-measuring resistor and substitution resistor are inserted in the cathode return has also been used. This method has the advantages that the plate current can be adjusted independently of the signal voltage and that the tube need not be driven through current cut-off where the non-linearity of the tube characteristic makes it difficult to match the voltage across the current-measuring-resistor with the balancing voltage.

c. The Transconductance Method

As noted in Section (a), the apparent transconductance of a multielectrode tube is a function of the interface resistance. If the transconductance of a tube is measured at two frequencies, one high enough so that the apparent interface capacitance shunts out the interface resistance, the second low enough so that the interface capacitance does not shunt out the resistance, the interface resistance may be computed from the two transconductances by the formula

$$R_i = \frac{1}{g_{m1}} - \frac{1}{g_{m2}}$$

in which g_{m1} and g_{m2} are the "low" and "high" frequency transconductances, respectively. Appropriate frequencies are 10 Mc and 0.01 Mc. If the lower frequency is chosen still lower, the long-time-constant effects begin to play a role. Much of our interface data has been acquired by this method. For low resistance values it suffers from the difficulties normal to all measurements or computations which depend on a small difference between large quantities.

d. A Bridge Method

This bridge method balances the unknown tube against a synthetic diode comprising a diode free from the defects under study in series with a suitable adjustable network (Fig. 6). The details of the bridge are described elsewhere.¹⁵ The bridge permits of considerable precision. However, in its present low-frequency form this bridge does not separate out oxide effects and interface effects. Hence, it is suitable for measurements of interface impedance only when the interface impedance is high compared to the oxide impedance. This is usually the case with well-activated tubes having a considerable silicon-content in the base metal, after the tubes have been aged at a low duty for some hundreds of hours. For making interface measurements early in the life of a tube, a pulse or high-frequency method is to be preferred to this bridge.

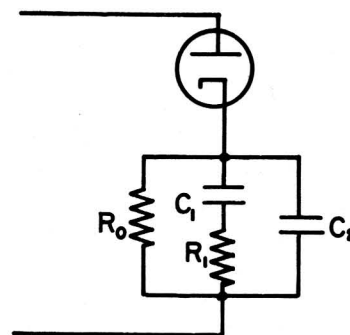


Fig. 6 - The equivalent circuit of a diode having an interface layer. The diode is presumed to satisfy the Child-Langmuir law.

In connection with the bridge circuit, it is worth noting that, in the form in which we have built it, the bridge may be balanced and then switched to display the plate currents of the unknown and standard tubes on the horizontal and vertical axes, respectively, of an oscilloscope. If the display shows a marked and abrupt deviation from linearity, one of the two tubes is emission-limited; which one is apparent from the direction of the deviation. In this measurement, true emission limitations, unconfused by deviations due to cathode impedances, can be found.

e. The Frost Method

The method of Frost places the tube under

test in its normal amplifier connection¹⁷. The grid is driven with a square wave from one-half of a phase inverter. A resistance having a magnitude equal to the reciprocal of the transconductance of the tube under test is connected between the control grid and the anode. The anode is driven out-of-phase by the other half of the phase inverter. Hence, the current through the load resistor is zero if the tube has no cathode impedance. An amplifier driving an oscilloscope is used to observe the voltage across the plate load. If there is cathode impedance, the apparent transconductance of the tube becomes frequency sensitive and is not matched by the reciprocal g_m resistor, and a signal appears across the plate resistor. This signal is balanced out by a network in the cathode return which is the dual of the interface impedance (a network complementary to that of Fig. 6). Because of the sensitivity of the circuit, stray capacitances must be balanced out by a neutralizing capacitor in order to achieve balance. Altogether, six parameters must be adjusted to achieve a balance: the reciprocal g_m resistor, the neutralizing capacitor, and the four elements of the complementary network.

This method is elegant and achieves a sensitivity and time-resolution which do not seem to be matched by any other method. It has disclosed two time-constants for interfaces in the microsecond range, one 0.1-1.5 microseconds; the second, 0.5-10 microseconds. Like all bridges which yield much information, a considerable amount of skill and time is involved in obtaining a balance. It is felt that this method is an elegant laboratory method but is not suitable for routine measurements on large numbers of tubes.

f. The Bartley and White Method

Bartley and White have used a comparison method for measuring interface impedance¹⁸. The tube under test is placed in its amplifier connection. The grid is driven by a square-wave voltage of several microseconds period.

¹⁷H. B. Frost, "The Measurement of Cathode Interface Impedance", (Abstract), *Proc. IRE*, Vol. 40, No. 2, p. 230, Feb., 1952. Also reported at Twelfth Annual Conference on Physical Electronics, MIT, 1952.

¹⁸W. P. Bartley and J. E. White, "Characteristic Shifts in Oxide Cathode Tubes", *AIEE Technical Paper*, pp. 52-53, December, 1951.

The output voltage of the tube is superposed on the square-wave input voltage in an oscilloscope display by an electronic switching circuit. Then any distortion of the output wave shape by interface impedance is apparent. This measurement makes possible the selection of "standard" tubes which show no appreciable interface effects. In the measurement of interface impedance, the output voltage of the unknown tube is superposed on the output voltage from a "standard" tube, with both tubes driven by the same grid voltage. The two wave shapes are then made coincident by introducing resistance and capacitance in parallel, both in series with the cathode return of the standard tube. When the output-voltage wave shapes coincide, the inserted resistance and capacitance are equal to the apparent resistance and capacitance of the interface layer of the unknown.

Aside from the switching circuits required to superpose the voltages to be compared, the method is simple and direct. If the oscilloscope is preceded by an amplifier of adequate gain and bandwidth, it should be capable of considerable sensitivity and accuracy.

g. The McNarry Method

McNarry¹⁹ makes the tacit assumption that a cathode exhibits zero resistance except for interface resistance and proceeds as follows. The diode-connected unknown is compared with a three-element passive network in a bridge. The unknown is operated at the desired direct-current level and the bridge is driven with an a-c signal. The first of the three balances required to determine the interface impedance is made at a frequency of 10 Mc per second. At this frequency, the interface impedance is negligible compared to the plate resistance of the diode, so that balance is achieved by adjusting a resistor R_0 , which represents the plate resistance, in the standard arm of the bridge. The second balance is made at a frequency of 100 cycles per second. At this frequency, the apparent shunt reactance of the interface layer is large compared to the shunt resistance, so balance is achieved by inserting an additional resistance R_i , which represents the interface resistance, in series with R_0 . The third balance is made at a frequency of

¹⁹L. R. McNarry, "Bridge for Measuring the Interface Impedance of Oxide-Coated Cathodes", Report N.R.C. No. 2745 of the National Research Council of Canada.

100 kilocycles per second by shunting R_i with a capacitance C_i . If the bridge ratio is unity, the bridge is direct reading and R_i and C_i are the interface resistance and capacitance respectively. The bridge measures low interface resistances within one ohm.

Unfortunately, the cathode impedance of a tube with zero interface resistance is not zero; the oxide resistance remains and may be substantial. Hence the bridge does not measure interface resistance directly. Just what it measures depends on the details of the circuit, particularly the balance indicator.

All of these methods have their merits. The choice of circuit must be predicted on the application. For laboratory experiments where precision is desired, at the expense of time, naturally, certain circuits recommend themselves. For routine measurements of large quantities of tubes, other circuits are indicated. However, it must be stressed that the various methods will not yield the same results when applied to the same tubes. Methods which operate with a small signal superposed on a d-c bias are expected to yield a higher apparent interface resistance than those methods which employ a very small duty because the former measure resistance after the decay of Fig. 2 is complete and the latter make the measurement near the beginning of decay in Fig. 2. Furthermore, the "small-signal" methods may change the apparent interface impedance of tubes which have been aged under cut-off conditions if the d-c cathode current is substantial in the test. Until the effects of current on the activity of interface layers have been more thoroughly delimited, it seems wise to make measurements under conditions which resemble the aging conditions as closely as practicable.

Life Test

This section includes most of the pertinent data on interface effects in practical tubes which have been accumulated. Some of the data have been reported orally at various conferences. They are included here because of the evident interest in them.

a. 6SN7-GT's and 6SL7-GT's from Multiplex Equipment

Certain tubes operating at low-duty cycle in time-division multiplex terminal equipment had failed. These tubes were sent to RCA Laboratories for study after their cathode resistances had been checked by the transconductance method described in the preceding section. The low-frequency transconductances were then computed from the measured high-frequency transconductances and measured cathode resistances for comparison with the measured low-frequency transconductances. The results are shown in Tables I and II. The columns in Table I are, from left to right:

1. The tube number
2. I_p , the peak current to which the tube was driven in the bridge
3. R_k , the apparent cathode resistance at 60 cps.
4. V_k , the peak voltage drop across the apparent resistance
5. V_p , the peak applied plate voltage
6. V_k/V_p , the fraction of the plate voltage which appears across R_k
7. $I_p/V_o^{3/2}$, where $V_o = V_p - V_k$. This is the perveance of the tube.

It should be noted that in some cases the cathode drop amounts to 50 per cent of the applied voltage.

Table II compares the bridge measurements with the transconductance measurements. The columns from left to right are:

1. The tube number
2. g_{mo} , the transconductance at 10 Mc. This is assumed to be the true transconductance of the tube.
3. R_k , as given in Table I
4. g'_m , the apparent transconductance computed from

$$g'_m = \frac{g_{mo}}{1 + g_{mo}R_k}$$

5. g_m , the transconductance at 10 kc.
6. The ratio of computed and measured transconductance at 10 kc.
7. The duty at which the tubes had operated in the multiplex equipment.

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Table I

Multiplex Service							
Tube Type	Tube No.	I_p Amps	R_k Ohms	V_k Volts	V_p Volts	V_k/V_p	$I_p/V_o^{3/2}$ $\times 10^6$
6SN7-GT	1a	0.068	44	3.00	21.2	0.141	873
	b	0.032	317	1.01	19.8	0.510	1060
	3a	0.060	84	5.04	21.2	0.238	923
	b	0.034	322	11.1	21.2	0.528	1070
	14a	0.025	178	4.45	15.6	0.285	680
	b	0.042	213	8.9	21.2	0.419	966
	18a	0.025	250	6.25	17.7	0.354	618
	b	0.042	187	8.23	21.2	0.388	933
	30a	0.030	130	11.3	21.2	0.486	980
	b	0.044	179	7.9	21.2	0.372	900
6SL7-GT	1a	0.0216	480	10.4	21.2	0.491	610
	b	0.0136	256	3.48	10.0	0.348	825
	2a	0.0202	81	1.6	10.0	0.160	1030
	b	0.0184	142	2.6	10.0	0.260	920
	3a	0.016	203	3.2	10.0	0.320	905
	b	0.0106	483	5.1	10.0	0.510	980
	4a	0.0057	1010	5.8	10.0	0.580	670
	b	0.0088	615	5.4	10.0	0.540	890
	14a	0.0044	1670	7.3	10.0	0.730	995
	b	0.0104	465	4.83	10.0	0.483	881

Table II

Multiplex Service							
Tube Type	Tube No.	g_{mo} 10 Mc	R_k Ohms	g'_m Comp.	g_m 10 kc	g_m/g'_m	D Duty
6SN7-GT	1a	2480	44	2230	2060	0.923	0.97
	b	2520	317	1400	1340	0.958	0.041
	3a	2520	84	2080	2140	1.03	0.97
	b	2560	322	1400	1420	1.01	0.041
	14a	2520	178	1760	1900	1.08	0.57
	b	2500	213	1630	1100	0.67	0.041
	18a	1440	250	1060	1460	1.36	0.45
	b	1060	187	885	400	0.45	0.041
	30a	1260	370	880	760	0.86	0.090
	b	2520	179	1740	1040	0.60	0.041
6SL7-GT	1a	1700	480	935	1120	1.20	1.0
	b	1680	256	1180	1320	1.12	1.0
	2a	1840	81	1600	1460	0.912	1.0
	b	1660	142	1340	1320	0.985	1.0
	3a	1740	203	1280	1340	1.05	1.0
	b	1580	483	893	1040	1.16	1.0
	4a	1100	1010	524	680	1.30	1.0
	b	1560	615	798	1040	1.30	1.0
	14a	1120	1670	582	500	0.860	1.0
	b	1100	465	730	800	1.10	1.0

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Table III

6AG7 - Life Test							
Test No.	Tube No.	I_p Amps	R_k Ohms	V_k Volts	V_p Volts	V_k/V_p	$I_p/V_o^{3/2}$ $\times 10^6$
49 x 149	1	0.038	180	6.8	10.7	0.64	4430
	2	0.064	78.4	5.0	10.9	0.46	4480
	3	0.064	91.3	5.8	11.7	0.50	4480
	4	0.058	113	6.6	12.1	0.55	4530
	5	0.064	71.5	4.6	10.6	0.43	4360
	6	0.052	86.2	4.5	9.5	0.47	4550
	7	0.051	83.5	4.3	9.2	0.47	4740
	8	CATHODE LEAD OPENED					
49 x 150	1	0.058	228	13.2	18.7	0.70	4570
	2	0.030	136	4.1	7.6	0.54	4600
	3	0.030	226	6.8	10.1	0.67	5000
	4	0.033	162	5.4	9.4	0.57	4150
	5	0.033	253	8.4	12.2	0.69	4480
	6	0.029	226	6.6	9.9	0.67	4870
	7	0.021	351	7.2	10.2	0.71	4070
	8	0.029	273	8.0	11.4	0.69	4610
	9	MISSING					
49 x 160	1	0.067	37.3	2.5	8.5	0.34	4560
	3	0.042	106	4.5	9.2	0.49	4120
	7	G_1 - K SHORT					

Table IV

6AG7 - Life Test						
Test No.	Tube No.	W/W_o Calc.	W/W_o Meas.	R_k Calc.	R_k Meas.	Life Hours
49 x 149 N-34A Cutoff	1	0.195	0.234	115 Ω	180 Ω	1545
	2	0.615	0.472	25	78	2041
	3	0.402	0.350	53	91	2041
	4	0.490	0.380	39	113	2041
	5	0.640	0.432	23	72	2041
	6	0.326	0.339	66	86	1545
	7	0.390	0.370	55	83	2041
	8	0.222	0.205	102	--*	1545
49 x 150 N-34A Conduction	1	0.435	0.478	47	228	3053
	2	0.080	0.061	231	136	3053
	3	0.081	0.081	229	226	3053
	4	0.105	0.090	190	162	3053
	5	0.113	0.087	180	253	3053
	6	0.098	0.086	199	226	3053
	7	0.051	0.116	310	351	3053
	8	0.070	0.067	251	273	1545
	9	0.060	0.056	280	--+	--+
49 x 160 N-81 Conduction	1	0.338	0.303	66	37	3053
	3	0.191	0.305	117	106	3053
	7	G_1 - K SHORT				
*Cathode Lead Open				+Missing		

In some instances, the ratio of g_m/g'_m is considerably less than unity. This may be due to the fact that some of these tubes were subjected to emission checks after the transconductance measurements and before the bridge measurements. Operation of tubes under high current conditions reduces R_k , as was pointed out earlier. All of these tubes were checked for emission limitation up to at least one-half ampere after the bridge measurements. In no instance was an emission limitation found.

b. Life-Test of Special 6AG7 Tubes

A group of 6AG7's having various cathode base metals were operated on life test for periods up to 3050 hours. The life-test data comprise the plate current at a standard voltage versus time and the power output of the tubes into a standard load versus time. Table III shows the results of bridge measurements on these tubes. The columns correspond to those of Table I. The tubes 49 x 149 and 49 x 150 have a high-silicon-content base metal (0.15 - 0.25 per cent silicon) and were run under cut-off and conducting conditions, respectively. Tubes 49 x 160 have a low-silicon-content base metal (<0.01 per cent silicon) and were run under conducting conditions. It is worthy of note that in some of these tubes about 70 per cent of the applied voltage appears across the cathode.

Table IV compares the bridge measurements with the life-test data. The cathode resistance may be computed from the plate currents at the beginning and end of life if the drop in plate current is caused solely by an increase in cathode resistance. The required relation is

$$R_k = \frac{i_o^{2/3} - i^{2/3}}{p^{2/3} i}$$

in which i_o is the initial current, i is the final current and P is the perveance of the tube.

Columns 5 and 6 in Table IV compare the computed cathode resistances with those measured in the bridge. The ratio of the final g_m to the initial g_{m0} may be computed from the relation

$$\frac{g_m}{g_{m0}} = \frac{1}{1 + g_{m0} R_k}$$

The ratio of the final power output into a

standard load to the initial power output into the same load is approximately the ratio of the final to initial g_m squared. Columns 2 and 3 of Table IV compare the ratio of final to initial output as computed and measured. It appears that the major cause of the decrease of plate current with life was the increase of interface resistance with life. The column on the extreme right shows the time at which the tubes were removed from the life-test racks. These tubes were also checked for signs of emission limitation up to about 0.5 ampere and none was found.

c. Current Life-Test Data on Special 6SN7-GT and 6SL7-GT Tubes Operating in Time-Division-Multiplex Terminal Equipment

The time-division-multiplex terminal equipment mentioned under (a) is now equipped with a series of 6SL7-GT's and 6SN7-GT's having various silicon-content base metals. These tubes are operated at a heater voltage of 6.0 volts to retard interface growth. After each 1000 hours of operation, the 10-Mc and 10-kc transconductances of these tubes are read. From the transconductances, the apparent interface resistances are computed. The data for the first 5000 hours were examined for significant differences which might be associated with the silicon content of the base metal, the average plate current and the duty. The data were then grouped in accordance with the operating conditions which seemed to produce differences. The average resistances versus life for each of the groups are shown in Figs. 7, 8 and 9. An examination of the curves suggests that the original subdivisions were too fine and that the statistical variations far exceed the suspected correlations with plate current and duty. Fig. 7 shows the variation of resistance with life of a group of 106 triode units with a relatively high silicon content in the base metal. The conditions of operation corresponding to each curve are shown in the box in the figure. It will be noted that the apparent resistance rises quite rapidly to a value of the order of a thousand ohms in the first 8000 hours and then shows a tendency to level off.

Fig. 8 shows similar data on a group of 50 triode units having a lower silicon-content base metal. The silicon content is less than 1/3 of that of the tubes of Fig. 7 and the apparent resistance approaches a value of the

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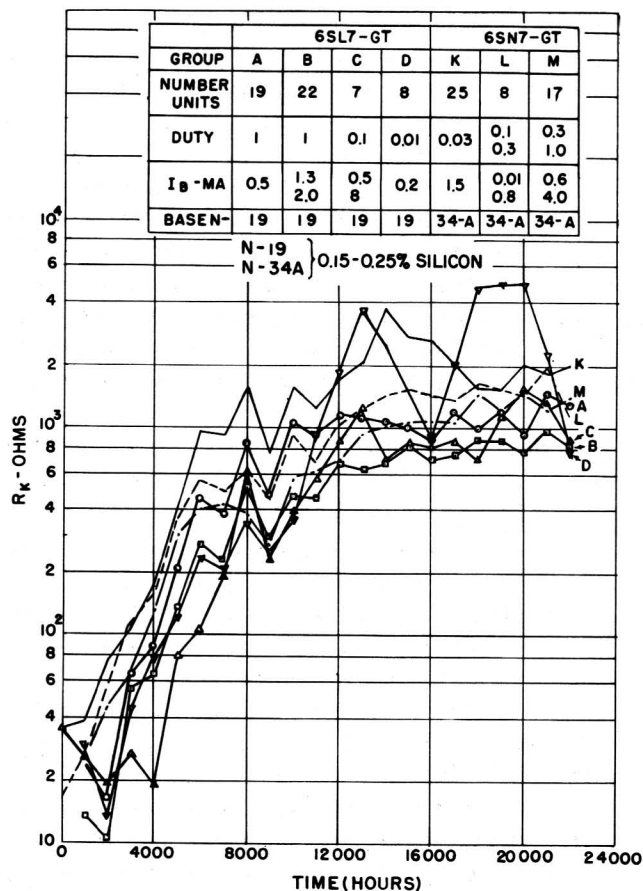


Fig. 7 - The interface resistances versus time of a set of tubes having 0.01-0.05 per cent silicon in the base metal.

order of 1/5 of that of the tubes of Fig. 7. The same rapid initial rise of resistance with life as observed previously is noticeable.

Fig. 9 shows similar data on a group of 92 triode units some of which have a still lower silicon content. The same general behavior with life is observed. The resistance appears to level off at about 70 ohms.

Because there appears to be no clear-cut correlation with plate current or duty, at least for the ranges of plate current and duty encountered in the multiplex equipment, the data were reduced to a unit cathode area basis and averaged by base metal. The results are shown in Fig. 10. Two general conclusions can be drawn:

1. The interface resistances increase rapidly with time during the first 8000 hours and then show a tendency to saturate.
2. The "final" resistances are about in proportion to the original silicon contents of the base metals.

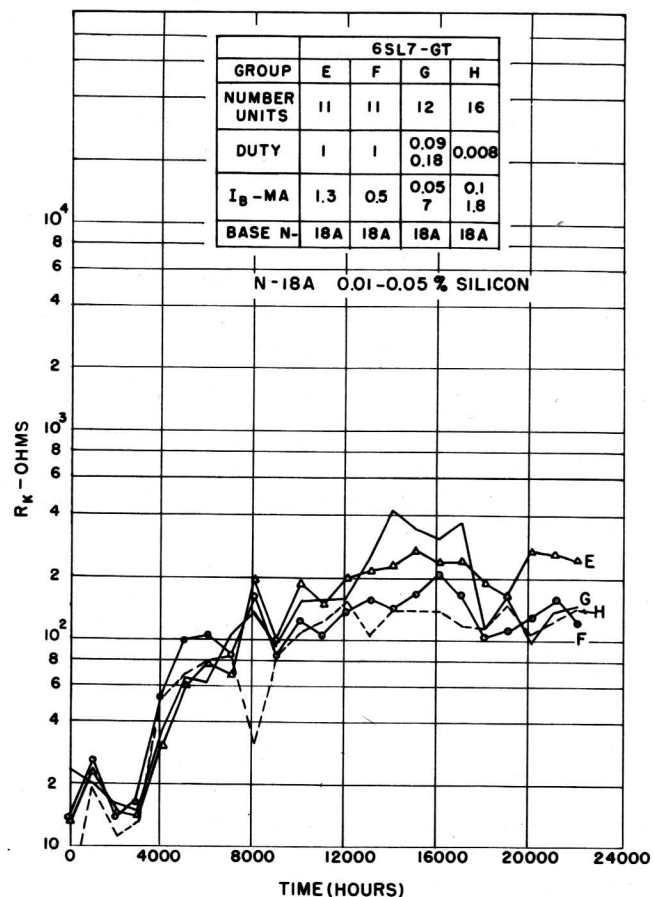


Fig. 8 - The interface resistance versus time of a set of tubes having 0.01-0.05 per cent silicon in the base metal.

It is worth noting that the behavior of the resistance with time during the first few thousands of hours does not give a clear indication of what will happen subsequently.

Considered from an engineering standpoint, the implications of these data are self-evident. In view of the considerable investment in time required to obtain such data, it seems desirable to glean whatever further information is possible from them. The amount of fundamental physical information which can be abstracted is probably very small because:

1. The increase of interface thickness with time is not known. Hence, the dependence of interface resistance on layer thickness cannot be established. Furthermore, the process which determines the rate of growth cannot be separated out. The dominant process may be the rate of diffusion of silicon out of the base metal, the rate of diffusion of silicon or barium oxide through the interface layer, the rate of reaction between silicon and barium

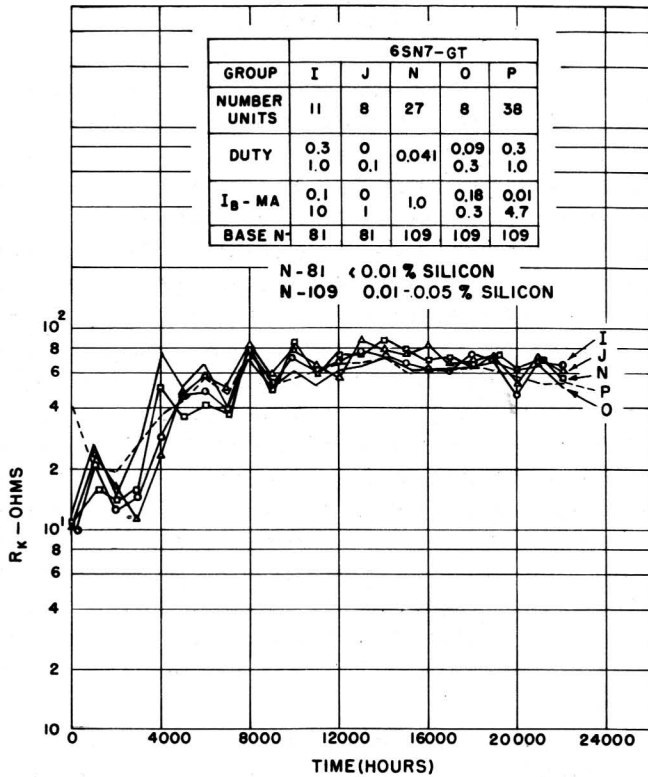


Fig. 9 - The interface resistances versus time of a set of tubes having <0.01-0.05 per cent silicon in the base metal.

oxide or perhaps one of these mechanisms early in life and another later.

2. It is not certain that the measurements from which the resistances are derived do not affect the resistances and their rate of growth. The transconductances of the 6SN7-GT tubes are read at a plate current of 12 ma and the transconductances of the 6SL7-GT tubes at a plate current of 4 ma. These currents exceed the currents at which the tubes operate in the life test with a few exceptions. If the usual pattern of behavior applies, the decrease of interface resistance with current noted in Section III, the currents drawn during the measurements reduce the resistances at each reading. As the resistances increase with life the effect of the measurement current may also increase in such a manner that the asymptotic resistance observed in the life curves is simply an equilibrium between the rate of growth of resistance and the reactivation during each measurement. This possibility is suggested by the results shown in Figs. 4 and 5.

To explore how the measurements might affect the life curves, suppose that the re-

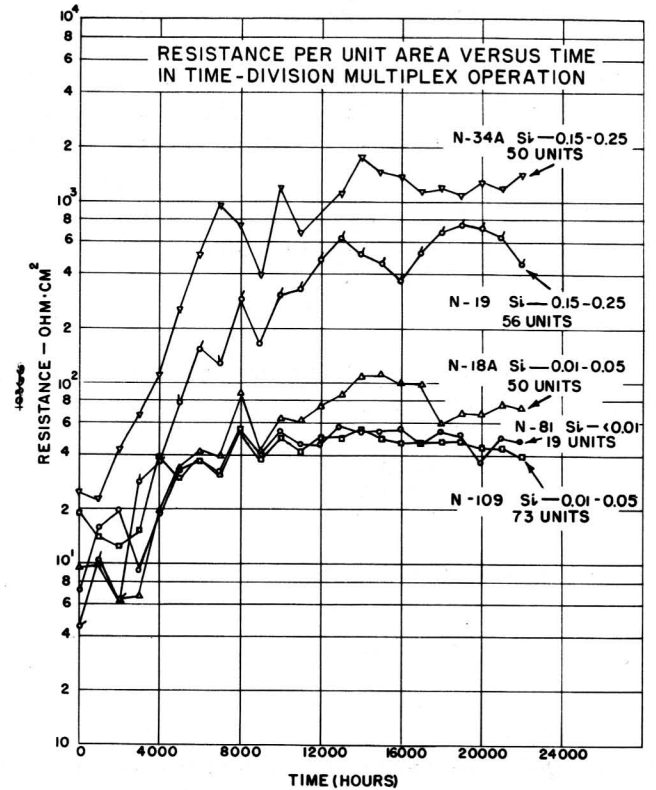


Fig. 10 - The data of Figs. 7, 8, and 9, reduced to a unit cathode area basic, with the type of base metal as a parameter.

sistance of the layer is proportional to its thickness and that the thickness is determined solely by the diffusion of silicon out of the nickel. Then it can be shown that after the first thousand hours of life or so the resistance should approach an asymptotic value R_{∞} according to the formula

$$R = R_{\infty} \left[1 - \left(1 - \frac{R_0}{R_{\infty}} \right) e^{-t/\tau} \right]$$

in which

R_0 = resistance at the beginning of the life test

$$\tau = \frac{1}{D} \left(\frac{d^2}{\pi} \right)$$

D = diffusion constant of silicon in nickel

d = thickness of the nickel

Hence the rate at which the resistance increases is

$$\frac{\partial R}{\partial t} = \frac{R_{\infty} - R}{\tau}$$

Now suppose the measurements reduce the resistance at the time of measurement in proportion to the resistance as in Fig. 5. If this reduction is averaged over the time between readings, the differential equation becomes

$$\frac{\partial R}{\partial t} = \frac{R_{\infty} - R}{\tau} - \alpha R$$

where αR is the reduction due to the measurement. The asymptotic resistance then becomes

$$R'_{\infty} = \frac{R_{\infty}}{1 + \alpha \tau}$$

and the time constant becomes

$$\tau' = \frac{\tau}{1 + \alpha \tau}$$

Hence, the life behavior is determined in part by the measurement, both as to the asymptotic resistance and the time constant.

This example has been used to stress a point made earlier, namely, that life data must be interpreted in terms of how the life tests are conducted and how the status of the tubes during life is determined. While life-test data on tubes periodically subjected to a current in excess of the operating current are of interest, it is also of interest to have data in which excess current is not drawn.

Conclusion

The reducing agents included in the base metal of oxide cathodes lead to the formation of insulating layers at the interface between the base metal and the oxide. The layer which forms when silicon is one of the reducing agents exhibits a resistance which is apparent early in the life of a tube and seriously impairs its performance in the course of time. Life data on tubes in practical applications are presented. It is found that tubes with 0.01 per cent silicon in the base metal develop an interface resistance of about 50 ohms for a square centimeter of cathode area and that tubes with 0.15 - 0.25 per cent silicon in the base metal develop an interface resistance of about 1000 ohms for a square centimeter of cathode area. These values are reached in about 10,000 hours after which the values remain more or less constant. The data extend to 22,000 hours.

Exploratory studies of the physical phenomena which account for the complex behavior of the interface layer are described. These studies lead to no firm physical model. However, they suggest certain precautions to be observed in making measurements of interface resistance if consistent results are to be obtained. The most important of these precautions is that measurements of interface resistance should be made at the cathode current at which the tubes normally operate; otherwise, the measurement itself may obscure the effect of the previous experience of the tube.

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