Assessment and Control of Cathode Interface Impedance*

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PRESENTLY, almost all receiving-type electronic valves employ an oxide-coated cathode that consists basically of a nickel sleeve carrying a coating of alkaline-earth oxides. Between the sleeve and coating there exists an interface layer whose effect on the cathode performance is normally negligible during the first thousand hours of operation. The structure of the cathode is illustrated in Figure 1, with its equivalent electrical circuit.

In general, the coating behaves as an *n*-type semiconductor whose impurity centres are free metal ions caused by oxygen deficiencies in the lattice. It normally consists of an equimolar mixture of barium and strontium oxides with a little calcium oxide, which is activated by free barium ions. These are released in the coating through the action of reducing agents such as magnesium, silicon, and aluminium, which diffuse from the sleeve when the cathode temperature is raised to about 1300 degrees Kelvin during processing. A typical reaction with the coating is

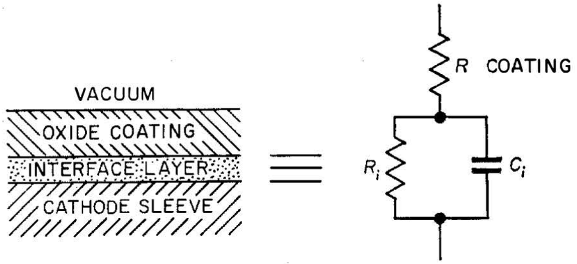

Figure 1—Structure and equivalent circuit of the oxide-coated cathode.

$$\mathrm{Si} + 4\mathrm{BaO} = \mathrm{Ba_2SiO_4} + 2\mathrm{Ba}. \tag{1}$$

This shows that barium orthosilicate is formed in addition to free barium, and this compound has been identified in the interface layer of cathodes based on sleeves containing silicon. Also free barium will be released both in the layer and in the coating. During the life of the cathode at a temperature normally between 1000 and 1100 degrees Kelvin, this reaction will proceed slowly until all the reducing agent is used up. At the same time barium will be lost by evaporation from the coating and replenished by diffusion from the interface layer. Eisenstein[1] has shown that barium orthosilicate is also an *n*-type semiconductor, so that as the excess barium content of the interface layer is reduced, its resistance will rise until it reaches a limiting value determined by its intrinsic resistivity. Values up to 1000 ohm–centimetres^{-2} of coating have been observed for British valves.

It is found that the rate of growth of the resistance is larger for higher cathode temperatures due to the higher rate of chemical action but is decreased when cathode current flows. This is probably due to the potential gradient between the cathode sleeve and the emitting surface, which opposes the flow of positively charged barium ions out of the interface layer. For this reason, computer valves that spend a large part of their lives in the quiescent state are particularly prone to the build-up of interface resistance.

As shown in Figure 1, the resistance is associated with capacitance in parallel so that to a first approximation the valve acquires a cathode time constant that may vary from about 5×10^{-7} to 5×10^{-6} second.

The value of interface resistance R_i is given by

$$R_i = \rho d/s, \tag{2}$$

where

ρ = resistivity of the interface layer at the operating temperature
d = thickness of the layer
s = coated area of the cathode.

Thus, miniature valves with small cathode areas will be particularly prone to deterioration through interface development.

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* Originally published under the title, "Computer Valves and Cathode Interface Impedance," in the *Journal of Electronics and Control*, First Series, volume 3, pages 107–125; July, 1957.

[1] A. Eisenstein, "Leaky-Condenser Oxide Cathode Interface," *Journal of Applied Physics*, volume 22, pages 138–148; February, 1951.

The effect of interface layers was first observed with cathodes from which pulse currents of high density were drawn. Under these conditions high potential gradients were produced across the layer, preventing the maximum current being drawn from the cathode and distorting the pulse shape. In extreme cases the Joule heating effect would cause sparking and damage to the cathode. The distortion that results from drawing current from a cathode with a high interface resistance is illustrated in Figure 2, where *B* is the current pulse from triode *2* of a high-slope double triode with a measured interface resistance of 630 ohms. This may be compared with Figure 2A, which is the pulse current from triode *1*, which although in the same valve, had no measurable interface resistance. The triodes were diode-connected in each case and the same pulse voltage applied. The rapid leading-edge decay and lower final current are evident for the triode with interface resistance. These effects are simulated in triode *1* by inserting a 600-ohm resistor in parallel with a 0·001-microfarad capacitor in the cathode lead, as illustrated in Figure 2C. This distortion will also occur if the valve is operated as a triode and a rectangular pulse signal is applied to the control grid, so that the output from a pulse amplifier will be seriously affected if any one of its valves has grown a high value of interface resistance.

Another effect of interface resistance is to place additional cathode bias on the valve. This will result in a fall of anode current, which may be serious when only a little bias is already employed, and also a lowering of the mutual conductance by negative feedback. The feedback will be frequency-dependent so that the effective mutual conductance is given by

$$g_m' = g_m/(1 + g_m R_i'), \qquad (3)$$

where

R_i' = real component of the interface impedance
g_m = mutual conductance when R_i is zero.

At frequencies above about 10 megacycles per second, $R_i' = 0$, so that $g_m' = g_m$, and below about 10 kilocycles per second, $R_i' = R_i$. As the frequency varies between these limits, so R_i varies from zero to R_i but it has been shown[2]

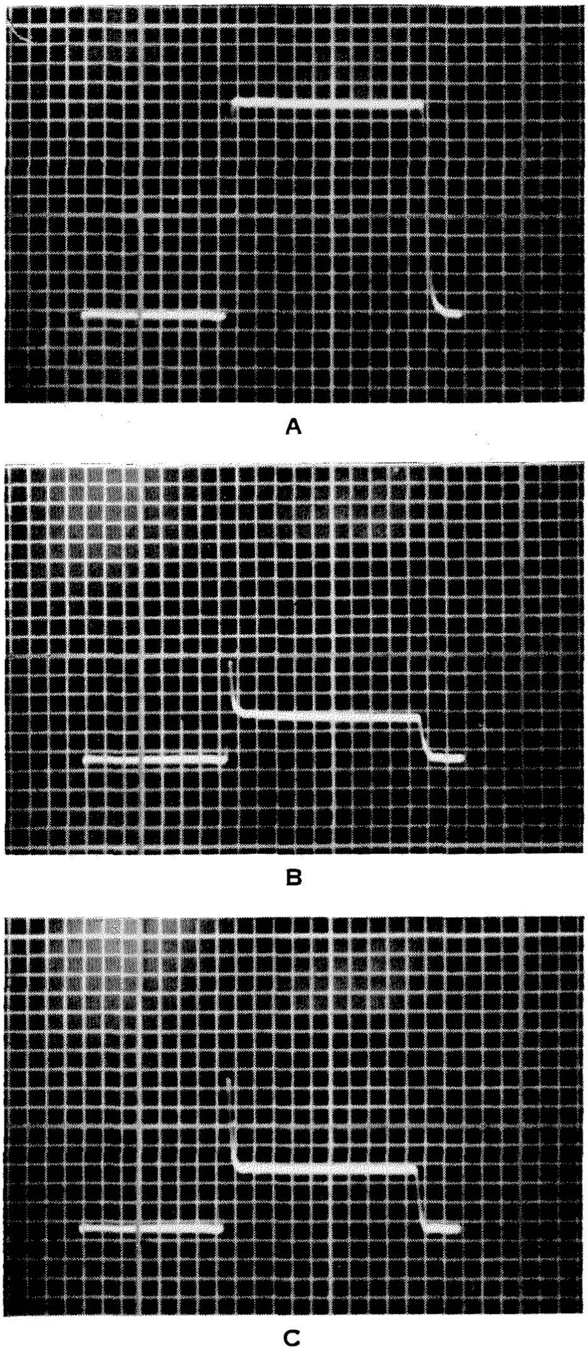

Figure 2—Cathode current waveforms for the two sections of the double triode for rectangular pulses of 10-microsecond duration repeated 50 times per second. *A* is for triode *1* having no interface impedance and producing a current of 68 milliamperes. *B* is for triode *2* and has a leading-edge current of 33 milliamperes and a trailing-edge current of 15 milliamperes. *C* is for triode *1* with 600 ohms in parallel with 0·001 microfarad in the cathode lead. The leading- and trailing-edge currents are 50 and 20 milliamperes respectively.

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[2] J. R. Tillman, J. Butterworth, and R. E. Warren, "Dependence of Mutual Conductance on Frequency of Aged Oxide-Cathode Valves and Its Influence on their Transient Response," *Proceedings of the Institution of Electrical Engineers*, volume 100, part 4, pages 8–15; October, 1953.

that a more-complicated resistance–capacitance network than the simple parallel combination of Figure 1 is required to explain the dependence of R_i' on frequency. However, this simple circuit is a useful approximation.

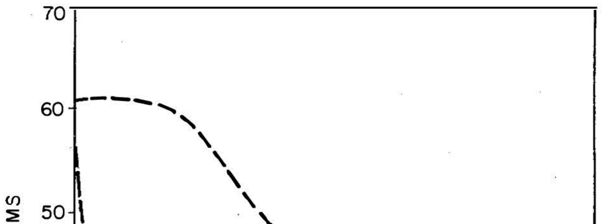

Figure 3—Values of interface resistance as a function of time. Direct-current measurements were made.

1. Some Properties of Interface Resistance

1.1 EFFECT OF CATHODE CURRENT

Figure 3 illustrates the effect on the interface resistance of six high-slope pentodes of passing a cathode current I_k of 7 milliamperes with a heater voltage V_h of 6·3 volts. The resistances were measured by the direct-current method described in a later section, where I_k = 7 milliamperes is needed to give the required mutual conductance for balance. The solid curves apply to three valves that had been run for 1000 hours with I_k = 12 milliamperes and V_h = 6·3 volts, while the dotted curves apply to three other valves that had been run for 1000 hours with I_k = 0 and V_h = 8·0 volts. It may be seen that the valves in which R_i had increased with current flowing showed little change during measurement, while those that had been run under zero-current conditions could show a marked fall in R_i during measurement. This behaviour is thought to be due to activation of the interface layer by barium ions diffusing back from the cathode coating.

1.2 EFFECT OF CATHODE TEMPERATURE

Since the interface layer is a semiconductor, its resistance should be strongly temperature dependent. The relation between R_i and V_h, which determines the cathode temperature, is illustrated in Figure 4 for the pentode and double-triode types mentioned above. Both groups had been run for about 6000 hours with I_k = 0, the triodes at V_h = 6·3 volts and the pentodes at V_h = 8·0 volts. The value of R_i is about doubled when V_h is lowered from 6·3 to 5·5 volts, while for a 10-per-cent variation of V_h about the rated value of 6·3 volts, there is approximately a 40-per-cent variation of R_i.

Metson[3] has published a curve relating the dependence of cathode temperature on heater voltage for a cathode of the pentode type and in Figure 5 the observed R_i values for four valves are plotted logarithmically against these temperature values. A straight-line relation is obtained, which tends to confirm the view that

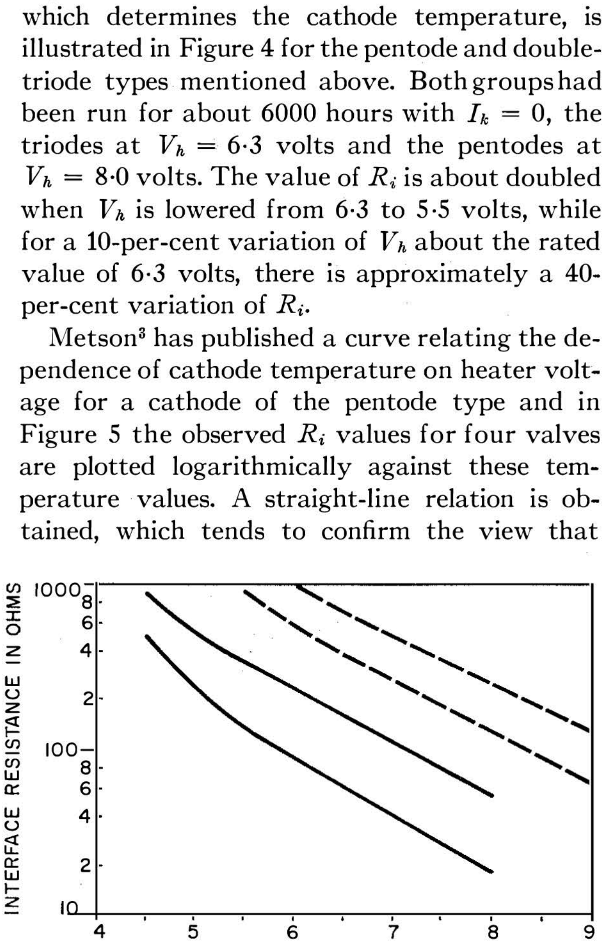

Figure 4—Interface resistance as a function of heater voltage. The two dashed curves are for two sections of a double triode and the two solid-line curves are for pentodes.

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[3] G. H. Metson, "Life of Oxide Cathodes in Modern Receiving Valves," British Post Office Research Report number *12 944;* 1951.

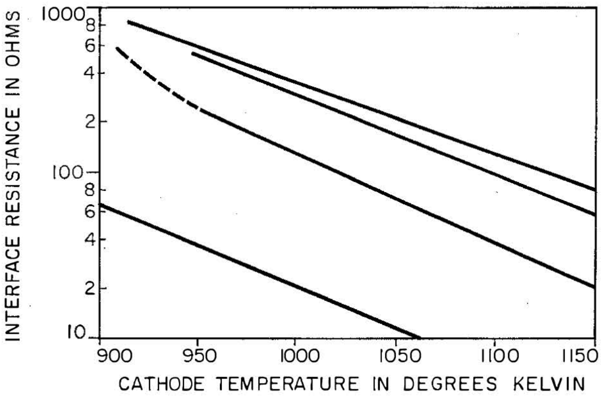

Figure 5—Interface resistance as a function of cathode temperature.

the interface layer is semiconducting. These measurements were made using a pulse method described later.

1.3 Effect of Running Conditions

Figure 6 shows the effect on the growth of R_i of running pentodes at normal cathode temperature with zero and normal cathode current, and also at increased cathode temperature and zero cathode current. The curves were plotted from points representing the mean of four values. At normal cathode temperature there is a small difference between the effect of zero and normal cathode current on R_i growth, but when the temperature is increased to about 1150 degrees Kelvin at $V_h = 8{\cdot}0$ volts, the rate of growth of R_i is greatly increased and the curve shows signs of saturation at 230 ohms and 4700 hours. As outlined above, the increase in resistance is thought to be due to the loss of barium ions from the interface layer; this process will occur more rapidly as cathode temperature is increased, but will be retarded as cathode current is increased. However, heat will be dissipated in the electrode collecting the current and some gas molecules will be liberated; as a result, gas ions will enter the cathode and combine with barium ions in the coating and interface layer so that the activating effect of the current will be counteracted. Hence, there may be only a small difference in the rate of growth of R_i between zero and normal-current life conditions at normal cathode temperature.

When all the barium ions have been removed from the interface layer due to diffusion into the coating and recombination with gas ions, the interface resistance should remain constant at its highest value unless cathode current causes it to fall. This state appears to have been reached on the valves run at $V_h = 8{\cdot}0$ volts and it is apparent that it will be many thousands of hours before it is reached at $V_h = 6{\cdot}3$ volts. For this reason, accelerated life tests at high cathode temperature are useful to indicate differences in the rate of R_i growth between different cathode materials, since the time required to reach a limiting value is short compared with tests at normal temperature.

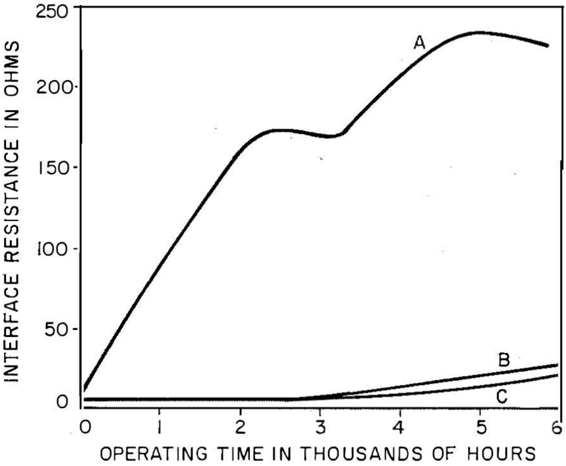

Figure 6—Dependence of interface growth on operating conditions of pentode. For A, $V_h = 8{\cdot}0$, cathode current $= 0$; for B, $V_h = 6{\cdot}3$, cathode current $= 0$; for C, $V_h = 6{\cdot}3$, cathode current $= 11$ milliamperes.

2. *Methods of Measuring Interface Resistance*

2.1 Direct-Current Methods

The two main effects described above provide two different methods of measuring interface resistance; namely, the dependence of mutual conductance on frequency and the distortion of a rectangular voltage pulse. Methods based on the reduction of mutual conductance have been described by Metson,[3,4] Eaglesfield,[5] and others

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[4] G. H. Metson, S. Wagener, M. F. Holmes, and M. R. Child, "Life of Oxide-Coated Cathodes in Modern Receiving Valves," *Proceedings of the Institution of Electrical Engineers*, volume 99, part 3, pages 69–81; March, 1952.

[5] C. C. Eaglesfield and P. E. Douglas, "Method of Measuring Interface Resistance and Capacitance of Oxide Cathodes," *British Journal of Applied Physics*, volume 2, pages 318–320; November, 1951.

and entail using the valve as an amplifier with a gain of less than unity, or as a cathode follower. These may be called direct-current methods since direct cathode current flows during measurement.

If the anode impedance of the valve is large compared with its load resistance R_L, then at a high frequency where R_i' is negligible, the gain is

$$S_1 = g_m R_L. \tag{4}$$

At a lower frequency where $R_i' = R_i$, the gain is

$$S_2 = g_m R_L / (1 + \alpha g_m R_i), \tag{5}$$

where $\alpha =$ (cathode current)/(anode current). If R_L is increased by resistance R_x so that $S_1 = S_2$,

$$\frac{g_m\,(R_L + R_x)}{1 + \alpha g_m R_i} = g_m R_L.$$

Hence

$$R_i = R_x / \alpha S_1. \tag{6}$$

The circuit used to measure the values of R_i is shown in Figure 7 for a triode ($\alpha = 1$). A known fraction $R_4/(R_3 + R_4)$ of the input signal is mixed with the output signal at P. When the two signals are equal in amplitude and exactly 180 degrees out of phase, a null signal is obtained at P, so that

$$S_1 = R_4/(R_3 + R_4) \tag{7}$$

and hence

$$R_i = R_x(R_3 + R_4)/R_4. \tag{8}$$

In practice, 10 megacycles per second is used as the high frequency and 1 kilocycle per second as the low frequency with separate amplifiers and detectors for each signal. The 10-megacycle-per-second amplifier is a conventional tuned-anode–tuned-grid type with a gain of about 700, feeding a valve voltmeter, while the 1 kilocycle-per-second amplifier is resistance–capacitance coupled with a gain of about 100 000, connected to a cathode-ray-type tuning indicator. Measurement of R_i is effected by adjusting the cathode bias rheostat R_k for null indication with the 10-megacycle-per-second input and with this setting of R_k, the decade box R_x is adjusted for a null with the 1-kilocycle-per-second input.

It is found on valves with very-low values of R_i that it is not possible to obtain a null at 1 kilocycle per second. This will occur when $S_1 \neq S_2$, for then

$$R_i = \frac{R_x}{S_2} + \frac{S_1 - S_2}{S_1 S_2} R_L$$

or

$$R_i = (R_x/S_2) + R_0 \tag{9}$$

so that a zero-error resistance R_0 is introduced. A difference between S_1 and S_2 will occur when the anode and grid signals are not exactly 180 degrees out of phase at each frequency. At 10 megacycles per second, this is due to the transit time of electrons from the control grid to the

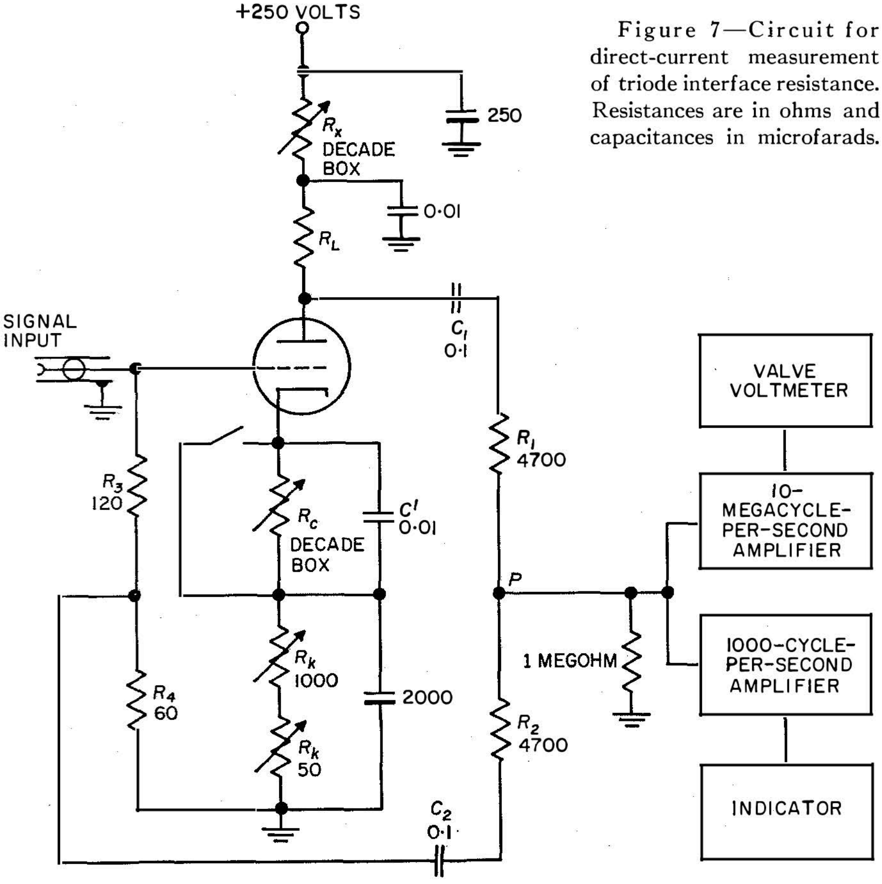

Figure 7—Circuit for direct-current measurement of triode interface resistance. Resistances are in ohms and capacitances in microfarads.

anode, distortion introduced by the valve, and valve and circuit stray capacitance. At 1 kilocycle per second, phase shift from 180 degrees is caused only by distortion of the input signal, which can be different from the 10-megacycle-per-second distortion since neither signal may be a true sine wave. The simplest way to determine R_0 is to calibrate the apparatus for each valve type to be measured by inserting an artificial interface impedance in the cathode lead. This is the decade box R_c by-passed by a 0·01-microfarad capacitor as shown in Figure 7. For a valve with low interface resistance, R_x' is determined for a range of values of R_c.

Then,

$$R_c + R_i = (R_x'/S_2) + R_0.$$

Subtracting from (9), where R_x is the reading for $R_c = 0$,

$$R_c = (R_x' - R_x)/S_2. \tag{10}$$

The graph of R_c against $R_x' - R_x$ is a graph of R_i against R_x and thus is the calibration curve. For the pentode and each half of the double triode, the curves correspond to:—

$$\text{Pentode } R_i = (3{\cdot}96/\alpha)\, R_x + 1 \tag{11}$$

$$\text{Triode } R_i = 2{\cdot}73\, R_x, \tag{12}$$

so that R_0 is 1 ohm for the pentode and zero ohms for the triode.

Apart from the constant zero error, the greatest source of inaccuracy arises from setting R_k to obtain a null signal at 10 megacycles per second since an appreciable rotation of R_k may produce no visible change on the detector. This results in an error in setting S_1 that corresponds to an error in the indicated values of R_i of ± 1 ohm for both valve types.

2.2 Pulse Methods

Methods based on the distortion of a rectangular pulse have been described by Waymouth,[6] Wagner,[7] and others where direct cathode current may or may not be drawn. Pulse methods can be applied to diodes as well as multi-electrode valves. For a diode (or a multi-electrode valve connected as a diode with the control grid as the anode) with a rectangular voltage pulse V developed across it, the instantaneous quantities are:

v = potential drop across interface impedance
i_c = current through C_i
i_r = current through R_i
i_k = total cathode current.

Then,

$$i_k = i_c + i_r$$

$$\frac{V - v}{r_D} = C_i\frac{dv}{dt} + \frac{v}{R_i},$$

where r_D is the diode impedance between cathode coating and anode. Hence it can be shown that

$$v = V\frac{R_i}{R_i + r_D}\left\{1 - \exp\left(-\frac{t}{RC}\right)\right\} \tag{13}$$

and

$$i_k = \frac{V}{r_D}\left[1 - \frac{R_i}{R_i + r_D}\left\{1 - \exp\left(-\frac{t}{RC}\right)\right\}\right], \tag{14}$$

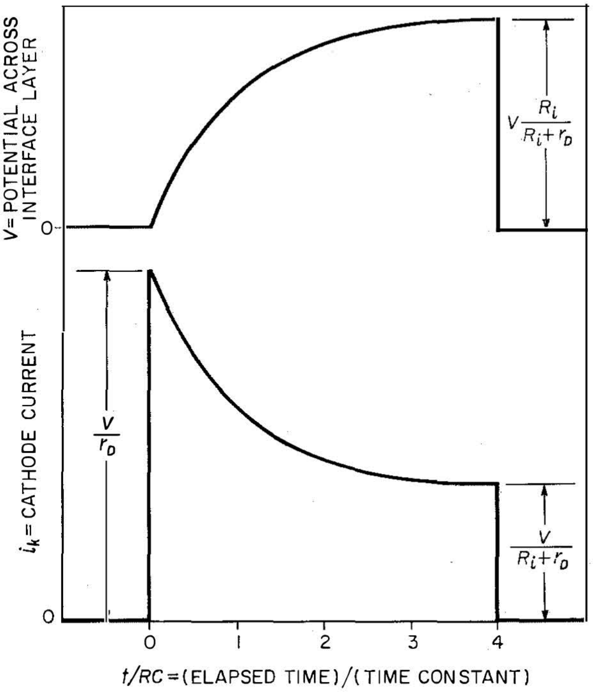

Figure 8—Theoretical curves of potential drop across an interface layer and cathode current of a diode with an interface layer as a function of t/RC.

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[6] J. F. Waymouth, Jr., "Deterioration of Oxide-Coated Cathodes Under Low Duty-Factor Operation," *Journal of Applied Physics*, volume 22, pages 80–86; January, 1951.

[7] H. M. Wagner, "Cathode Interface Impedance and its Measurement," *Proceedings of the National Electronics Conference*, volume 8, pages 553–561; 1952.

where

$$\frac{1}{RC} = \frac{1}{C_i}\left(\frac{1}{R_i}+\frac{1}{r_D}\right). \tag{15}$$

Curves of v and i_k against t/RC are shown in Figure 8. It may be noted that the resistance r_D, which includes cathode coating resistance, has the effect of reducing the time constant R_iC_i by appearing in parallel with R_i. Also, r_D will be constant throughout the pulse duration only if the difference between the leading and trailing edge currents is small since r_D is a function of diode current.

From (14) and Figure 8 it can be seen that the leading-edge pulse current is limited by the diode impedance r_D while the trailing-edge current is limited by $R_i + r_D$. These principles can be used to measure R_i by the simple circuit shown in Figure 9A. An adjustable calibrated resistance R_x is introduced in series with the test valve and i_k is observed on the oscilloscope when a rectangular voltage pulse is developed across the test circuit. If interface impedance is present, the i_k waveform will appear as in Figure 9B when R_x is zero. By increasing R_x, the new leading edge may be made the same height as the original trailing edge, so that $R_x = R_i$. A pulse duration sufficiently long to show the level part of the i_k waveform is required, so that the minimum time is about $4RC$. Values of R_iC_i have been observed in the range 5×10^{-7} to 5×10^{-6} second, so a pulse duration of from 2 to 20 microseconds is needed.

The sensitivity of this method is improved if the exponential part of the i_k waveform is studied alone and this can be done by cancelling the non-exponential part with an inverse rectangular waveform as illustrated in Figure 10. The resultant decay can then be amplified and observed alone; also, any decay due to droop of the applied voltage pulse is eliminated, so that a perfectly shaped pulse is not required.

The measurements described in the previous section were made in this way using the circuit shown in Figure 10. Here the rectangular voltage is developed across the valve diode in parallel with two adjustable resistances and, since the centre tap of the pulse-transformer primary winding is earthed, the difference between the two primary currents flows in the secondary winding and can be observed on an oscilloscope connected across it. In practice, R_1 is continuously adjustable from 0 to 1000 ohms and R_x is adjustable in decades 0 to 10, 0 to 100, and 0 to 1000 ohms. Both R_1 and R_x must be non-inductive or they will distort the fast-rising pulse leading edge. In a later development of this system, the currents in each arm are compared by a difference amplifier. With R_x = zero, R_1 is adjusted until the trailing edge of the secondary output is level with the main trace so that $R_1 = r_D$. R_x is then adjusted until the leading edge is level, when $R_x = R_i$.

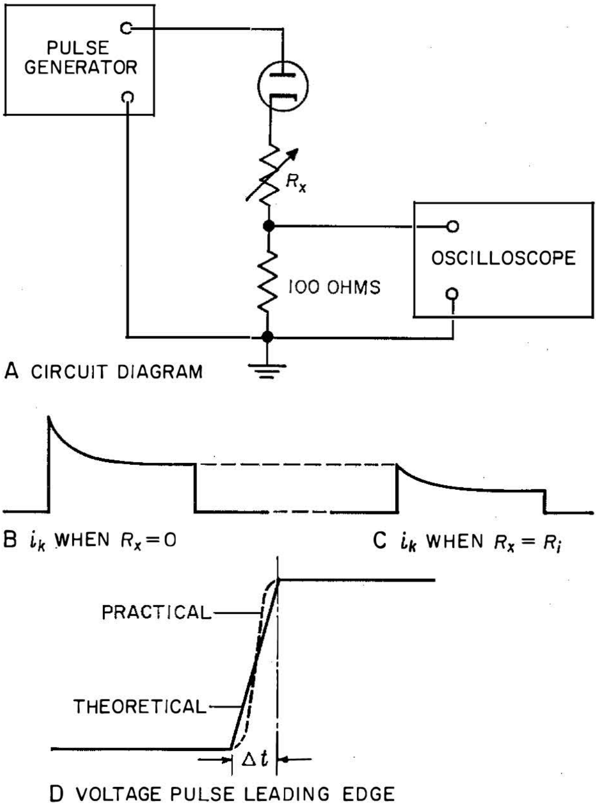


Figure 9—Circuit and cathode current waveforms for a simple pulse method of measuring interface resistance.

It has been assumed so far that the applied voltage pulse reaches its maximum value V in an infinitesimally short time. This is never true in practice and it may be assumed that the voltage increases linearly from zero so that at any time t after the beginning of the pulse, where $t = 0$, its height is given by $V' = at$. This means there will be a small voltage v_0 developed across the interface impedance in the time Δt that the pulse has taken to reach its maximum value (see Figure 9*D*); it may be shown that

$$v_0 = V\frac{R_i}{R_i + r_D}\left[1 - \frac{RC}{\Delta t}\left\{1 - \exp\left(-\frac{t}{RC}\right)\right\}\right], \tag{16}$$

where $VR_i/(R_i + r_D)$ is the potential drop across the interface at the end of the pulse and may be written as V_f. Hence

$$V_0/V_f = 1 - (RC/\Delta t)\{1 - \exp(-t/RC)\}. \tag{17}$$

If $\Delta t > 0{\cdot}1\ RC$, a fraction V_0/V_f of the final potential drop across the interface will occur at the beginning of the pulse, so that the indicated value R_x will be less than the true value R_i.

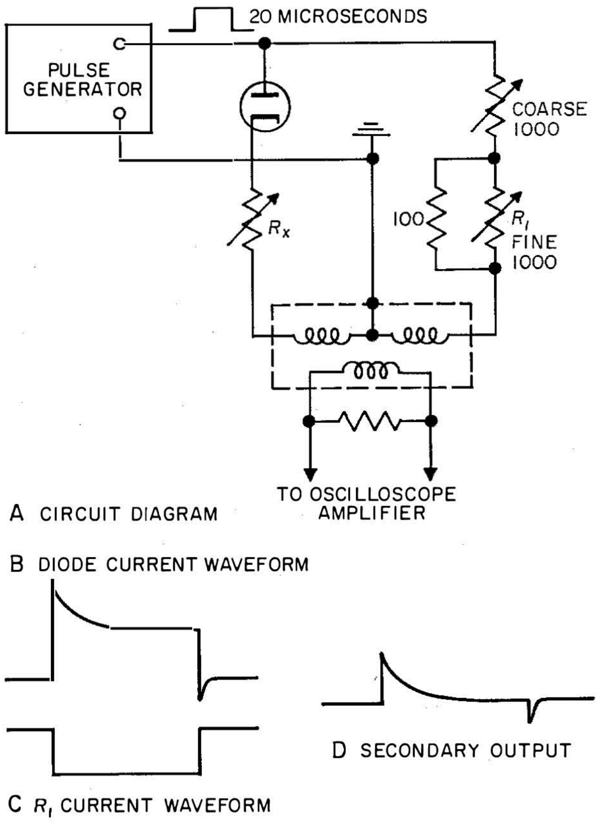
For a typical r_D value of 150 ohms, and allowing $R_x \nless 0{\cdot}9\ R_i$, the maximum allowable pulse rise time Δt when $RC = 10^{-7}$ second is $0{\cdot}05$ microsecond. As RC increases, the error in R_i will decrease for a fixed rise time. If Δt is small compared with RC, C_i can be deduced from the whole i_k waveform by

$$C_i = (i_1/i_2)(T/R_i), \tag{18}$$

where

i_1 = leading edge current
i_2 = trailing edge current
T = time for decay curve to discharge by 63 per cent.

The factor i_1/i_2 takes into account the shunting effect of r_D and any load resistors.



A CIRCUIT DIAGRAM

B DIODE CURRENT WAVEFORM

C R_I CURRENT WAVEFORM

D SECONDARY OUTPUT

Figure 10—Circuit and waveforms for measuring interface resistance using a pulse transformer.

2.3 COMPARISON OF DIRECT–CURRENT AND PULSE METHODS

The pulse method is capable of an accuracy similar to the direct-current method until the interface time constant becomes small enough to cause an error due to the pulse rise time. It has an advantage over the direct-current method in that no R_i change occurs during measurement due to the low duty factor of the cathode current. For a 20-microsecond pulse at 50 cycles per second, 50 milliamperes of pulse current is equivalent to 50 microamperes of direct current, compared with 7 milliamperes of cathode current flowing during measurement by the direct-current method. A further advantage is that all types of valve can be measured, while the direct-current method is only applicable to multigrid valves with a mutual conductance greater than about 2 milliamperes per volt. Also, the pulse method provides simple visual indication of interface presence and indicates deviations from the exponential decay curve. The main disadvantage is that a high-quality pulse generator and oscilloscope are required while the apparatus for the direct-current method is comparatively simple.

When valves operating under conditions known to cause growth of interface resistance are measured by pulsed and direct-current methods, it is found in general that the pulsed values are about 10-per-cent greater than the direct-current values, which may be explained by the activating effect of the direct current. It has been found that measurements made on some valves before operation or after a short period of operation under current-drawing conditions gave pulsed R_i values of several hundred ohms, but direct-current R_i values of only a few ohms. The time constant of these pulsed currents was much longer than would be expected from a cathode interface layer and the difference in observed R_i values can be explained by the existence on the control grid of an impedance of a similar nature to the cathode impedance but of longer time constant. This could be caused by a very-thin high-resistance film on the grid lateral wires and supports, or on the anode of a diode. Whenever pulsed grid current flows, its waveform shows a decay and when the pulse has finished, a negative charge will remain on the grid and can cut off the anode current until it has leaked off. Such effects limit the performance of pulse amplifiers and switching circuits and the phenomenon is still a subject of investigation.

TABLE 1

CATHODE SLEEVE COMPOSITIONS IN PERCENTAGE BY WEIGHT*

Element	Cathaloy *A-30*	Cathaloy *A-31*	Cathaloy *A-32*	*0* Nickel	*ST* Nickel
Aluminium	0·03–0·08	0·04	0·05–0·10	0·02	0·005
Carbon	0·03–0·10	0·03–0·10	0·03–0·10	0·04	0·08
Cobalt	0·40–0·60	0·40–0·60	0·40–0·60	0·90	0·10
Chromium	—	—	—	0·03	0·03
Copper	0·05	0·10	0·05	0·1	0·05
Iron	0·10	0·10	0·10	0·20	0·10
Magnesium	0·01–0·06	0·01–0·06	0·01–0·06	0·05–0·10	0·03–0·07
Maganese	0·05	0·05	0·05	0·05	0·05
Sulphur	0·005	0·005	0·005	0·005	0·005
Silicon	0·02	0·02–0·06	0·02	0·05	0·03
Titanium	0·01	0·02	0·01	0·02	0·005
Tungsten	—	3·75–4·25	2·0–2·50	—	3·50–4·25
Nickel	Balance	Balance	Balance	Balance	Balance

* Except where a range of percentages is given, all figures represent the maximum permissible content.

3. *Growth of Interface Resistance in Valves*

Double triodes are vital components in some computers and life tests have been run to simulate the electrical conditions of this form of operation. With regard to the cathode, these conditions are normal temperature and negligible direct current irrespective of the components associated with the valve, so that the valves were run with heater voltages only applied and all electrodes unconnected. A control experiment with electrode voltages applied to cut off the cathode current of one triode and with the electrodes of the other triode unconnected showed there was no significant difference in the rate of interface growth between the two conditions.

After more than 6000 hours of operation, two distinct classes appeared; triodes in which R_i did not exceed 9 ohms at any time and triodes in which this value was exceeded and R_i continued to rise for periods from 340 to 6300 hours. Values at the end of operation ranged from 32 to 342 ohms with the largest occurring in valves where R_i began to rise earliest and a good correlation existing between low values of cathode current and transconductance and high values of R_i. This erratic behaviour prevents any accurate prediction of R_i values during operation and so leads to uncertainty in estimating valve performance at any time.

4. *Effect of Cathode Sleeve*

All the valves mentioned so far used the *0*-nickel cathode sleeve that is standard throughout the British valve industry. During an investigation to evolve an oxide-coated cathode that does not suffer from interface growth and can still be employed in mass-produced valves, experiments were carried out using nickel sleeves with various constituents added. In particular, the American Cathaloy *A-30, A-31,* and *A-32* sleeves were compared with *ST* nickel, an alloy being developed in conjunction with the British Post Office, and *0* nickel. The compositions of these materials are given in Table 1, and it may be seen that Cathaloy *A-30* has aluminium and magnesium as its main active constituents; *A-31* has magnesium and tungsten; *A-32* has aluminium, magnesium, and tungsten; *ST* nickel has magnesium and tungsten; and *0* nickel has magnesium and silicon. The effect of these materials on R_i is illustrated in Figure 11, based on accelerated life tests run by the British Post Office. It is clear that the materials containing appreciable amounts of aluminium or silicon favour R_i growth, while *ST* nickel containing magnesium and tungsten only, shows no signs of R_i growth until after 15 000 hours of operation. Examination of these sleeves showed that the concentration of aluminium had increased during operation probably due to migration from the other parts of the valve. Research is being carried out on the elimination of the sources of this impurity and it is considered that, even at present, valves employing *ST* nickel should not develop interface resistance before 20 000 hours of operation at normal current.

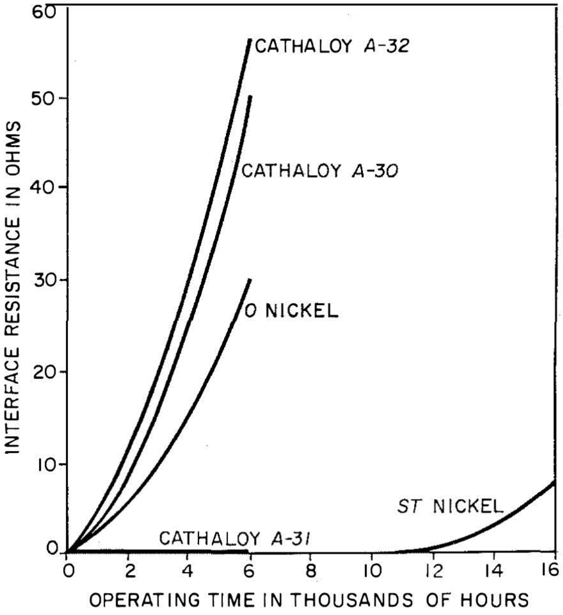


Figure 11—Accelerated life tests on pentode with various cathode sleeve materials. $V_h = 7{\cdot}0$, cathode current $= 0$.

The new alloy is being introduced in the manufacture of special-quality valves at the Brimar factory at Footscray and its effect on the maintenance of mutual conductance is shown in Figure 12 for double triodes. As expected, the improvement during zero-current operation is even more pronounced than during normal operation.

5. *Discussion of Results*

If the silicon content of the cathode sleeve is kept low, this in itself discourages the formation of a barium orthosilicate layer, but Rittner[8] has suggested the following explanation of the beneficial effects of tungsten in reducing interface growth. While the cathode coating is being broken down during exhaust, the following reaction proceeds quickly:—

$$3BaCO_3 + W = Ba_3WO_6 + 3CO \qquad (19)$$

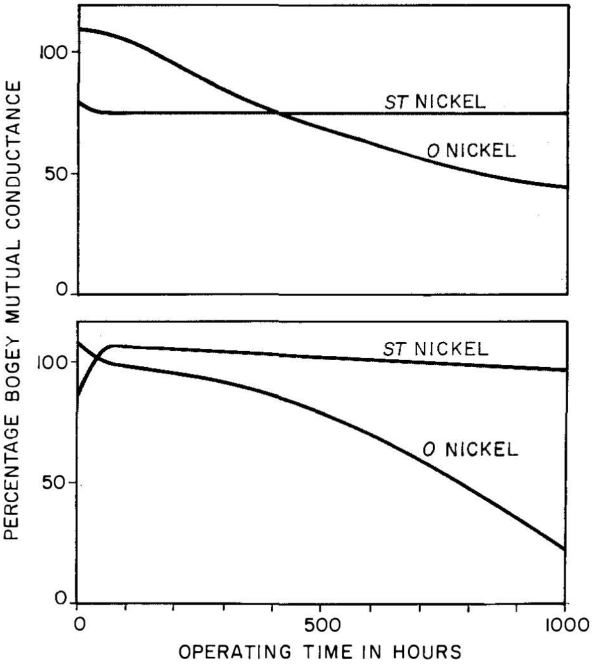


Figure 12—Comparison between effect of *0* nickel and *ST* nickel on mutual conductance in double triodes. Top graph for normal operation and bottom graph for operation with zero cathode current.

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[8] E. S. Rittner, "Theoretical Study of Chemistry of Oxide Cathode," *Philips Research Reports*, volume 8, pages 184–238; June, 1953.

and any good reducing agent, A, such as magnesium or silicon, will react to form free barium thus,

$$Ba_3WO_6 + 6A = 6AO + W + 3Ba. \quad (20)$$

In this way free barium is formed by reaction with the layer itself so that a very-long time is required to deactivate it and cause interface resistance to rise. Furthermore, if silicon is present, it will react with the barium tungstate layer to form free barium rather than with the coating to form barium orthosilicate.

Previous reports have suggested that aluminium inhibits interface growth, but this has been proved untrue under production conditions. It seems that aluminium is as harmful as silicon in promoting interface growth and for this reason aluminum content in *ST* nickel is kept as low as possible. Magnesium is included since its presence does not annul the beneficial effects of tungsten and it is necessary as a reducing agent to ensure adequate electron emission from the cathode coating. The magnesium content is not more than that of *0* nickel, since any further increase results in the formation of low-resistance films on the valve insulators causing undesirable leakage and noise effects.

6. *Conclusion*

Although British valves suffer less from the growth of cathode interface resistance than other valves employing cathode sleeves with a higher silicon and aluminium content, the unpredictable nature of interface growth makes desirable its elimination. It is considered that good progress on a production scale has been made with the introduction of *ST* nickel and further progress is being made in overcoming manufacturing difficulties caused by removing reducing agents from the cathode sleeve. It is therefore expected that the complete range of Brimar special-quality valves will employ interface-free cathodes in the near future, with a consequent improvement in stability of characteristics and pulse performance.

7. *Acknowledgment*

Acknowledgment is made to the British Admiralty for permission to make use of the information contained in this paper.