Cathode/heater-insulation failure in oxide-cathode valves

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Synopsis

Heater/cathode insulation in indirectly heated valves, is considered as a two-part phenomenon: the comparatively slow deterioration during operational conditions followed by a rapid thermal breakdown, which is caused directly by the sudden passage of a large current between heater and cathode.

Examination of heater/cathode failures in valves tested under rigidly controlled conditions has indicated some of the laws governing the deterioration of the insulation. The effects of various parameters such as temperature of operation, thickness of insulation and applied potential have been studied, and comparisons have also been made for different heater and cathode materials.

The experimental evidence is discussed in an attempt to explain the failure mechanism involved, and the conclusion that electrolysis is the principal factor is supported by the results of a number of experiments carried out with specially designed electrode structures.

1 Introduction

The modern indirectly heated radio valve is subject to few types of catastrophic failure on life, and these are usually readily explicable in terms of some mechanical defect, or, as with broken heaters, in terms of inferior or badly processed materials. A most important exception to this generality is the particular defect commonly known as cathode/heater breakdown, a phenomenon which occurs when the valve is operated on life with a voltage applied in either direction between heater and cathode, and takes the form of an effective short circuit between these components.

Although the existence of this defect has been known for many years,[1] it was not until the investigations of Metson and his coworkers[2,3] that any detailed study of it was published. However, neither these publications, nor the papers[4,5,6,7] which have since appeared, contain all the systematic information required by the engineer who is attempting to improve the reliability of the valve or the user who wishes to know the life expectancy of the valve under particular circuit conditions. To provide such information has been one of the purposes of the present investigation, which has thus been concerned largely with tests of the conventional cathode/heater system run under conditions not too remote from normal operation. It is, presumably, for this reason that some of the results to be reported differ from those of Metson *et al.*,[2] and of Veith and Kallweit,[7] whose interest in establishing the mechanism of the defect involved experiments with laboratory models under conditions remote from those appertaining in practice.

What the valve engineer commonly describes as cathode/heater breakdown is a two-stage process. The first stage is the slow degradation of the insulation, a process which may occupy a few minutes or more usually many hours; the second stage is the thermal breakdown of the remaining insulation, a process which usually occurs in a fraction of a second. To prevent confusion, we prefer to call the whole sequence cathode/heater failure. It is the slow degradation of the insulation with which this paper is mainly concerned, and the investigation of the influence of various operational conditions, as well as the study of a number of physical-chemical properties of the component materials in the cathode/heater system, has led to a better understanding of the nature of the underlying mechanism.

Paper 4796 E, first received 15th August 1964 and in final form 27th April 1965

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2 Experimental procedure

2.1 General considerations

Often, in normal use, the impedance of the external circuit in which the voltage between heater and cathode is produced is very low. In such circumstances, if breakdown occurs, it is catastrophic and either the valve or the external circuit or both are presumably damaged. However, if the valve is left operating in a circuit containing a resistance to limit the short-circuit current, as has been the case during the tests carried out for this investigation, then, after breakdown occurs, the valve often recovers. The interval between failure and recovery has been found to be anything from several hours down to a lower limit which has not been determined but is thought to be a fraction of a second. After the initial failure, the valve usually recovers and breaks down repeatedly at irregular intervals. From the observation of the occurrence of failures lasting only a fraction of a second it seems possible that such a failure could occur in a circuit with very low limiting impedance, resulting only in the probable injection of a pulse into the signal path, the cause of which is never detected.

These circumstances make difficult the formulation of a working definition of cathode/heater failure. It was found expedient to consider the end of the life of the insulation as the first time at which a current of at least 1 mA passed in the circuit in which the maximum current was limited to about 20 (say 10–30) mA. The value of 1 mA was chosen since it was well above the largest steady leakage current ever observed and, at the same time, was sufficiently below the short-circuit current to ensure that the voltage across the insulation had not dropped substantially on account of the limiting resistance before the indication of failure was obtained. Recordings showed that failures of very short duration were fortunately most prolific just prior to a failure lasting for appreciable time so that it would be registered by the testing equipment. Thus the errors due to missing the former were not great, and exact control of the time for which the current of 1 mA flowed in order to operate the failure indicator was unnecessary. The suitability of the definition was indicated by the fact that no significant difference was obtained in the mean life times of the two halves of a batch of valves, one half being tested according to this definition and the other half using the rupturing of a 25mA fuse in the cathode/heater circuit as the failure indicator.

2.2 Standardised test valve

In order mainly to carry out comparative tests, a standardised test valve was used. This had a heater designed for operation at 6·3V and approximately 3W and consisted of a tungsten helix bent so as to form two limbs, the wire being 100μm in diameter and wound on a 200μm diameter mandrel at a pitch of 130μm (77 turns per cm length). The cathode tube was cylindrical, 23mm long and 1·35mm internal diameter, and was usually used without an external emissive coating. Except in some special cases, the assembly was suitably mounted in a subminiature glass envelope. This valve type was chosen since it was simple in construction and small—an advantage when testing in batches—yet contained a heater/cathode system of convenient size. The components for the valves were processed and the valves pumped and assembled under laboratory conditions.

The valves were tested in batches on equipment which automatically and continuously recorded the state of the insulation of each valve. Except where these parameters were the subject of a particular test, the heater voltage was set at 8·0V and the heater–cathode voltage when the heater was positive (the polarity under which most of the tests were carried out) was maintained at 200V. The voltage stress was thus a little higher than the recommended maximum for valves with this type of cathode construction, and the temperature of the heater wire was higher than normal. These overrun conditions were found to give suitable failure times in most cases, and yet were not too far removed from the normal operating conditions.

2.3 Statistical life-time distribution

At the outset, it was necessary to determine the form of the distribution of lives in a batch of valves, firstly, in order to find a suitable parameter representative of the behaviour of the batch and, secondly, to obtain a means of estimating the significance of differences between the results of different batches. For this purpose, a Weibull analysis[8] was found useful and indicated that the distribution of life times was more complex than had been suggested in previous work. In the main, the distribution had a log-normal character representing a deterioration process taking place in the insulation during life. However, there were superimposed small but significant Gaussian distributions associated with the very early and very late failures. These latter components were more in evidence when the applied breakdown stress was high. Nevertheless, for most investigational purposes it was sufficient to describe the behaviour of a batch of valves in terms of a characteristic life time (the halflife of the batch) and the standard deviation of the common logarithm of the life time. The life time of 100 valves plotted on a log-normal grid are shown in Fig. 1. These were standard test valves run at a mean heater temperature of 1250°C, the heaters being maintained at 200V positive with respect to the cathodes.

The Gaussian part of the distribution assumes more importance when a valve maker is attempting to control a small percentage of early failures. It would seem that judgment of the expected performance of a production batch should be based on a test carried out on an adequate scale under operating conditions as near as is practicable to those at which the valve is required to work normally. Misleading results may be obtained if the test is made under overrun conditions, when the distribution laws governing the life times may be different from normal. It may be of value to record that some results suggest that the random element is reduced when the characteristic life of the batch is increased, for instance, by lowering the operating temperature and also when the standard deviation is reduced by careful control of the consistency of components.

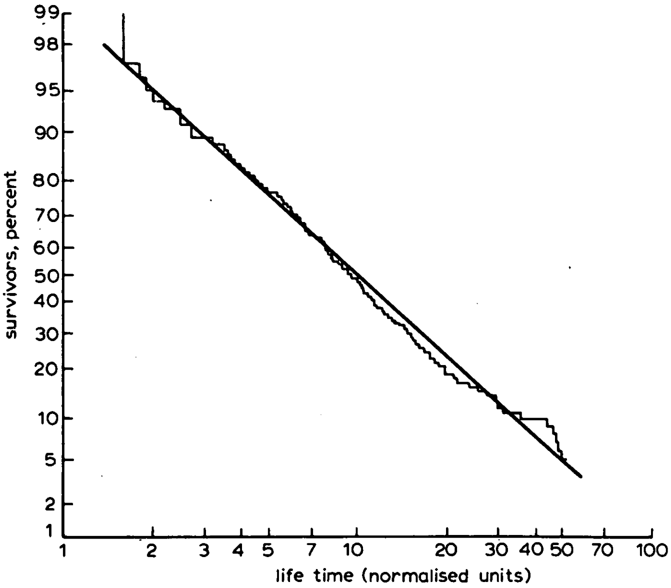

Fig. 1
Log-normal plot of life-time distribution

3 Influence of applied voltage

3.1 Direct voltage

The effect of variations in the voltage applied between heater and cathode in both the heater positive and heater negative direction was determined. Standard test valves were used at a constant heater voltage of 8·0V on the nominal 6·3V heater, the range of heater–cathode voltages used being controlled by suitability of the resultant life times for measurement. Batches of at least 12 valves were used for each value of voltage, and the individual results were plotted on log-normal paper in order to obtain the characteristic life times. These are quoted in the results which are plotted in Figs. 2 and 3.

In both cases, the results appear to follow the relationship

$$t \propto \frac{1}{V^b} \quad \text{where } t = \text{characteristic life time}$$
$$V = \text{applied heater to cathode voltage}$$
$$b = \text{constant}$$

The value of b was different for the two polarities of the applied voltages. Tests over the range 100–250V with heater positive gave $b = 3$, and, with heater negative over the range 250–450V, $b = 2$ was obtained.

A comparison of the two polarities of operation shows that, with the standard test valve, 450V with the heater negative gave approximately the same life time as 200V with the heater positive.

3.2 Alternating voltage

Experience had shown that the electrostatic forces set up between heater and cathode by voltages of the order used in failure tests could cause movement of the heater, particularly if this showed some mechanical resonance at the appropriate frequency. In order to eliminate the effect of any such vibration from the results, three tests were made. In the first, pure alternating voltage was applied between heater and cathode; in the second, unidirectional varying voltage of

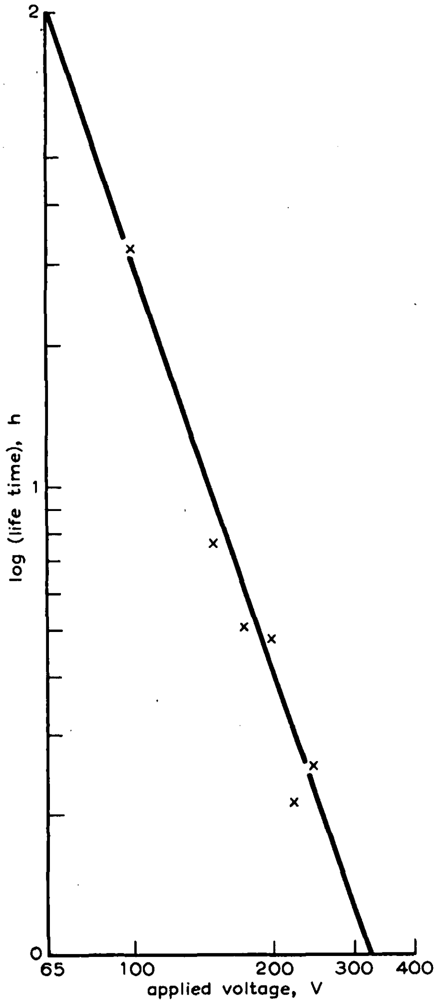

Fig. 2
Effect of applied voltage (heater positive)

approximately the same peak value, the heater being positive; in the third test, steady direct voltage of the same average value as that in the second test. The frequency was 1000c/s, and the heaters, in all tests, were operated at the standard overrun temperature. The results were as follows:

Heater/cathode voltage	Life time
200Vr.m.s. a.c.	>400h
100Vr.m.s. a.c. + 150V d.c.	38h
150V d.c.	25h

The similarity in the last two results shows the vibration effect to be negligible, and therefore the greatly increased life time obtained with alternating voltage must be attributed to an electrical effect.

3.3 Intermittent operation

Two batches of valves were run, one with a continuously applied voltage, the other operated so that the heater/cathode voltage was applied for a period of only 1·6min in every 18min by means of a mechanical switch. During the time when the voltage was not applied, the external cathode/heater circuit was open. Under otherwise standard test conditions, the characteristic lives were

Continuously applied voltage	4·7h
Intermittent voltage	50h

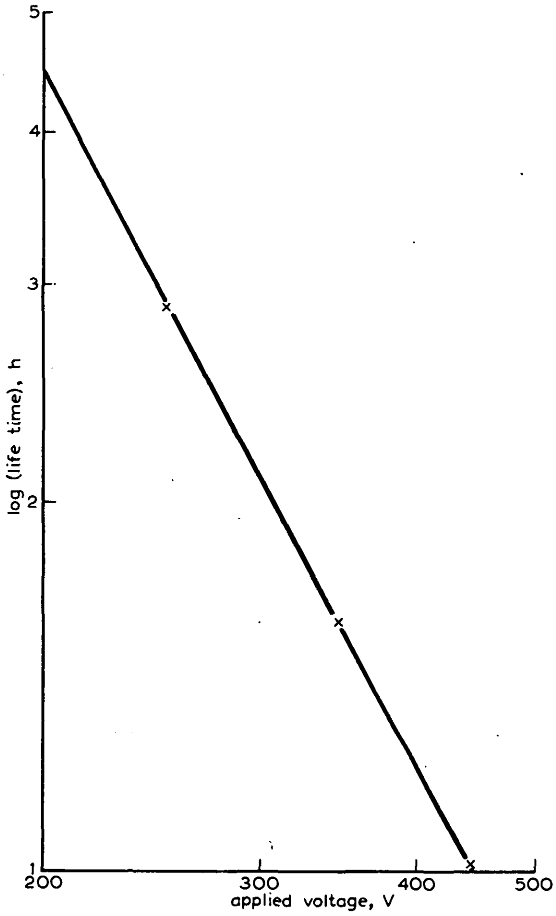

Fig. 3
Effect of applied voltage (heater negative)

Since the duty cycle of the intermittent operation was about 9%, the lives were the same in terms of total time of applied voltage, indicating that insulation deterioration occurs only during application of the applied voltage and is unaffected by the periods in between. This is contrary to the behaviour of the leakage current, which measured on one valve showed a steady fall during each 1·6min period but recovered during each rest period.

4 Influence of temperature

In considering the effect of temperature, it must be remembered that the cathode/heater system is not all at one uniform temperature. In a system of normal design, there is a considerable difference between the mean temperature of the cathode surface and that of the heater wire and, moreover, some difference between various points on both surfaces. The insulating coating has a temperature between the two and, in general, will have some thermal gradients both through its thickness and along its length. Consideration of the thermal conductivity of alumina showed that the temperature drop across the insulation of the standard test valve under overrun conditions would be 5–10degC, and that the bulk of the temperature difference found between heater wire and cathode surface could be accounted for by radiation from the heater coating surface to the cathode tube. The temperature of the insulating coating would be substantially the same as that of the heater wire. There were thus two distinct temperature regions: the cathode and the coated heater. In determining the effect of temperature on life, the two regions were considered separately.

4.1 Influence of the cathode temperature

In order to investigate the effect of the cathode temperature, as distinct from the heater temperature, it was necessary to be able to vary the two independently whilst keeping the internal cathode/heater structure constant. In one experiment, this was achieved to a limited extent by blackening the outside of some of the cathode tubes, thus increasing their radiating efficiency and causing them to operate at a lower temperature than normal for the same heater temperature. The cathode temperatures were measured by optical means, the otherwise unblackened tubes having small blackened spots on which to sight the pyrometer.

Table 1

RESULTS OF THREE LIFE TESTS UNDER DIFFERING CONDITIONS IN THE HEATER-POSITIVE OPERATION

Cathode type	Heater temperature	Cathode temperature	Characteristic life time
	degC	degC	h
Bright . .	1230	940	5
Black . .	1230	700	8
Black . .	1360	800	<0·1

The first two results taken together show that there is no significant difference in the life times for a difference of 240degC in cathode temperature. Unfortunately, the blackening was so effective that it was not possible by this method to carry out the complementary comparison of differing heater temperatures at the same cathode temperature. However, the third intermediate set of conditions shows the comparatively enormous effect on life time produced by changing the heater temperature.

In further experiments, the nickel cathode tube was replaced by a spiral wire of similar dimensions. This could be adjusted to a wide variety of temperatures by passing a heating current, and also different materials could easily be used for this electrode. The results obtained under some particular conditions are given in Table 2.

Table 2

EFFECT OF VARYING HEATING CURRENT AND MATERIALS

Heater temperature	Spiral temperature	Spiral material	Characteristic life time
degC	degC		h
1300	1300	tungsten	$5\frac{1}{2}$
1300	670	tungsten	>300
1300	670	nickel	75

These results show, in the case of a tungsten outer electrode, a substantial change in characteristic life brought about by a 600degC change in temperature. Thus the effect of temperature of the outer electrode on life time is a function of the material of this electrode. Comparing the result for nickel with that for tungsten under the same conditions, it can be seen that, in the case of the former metal, the life is shorter. The rate of evaporation of material from nickel would be greater than from tungsten at the same temperature, and it may be, therefore, that the effect of the cathode temperature on life is operative in controlling the rate of production of impurities which contaminate the insulating coating.

4.2 Effect of heater temperature

The temperature of the heater was determined by the only suitable method: that of measuring the resistance of the heater wire. This involved a considerable amount of calibration and also devising a means of checking the resistance/temperature relationship, which was found to vary, not only from one sample of tungsten to another, but also for a particular valve heater during life. The temperature obtained was an average over the temperature gradient in the heater. For coated heaters without the surrounding cathode, it was found that this value was 15–50degC below the true temperature of the hottest part; in the complete system the discrepancy would be a little less. It is in the hottest part that the majority of breakdowns occur; thus it must be accepted that the relevant temperature is measured on a slightly arbitrary scale.

Since the cathode temperature had so little influence compared with the heater temperature in the normal system, the effect of the latter was investigated by operating test batches at various heater voltages and relating the life times obtained to the corresponding measured temperatures. The results of such tests, carried out with heater positive, are plotted in Fig. 4 and conform to the formula

$$1/t = A \exp(-B/T)$$

where T = absolute temperature

A, B = constants

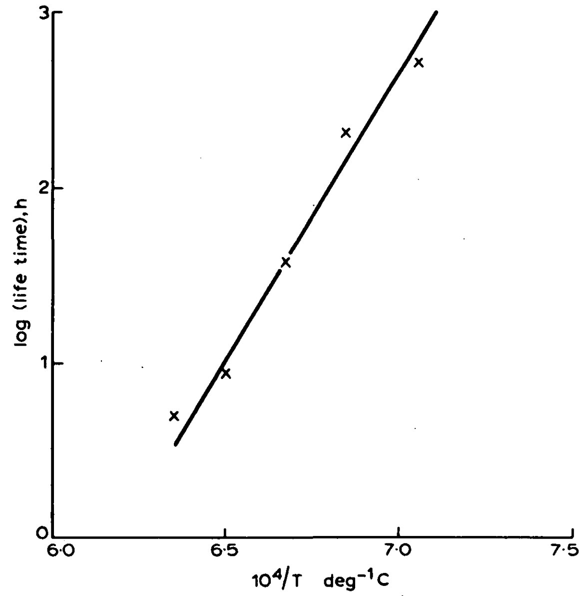

Fig. 4

Effect of temperature on life time

$1/t$ is a measure of the rate of deterioration of the alumina, and hence B represents the activation energy of the process causing it. The experimental results yield a value of 3·3eV for this.

The significance of this relationship can be realised from the fact that in the normal-operating-temperature region an increase in heater temperature of 50degC will decrease the life by a factor of about 10.

Considering the varations that occur among the individual valves in a batch, if the temperatures follow a normal distribution, then the life times will have a log-normal distribution as a consequence. By differentiating the relationship between life time and temperature, the relationship between the standard deviations of the log of the characteristic time and the temperature is obtained:

$$\sigma_T = \frac{T^2}{3 \cdot 33 \times 10^4} \sigma_L$$

where σ_T = standard deviation of temperature

σ_L = standard deviation of log of characteristic time

For the overrun-test conditions, this reduces to

$$\sigma_T = 47\sigma_L$$

Thus a standard deviation of the log of the life time of 0·4, a common value, could be accounted for entirely by a distribution of operating temperatures having a standard deviation of 19 degC.

An experiment was carried out in which a batch of standard valves was operated on life with the heater temperature for each valve kept constant within ±2 degC by controlling the hot resistance. Under these conditions, the standard deviation of the logarithm of the life time was reduced from 0·4 to 0·17, confirming that much of the spread of the life times was due to variation in operating temperature between individual valves.

Variations in operating temperature can be caused in a number of ways. Of these, in a batch of standard test valves a maximum divergence of 6 degC was traced to variations in cold resistance of the heater and a maximum divergence of 24 degC to variations in temperature coefficient of resistance. Batches of typical production valves showed a measured standard deviation of the running temperature of 17 degC.

During life, it has been found that there is a decrease in running temperature of a valve. The rate of decrease is more rapid at the start, but over the course of several thousand hours it can amount to well over 100 degC. This is far more than can be accounted for by the measured changes in cold resistance and temperature coefficient. It is thought to be due to increase in the efficiency of heat transfer through the valve caused by deposition of evaporated dark material on various surfaces, particularly those within the cathode. Such effects would also occur under normal running conditions, but, at a slower rate, the maximum drop in temperature attained depending on the original efficiency of heat transfer. The effect may well account for the divergence from the log-normal distribution law associated with the valves having the longest lives of the batch.

5 Influence of coating variations

5.1 Coating thickness

One of the factors which one might reasonably expect to have a direct bearing on the life time is the thickness of the insulating coating. In practice, it has been observed that the cataphoretically coated insulations had sensibly uniform thickness throughout about 85% of the length of the heater, although the radial uniformity is less certain. The thickness measurements were therefore made by microscopic examination in the direction in which the heater coatings would touch the cathode tubes, i.e. in the directions in which breakdown would occur. Many measurements were taken in order to get good average values, and the method, although tedious, permitted due allowance to be made for any abnormalities in the coating.

A series of heaters of differing coating thicknesses was obtained by varying the cataphoretic-coating time and then processing under otherwise constant conditions. The characteristic life time for each thickness was then determined.

From Fig. 5, it can be seen that, over the range studied (10–80 μm), the results take the form

$$\log t = dD - c$$

where D = coating thickness

c, d = constants.

This equation has been confirmed in numerous subsequent experiments in which, although c varied, d remained constant at 0·040.

From a practical point of view, the result means that an extra, say, 10 μm of coating thickness will prolong the life by

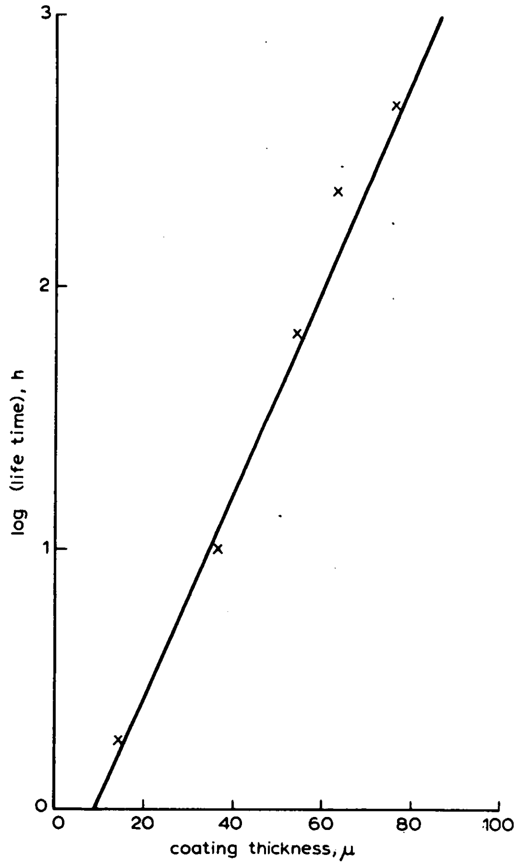

Fig. 5
Effect of coating thickness on life time

a factor of $2\frac{1}{2}$ times, whatever the starting thickness, provided this is above a certain minimum.

The corresponding relationship between the standard deviations is given by

$$\sigma_D = \frac{\sigma_L}{d}$$

i.e. $\sigma_D = 25\sigma_L$

Typical factory-coated heaters have shown standard deviations of 4–5 μm, which could therefore produce a standard deviation of the log of the characteristic life time of 0·2.

The logarithmic nature of the effect of both temperature and thickness variations on life time agrees with the logarithmic distribution of life times within a batch which was found, and indeed the total variance of the distribution is well accounted for by the measured variances of these two parameters.

5.2 Other coating variations

A preliminary test showed that sintering the coated heaters before assembly at 1750°C instead of the usual 1600°C reduced the failure life; this confirmed the trend found by Metson, Rickard and Hewlett.[2] A full-scale test with temperatures ranging from 1500 to 1750°C showed an optimum for cathode/heater life at about 1650°C.

Another set of experiments was carried out with heaters coated with alumina of different particle size—one batch less than 5μm and the other a coarse fraction greater than 15μm. Thickness of coating was also varied systematically in this test, and, while cathode/heater life varied with coating thickness as expected, the fine material consistently gave insulation lives of about one-tenth those of normal heaters, while the coarse material was not significantly different from normal.

Since it is at the contact points between heater and cathode that signs of eventual breakdown are observed, the effect of varying the fit of the coated heaters in cathode sleeves was tested. Valves were made using coated heaters from the same batch but with two different sizes of cylindrical cathodes of the same chemical composition (1·1mm and 1·4mm diameter). The characteristic life time of the batch with the bigger cathodes was seven times greater than the normal. This gain should be compared with the very much larger gain which could have been achieved if a thicker coating had been used. Obviously it is preferable to use the thickest coating compatible with no damage during assembly.

Most of the heater coatings were formed from 900-mesh Alundum. During processing, the impurity content was reduced considerably, the major impurities being then Na_2O and SiO_2 at about 0·01%. A batch of very pure alumina was made, with SiO_2 content at 0·002% and Na_2O at 0·01%, and heaters coated and compared with normal heaters. The insulation life of the heaters with pure alumina coatings was not significantly different from that of coatings of similar thickness prepared from the Alundum.

A series of experiments were also carried out in which the coating was applied in different ways. While no marked improvements in life were obtained by variations in the electrophoretic-coating technique (including anaphoresis), significantly better results than normal were had by using a 5% silica 95% alumina mixture. Melting the coating surface of the heaters before assembly gave a small improvement, but flame spraying the tungsten helixes with alumina gave a markedly longer life.

6 Heater and cathode materials

As far as the normal tungsten heaters are concerned, the only variation likely to be met with in practice is in the surface purity—in particular, the surface may be oxidised to some extent before the alumina is applied. In order to test the effect of this, a batch of valves was made up with heaters which had been anodically oxidised for 1 min in 10% nitric acid. These valves were operated heater positive and gave a characteristic life time of only 5% of that of the normal heaters given identical treatment, apart from the oxidation. This finding is in agreement with Jaccodine,[6] whose observations on the deleterious effect of a source of oxygen within the valve have also been confirmed.

A number of other metals have been used in place of tungsten, the most successful of which was a platinum/15% iridium alloy, which gave an eight-fold improvement over tungsten operated to give the same cathode temperature conditions. Other platinum alloys gave only marginal improvements, as also did rhenium and a 50 : 50 rhenium/molybdenum alloy.

A wide range of cathode–nickel alloys were tested, and it was clear that the magnesium content of the nickel has an important influence on the life of cathode/heater systems operated in the heater-negative condition—the life time improving with increase in magnesium content of the cathode nickel. This is probably due to the fact that, of all the activators concerned here, magnesium has the highest diffusion rate and is the most powerful reducing agent. Hence magnesium oxide could well be produced at the inner surface of the cathode, providing an excellent insulating film at the lower temperature of the cathode. This would retard the deterioration of the insulation, as does the well known process of deliberate internal coating of the cathode with a thin alumina layer.

7 Experiments to determine the mechanism

7.1 Observed effects of failure

If valves are run under test conditions in which the short-circuit current is limited so that catastropic destruction of the heater/cathode system does not take place on breakdown and the heaters from these valves are subsequently examined, then characteristic staining and other abnormalities in the heater coating are observed, particularly along the lines at which the coating touched the inside of the cathode tube. In the case where the heater is positive during operation, black lustrous pits are observed in the coating at sites where breakdown has occurred. The pit may be surrounded by a grey ring, from which it is often separated by an unstained ring. Greying may occur, generally over the insulation surface away from breakdown spots, and often tiny pinpoint black spots are seen without corresponding grey surrounding patches.

After heater-negative operation, the insulation surface is not so dark, and white excrescences, which have a puffed-up appearance, are seen at the breakdown sites. These white areas contain green crystals.

Analysis showed that in the heater-positive case the grey areas contained tungsten metal, whilst γ-alumina, i.e. the low-temperature form, was found on the inner cathode surface. The green crystals contained nickel, probably in the form of nickel aluminate.

7.2 Experiments on stain growth

In order to follow continuously the effects of the degeneration of the insulation and the simultaneous development of stain material during operation, a number of experiments were carried out, many with ceramic tubes made of alumina of the same high purity as the normal coatings but sintered at a much higher temperature in the absence of the heater wire.

In one illuminating experiment two wires, one of tungsten and the other of nickel, to simulate the heater and cathode of a normal valve, were wrapped closely together around a thick ceramic tube which contained a separate heater inside. With the tube hot and on applying a voltage between the two wires, the subsequent deterioration of the insulation took place primarily along its surface and could be continuously observed. With the nickel wire positive, a dark ring, followed by a continuous white area, spread from two points under the nickel wire, presumably where there was good contact with the alumina, and expanded uniformly in all directions. These areas were actually whiter than the bulk of the alumina. The ceramic in the region of the nickel contact became puffed-up and was subsequently found to be very soft and porous. In the centre of the area under the nickel wire, green crystals were found. With the tungsten wire positive, a white area again developed from the positive wire, followed, this time, by a black stain. In neither case was an experiment continued to breakdown. In all cases, the stains spread uniformly, irrespective of the electric field, and, in some cases, extended beyond the limits of the electrode system.

In another experiment, two alumina tubes of triangular cross-section were mounted in close contact with each other along one face, each tube containing a separate single wire electrode. Such an assembly was operated with one tube at 1300°C (brightness temperature) and the other at 1000°C and with 300V between the wires. Fig. 6 shows a photograph of a section of the hotter tube after operation; this tube also contained the positive electrode. The electrode wire was bent at the level shown in the section and was touching the inside of the bore. The other tube was touching this along the face closest to the wire, and the wire can be seen embedded in the side of the bore. The stain extended to a fairly well defined limit inside the two free sides of the tube, presumably at a line where the alumina temperature was too low to allow rapid diffusion. In the third side, the stain spread out completely to the edge and could be seen on the face of the tube.

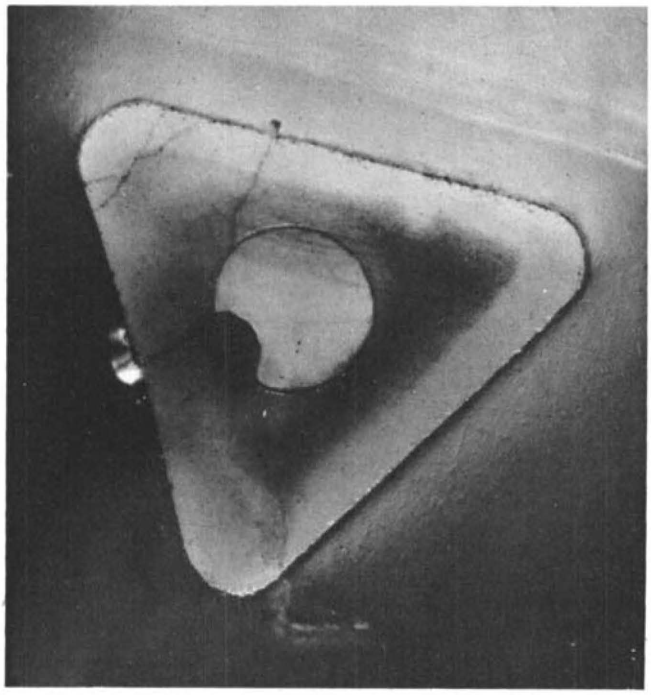

Fig. 6
Section of alumina tube showing stain growth after operation in contact along one face with a similar tube

Further experiments in which the deteriorating field was through the alumina confirmed that the stains originated from the positive electrode and indicated that the disposition of the staining material was influenced by temperature gradients rather than by electric fields, suggesting that it spread by a process of diffusion. Such experiments were also carried out with normal cataphoretically produced coatings, with the same results.

7.3 Development of conducting path

Of more importance, perhaps, is the development of electrical conductivity of the insulation during life. Experiments using probes in ceramic material indicated that initially, with a uniform temperature system, there is an enhanced potential gradient near the positive electrode, whatever the material of the electrodes.

In one set of experiments, a system was used which consisted of an inner tungsten coil which was cataphoretically coated with a platinum probe wire buried in the coating and an outer spiral wire surrounding the coating and bonded to it by the application of more cataphoretic coating, the whole being finally sintered together. The inner and outer spirals could be heated independently by passing currents through them and also a voltage could be applied between them, the probe wire being connected to an electrometer to which a pen recorder was attached. The circuit was so arranged that, whenever breakdown occurred so that the system was conducting and all three wires were at substantially the same voltage, the recorder indicated 50% deflection. Zero and full scale on the recorder indicated the probe at the voltage of the inner and outer wire, respectively.

The system was heated by passing currents through the spirals to a suitable temperature, and a voltage was applied between the inner and outer spirals. It was found that in all cases the probe voltage drifted towards that of the positive electrode during operation, and, in no case, was the voltage of the negative electrode attained before breakdown occurred. When recovery occurred after breakdown, the probe might be left at the voltage of either the positive or negative electrode.

These results indicate that, as in the case of the stains, conducting material also originates from the positive electrode.

An interesting result arose in an experiment using a double-bore ceramic tube. Each bore contained a tungsten spiral, and, by means of these, the tube was heated to the normal operating temperature of a valve heater. At the same time a voltage was applied between the two wires so that a small current passed between them through the ceramic. The material of the tube was rather impure alumina containing much more sodium (0·3%) than normal heater coating material. After a short time of operation, a deposit of sodium metal was formed on the glass bulb, the deposition of which could be started or stopped by turning on or off the current between the two spirals, thus indicating the possibility of electrolysis of alumina material.

8 Conduction processes in the system

8.1 Electron emission

In a typical valve, such as our test valve, if the heaters were not coated with alumina, the temperature-limited electron emission of the tungsten at the normal operating temperature could be of the order of 10^{-7}A (assuming a work function of 4·5eV for tungsten); the corresponding electron emission from a pure nickel surface operating at the much lower temperature would be of the order of 10^{-15}A. The presence of the alumina coating on the tungsten would tend to reduce the possible electron emission to even lower levels. The higher work function of the nickel surface may be considerably reduced if contaminating deposits are allowed to form on it. With lock-seamed cathodes, for example, there is this danger, and, if material from the external coating is present inside the cathode/heater system, considerable electron currents can arise.

It has been suggested[2, 3] that one of the main causes of cathode/heater insulation failure is, either directly or indirectly, electron bombardment. If so, since it is well established that insulation failure occurs more readily with heater-positive operation, it follows that the inner surface of the cathode would be the most probable source of the electron emission. Except in an experiment where the interior of the cathode was known to be contaminated with emissive material from the exterior cathode coating, no evidence of electron currents has been observed. A powerful argument against electron bombardment of the alumina arises from a consideration of the location of the insulation breakdown sites. These always occur at points of contact between cathode and alumina, and at these points the potential gradients are such as to favour electron-bombardment effects from the heater rather than the cathode.

Electrical currents can also arise owing to the formation of conduction paths across the micas and glass insulation between heater and cathode leads. This could result from evaporation from the cathode, getter or other electrode, processed at high temperatures, or may be due to bombardment of electrodes by ions or electrons during normal operation. Some of the early tests, carried out with cathode–nickel alloys of high magnesium content and processed at higher than usual temperatures, resulted in early failures due to the evaporation of magnesium.

8.2 Positive ion currents

Even below normal operating temperatures, positive-ion emission is detectable from the heater and the cathode if alkaline contamination is present in the system. This is normally the case unless special processing of the materials and of the cathode/heater system has been carried out to eliminate the last traces of alkaline impurities. If alternating voltages appear between cathode and heater—and this is inevitable if an alternating current is used for the heater supply—asymmetrical currents can arise in the system owing to the effect of positive-ion movements superimposed on the normal reactive currents between cathode and heater. These currents are responsible for the well known 'hum' effect in preamplifier valves. Such ion currents usually decrease with time of operation as the alkaline contamination effuses from the cathode/heater system. Careful tests, designed to show any correlation between the magnitude of the measured ionic leakage currents and the failure life, have invariably shown negative results. Furthermore, the general decrease in positive-ion currents which occurs with operation was never reflected in any corresponding decrease in failure rate in later life in batch tests.

8.3 Electrolysis

Direct currents via the alumina coating are also more than a possibility. Although an excellent insulating material in its pure state, alumina at the high operating temperatures will allow some current to flow and traces of impurities can increase this conduction, so that it would appear possible that the cumulative effects of this process, if electrolytic in nature, could cause deterioration of the insulation. Any diffusion or chemical reactions which alter the insulating material with time could also accelerate this process. A number of experimental observations have revealed strong evidence of an electrolytic process governing the life of the insulation. They are summarised as follows:

(*a*) The growth of an oxidised form of nickel, presumably as a result of anodic oxidation, is often to be seen at points corresponding to places of contact between the nickel tube and the alumina. The compound is clearly distinguished by its green colour, and the presence of nickel aluminate has been established by X ray-diffraction examination.
(*b*) The growth of stained material at the positive electrode, in the case of positive heater operation, is usually seen when the alumina coating is removed from the tungsten heater operated in this way.
(*c*) Prebreakdown stains in high-alumina ceramic tubes used as cathode/heater insulators have also shown the progress of stain growth from the positive electrode.
(*d*) Direct evidence of electrolysis was provided by experiments in which the insulator material was known to be rather impure. During these experiments, metallic sodium was evolved from the alumina but only while the cathode/heater voltage was applied; as soon as the latter was removed, the evolution of the alkali metal ceased.

9 Conclusions

The statistical examination of heater/cathode insulation failures has shown that it follows a log-normal probability distribution with time, and only a small percentage occur prematurely in a random manner. Other minor features of the distribution of life times have little practical significance and can be explained in terms of physical changes in the valves and in their operating conditions.

So far as the effects of different operating conditions are concerned, quantitative relationships have been established between heater/cathode insulation life and a number of parameters such as the heater temperature, the applied cathode/heater potential and its polarity. The temperature of the alumina during normal operation is essentially the same as that of the heater, and this has a powerful influence on the insulation life. Undoubtedly, a considerable improvement in life could be obtained by improving the thermal efficiency of the system, particularly by blackening the heater. The cathode temperature, on the other hand, is without detectable effect on the insulation life.

The relationship between insulation life and the various parameters concerned with manufacturing methods and materials has also been established. While the insulation life is an exponential function of the coating thickness, no marked improvement can be had by practical variations in the method of cataphoretic coating. The particle size of the alumina, the sintering temperature and the degree of contact between heater and cathode all have small, though real, effects on the insulation life. The use of platinum alloys instead of tungsten for the heater can be advantageous if the system is operated with heater positive, while the magnesium content of the cathode alloy is important with the system operated with heater negative. Purer alumina than that used commercially gives no gain, though the addition of a few percent silica can yield a substantial benefit. Oxidation of the tungsten, during manufacture or in operation, can lead to a serious reduction in insulation life.

The explanation which has been offered deals effectively with almost all the experimental observations and results: based on electrolysis, it contains a number of features of earlier ideas. Its confirmation must await the outcome of fundamental investigations on electrode processes with solid electrolytes, but since it is in accord with all the established facts concerning cathode/heater insulation failure under practical operating conditions, it provides an adequate working hypothesis.

10 Acknowledgments

The authors are grateful to the directors of the Mullard Radio Valve Co. for permission to publish this work.

11 References

1 BENJAMIN, M., COSGROVE, C. W., and WARREN, G. W.: 'Modern receiving valves; design and manufacture', *Proc. IEE*, 1937, **80**, p. 401
2 METSON, G. H., RICKARD, E. F., and HEWLETT, F. M.: 'Some experiments on the breakdown of heater–cathode insulation in oxide-cathode receiving valves', *ibid.*, 1955, **102 B**, p. 678
3 METSON, G. H.: 'On the electrical life of an oxide-cathode receiving tube', *Advanc. Electron.*, 1956, **8**, p. 403
4 RODENHUIS, K., SANTING, H., and VAN TOL, H. J. M.: 'Reliability of commercial amplifying valves', *Philips Tech. Rev.*, 1956, **18**, p. 181
5 JACCODINE, R. J.: 'Heater-cathode breakdown', *J. Electrochem. Soc.*, 1959, **106**, p. 530
6 JACCODINE, R. J.: 'Nodule growth on Al_2O_3 coatings', *ibid.*, 1960, **107**, p. 62
7 VEITH, K., and KALLWEIT, H.: 'Contribution on the problem of electrical breakdown between heater filaments and cathode sleeves of indirectly heated oxide cathodes', *Elektron. Physik*, 1961, **4**, p. 135
8 WEIBULL, W.: 'Statistical distribution function of wide applicability', *J. Appl. Mech.*, 1951, **18**, p. 293