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# THE OXIDE-COATED CATHODE

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MANUFACTURE



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## PREFACE

### VOLUME ONE

ALTHOUGH oxide-coated cathodes are used in the hundreds of millions of electronic valves that are manufactured every year, a comprehensive review of these cathodes is lacking. Realizing this we started work on this book as early as 1938 and tried to collect all existing information on both the manufacturing processes and physical behaviour of oxide cathodes. The work was greatly impeded during the war and only in 1944 was it possible to publish a first edition in German. Since then we have continued to incorporate new achievements in manufacture and the many new lines of scientific investigation which have been taken up. We are now pleased to present the first English edition of this work.

A review of the oxide cathode is complicated by the close interdependence between manufacture on the one hand and scientific investigation on the other. Many of the measures taken during manufacture can only be understood by virtue of their effect on the physical mechanism, whilst investigation of the physical phenomena must be based on a thorough knowledge of how to make a good cathode. If this latter point is not taken into account, phenomena may be investigated which are certainly interesting but of little importance for the cathodes which are actually used in commercial valves. For this reason the manufacture of the cathode has been dealt with first and forms the subject matter of the present volume. It is followed by a review of the physical phenomena in Vol. II.

The treatment is opened by an historical review of the oxide cathode and by a discussion of the different types and their applications. This introduction is followed by a description of the manufacturing processes and of the cathode characteristics. The volume is concluded with a description of some special types of cathodes, for instance, those in gas discharge tubes.

For the description of the manufacture a large number of patents had to be consulted, but only those patents are mentioned which either have found a wide application in commercial practice or which contribute to the understanding of manufacturing processes. The value of a patent should not, however, be inferred from its inclusion or exclusion.

## PREFACE

The present volume can be read independently, but frequent references to the second volume have been made which may be used for studying further details.

Much of the material presented here has been supplied by the firms Telefunken G.m.b.H., Allgemeine Elektrizitätsgesellschaft and Osram G.m.b.H. in Berlin, and the authors are much indebted to these firms, in particular to Dir. Dr. W. Statz and Dir. Dr. E. Wiegand. The translator wishes to express his appreciation to Dr. G. H. Metson who first suggested the translation of this book and to Mr. D. A. Wright of the G.E.C. Research Laboratories, Wembley, Miss C. M. Lovett, Mr. M. F. Holmes, Mr. R. W. Lawson and Mr. F. H. Reynolds, of the G.P.O. Research Station, Dollis Hill, who assisted in converting the translation into smooth English.

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## CHAPTER 1

### INTRODUCTION

#### 1. History of the Oxide Cathode

The phenomenon of electron emission from hot bodies was explained by Richardson at the turn of the century. His publications and all other early work, however, were only concerned with metals as electron emitters. In 1903 Wehnelt<sup>1, 2, 3</sup> investigated the phenomenon using a platinum wire emitter for decreasing the cathode fall of a gas discharge. An accidental observation made with this cathode was the starting point for discovering a new, better type of emitter, called the oxide-coated cathode.

Wehnelt observed that bright blue cathode rays were emitted from some areas of the platinum wire at low temperatures of 800 to 1000° C. and at low anode voltages of 10 to 100 volts. Owing to the low temperature of these areas, the cathode rays could not be due to the platinum itself. Wehnelt therefore explained the effect by assuming the existence of impurities at the appropriate areas of the platinum. He assumed that these impurities were metal oxides which originated from the grease used for the stopcocks of the pump. In pursuance of this theory Wehnelt undertook a detailed examination of various metallic oxides and found that the oxides of the alkaline earth metals in particular gave a considerable electron emission. The cathode consisting of metal oxides, now known as the oxide-coated cathode, or more shortly oxide cathode, was the direct outcome of these experiments.

Wehnelt soon found that Richardson's emission equation for metals was also valid for the electron current emitted by an oxide cathode. His collaborator Jentsch<sup>1</sup> ascertained the value of the work function, appropriate to Richardson's equation, for various metal oxides. While the values obtained for these work functions are no longer valid for modern commercial oxide cathodes, a theoretical note by Jentsch in the same paper corresponds very well with our modern ideas of the mechanism of the oxide cathode. Jentsch points out that a work function for the electrons emitted from an oxide cathode not only exists at the boundary between the metal oxide and the vacuum, as is the case with metals, but that a

work function may also be necessary in the interior of the metal oxide. This opinion of Jentzsch, the correctness of which may be emphasized here, was inspired by investigations of Koenigsberger<sup>1</sup> into the electrical conduction of chemical compounds.

The measurements of Wehnelt and of Jentzsch were not carried out under the best vacuum conditions. Soddy<sup>1</sup> employed all the means then known for producing a high vacuum, such as coconut charcoal cooled by liquid air and a calcium getter. He found that his oxide cathodes ceased to emit in such a high vacuum. This result is not, however, surprising to us, for neither the space charge laws nor the activation process of the oxide cathode were known at that time. Probably the emission was completely suppressed by an unfavourable configuration of cathode and anode in Soddy's experimental valve, and an activation of his oxide cathode was therefore not possible.

After these first publications Fredenhagen<sup>1, 2</sup> during the years 1912 to 1914 published another concept of the mechanism of the oxide cathode. He observed reactions between the oxide coating and the core metal occurring during the operation of the cathode. Furthermore, he found that the emission of the oxide cathode was influenced by gases (e.g. oxygen) and that his oxide coating was gradually consumed by these gases. Fredenhagen supplied an explanation for these phenomena from the results of Haber and Just,<sup>1</sup> according to which electrons of low velocities are emitted during the reaction between alkali metals and gases or vapours. Thus Fredenhagen assumed that part of the oxide decomposes during the operation of the cathode and that electrons are emitted when the products of the decomposition reunite. Similar results were obtained by Gehrts,<sup>1</sup> based on observations during the manufacture and the operation of battery-charging rectifiers containing oxide cathodes. It is noteworthy that both Fredenhagen and Gehrts considered the decomposition of the alkaline earth oxide to be necessary for the electron emission. Although this idea is superseded as a result of evidence obtained later, it first called attention to the fact that the electron emitter is not the pure alkaline earth oxide, but that part of the oxide must be decomposed in order to make emission possible.

Wehnelt<sup>4</sup> was the first to suggest the use of oxide cathodes in rectifier valves, especially in rectifiers\* for charging batteries. Of the first amplifier valves only those made by Lieben, which were

\* German Patent 157845.

filled with gas, were supplied with oxide cathodes. The high-vacuum valves made by de Forest were built with metal cathodes, because the oxide cathode at that time did not seem to be suitable for employment in a high vacuum. There were several reasons for this belief, one of them being the instability of the oxide cathode, which was mainly due to the insufficiently developed state of vacuum technique. Furthermore, due to the assumption of a decomposition of the oxide, there was a fear that oxide cathodes in operation would always give off gases and that such cathodes could therefore not be employed without interfering with the high vacuum. Lastly, Soddy's results mentioned above may have contributed to the popularity of tungsten and tungsten-thorium cathodes as opposed to oxide cathodes.

Progress in both the physics and manufacture of oxide cathodes was only made possible by improvements in vacuum technique, and especially by the introduction of diffusion pumps. The first investigation of oxide cathodes utilizing a diffusion pump was carried out by Germershausen,<sup>1, 2</sup> who also specified other conditions for reaching a high vacuum, such as avoiding greased ground joints, employing a liquid air-trap, baking the experimental valve, and heating the metal components. Germershausen proved by these means that some of the phenomena observed by Fredenhagen and Gehrts were mainly caused by an insufficiently high vacuum and that the electron emission of an oxide cathode is therefore not due to the continuous progress of a chemical process.

The first large-scale use of oxide cathodes in high-vacuum valves was made possible by advances in vacuum technique in the U.S.A. during the first world war. According to Arnold<sup>1</sup> half a million such valves were made before the end of the war, but these valves were far less consistent than those containing metal cathodes. The first oxide cathode valves were mostly used in stationary amplifiers for wire telephony both in the U.S.A. and later in England and Germany. As these amplifiers were to be operated for many hours without attention, the valves were required to have a low heater power and a long life with adequate amplification. Such requirements could only be adequately satisfied by an oxide cathode (cf. Gruschke and Pohlmann,<sup>1</sup> Nebel<sup>1</sup>).

A thorough investigation of the physical processes in the oxide cathode began about 1920. The works of Koller,<sup>1</sup> Espe,<sup>1</sup> Rothe,<sup>1</sup> Becker,<sup>1</sup> and Gehrts<sup>2</sup> proved that the emission of the cathode is due to the existence of excess metal in the oxide. It was shown by

various experiments that this excess metal is produced during the cathode activation process.

Espe, Rothe, and Detels<sup>1</sup> assumed the existence of the so-called barium islands on the surface of the cathode. According to this theory the oxide coating is activated by an electrolytic process during which oxygen escapes into the vacuum while barium accumulates at the surface of the coating in small emitting islands. These islands grow, until an equilibrium between the formation of barium and its evaporation from the surface is reached. The barium islands were assumed to possess the low work function of the metallic barium, which was assumed equal to the work function of the oxide cathode. The electron emission of the oxide cathode would then be identical with the purely metallic emission of the barium islands and the oxide coating would only supply the barium necessary for replacing losses by evaporation or oxidation. The following objections may be raised, however, against equating the emission from the activated oxide with that from the metallic barium:

- (a) The work function of the oxide cathode is still much lower than that of pure barium (2.52 eV). These two work functions, of course, were not known with sufficient accuracy at that time.
- (b) As the vapour pressure of barium in bulk is  $3 \times 10^{-2}$  mm. Hg (cf. Vol. II, Fig. 82) at the operating temperature of the oxide cathode (1000° K.), islands consisting of barium in bulk cannot exist on the surface of the oxide coating at this temperature.

These difficulties in the theory are removed, however, by assuming the existence of a monatomic barium layer instead of the barium islands at the surface of the cathode. Such a monatomic layer, called a barium film, would decrease the work function of the pure alkaline earth oxide and would thus produce the good emission of the oxide cathode. Such a layer can also exist at higher temperatures, as the rate of evaporation from these monatomic layers is considerably smaller than that from the same metals in bulk. This concept was developed during investigations by Koller<sup>1</sup> and Becker,<sup>1</sup> which will be discussed in detail in Vol. II.

Lowry,<sup>1</sup> when examining the influence of the metallic core of the oxide cathode, suggested that the electrons emerge from a barium layer on the core metal, the oxide coating being only a store for the

supply of barium. This concept was refuted by experiments of Becker and Sears,<sup>2</sup> who showed that by dropping the oxide coating from the core the emission current was decreased to 1/600 of its previous value. They also used a cathode whose coating contained an embedded probe, the surface area of this probe being one-third of the area of the core metal. The circuit used for the emission measurement was connected either to the core metal in the normal way or to the embedded probe or to both together. It was shown that the emission current obtained from the coating was exactly the same in all three cases and therefore independent of the surface area of the total core used. These results could not be explained if the emission of the oxide cathode originated from a layer on the core metal.

In spite of these contradictory explanations the commercial application of oxide cathodes spread rapidly. This success was mainly due to the introduction of getters and to the use of alkaline earth carbonates as a material for preparing the oxide coating.

From 1930 onward two lines of investigation may be identified. One line followed by de Boer is related to the properties of composite photo-electric cathodes, an example of which is caesium oxide with caesium atoms absorbed at its surface. The photo-electric behaviour of such a cathode is explained by the ionization of these Cs-atoms. De Boer assumed that the thermionic emission of the alkaline earth oxide could be explained in a similar manner by a thermal ionization of barium atoms adsorbed at the surface of the oxide coating.

Further research, however, showed that the processes in the interior of the oxide coating are as important as the processes at the surface and that there is a close relationship between the emission and the electric conductivity of the coating (Reimann and collaborators,<sup>1, 2</sup> Becker and Sears,<sup>2</sup> Meyer and Schmidt,<sup>1</sup> Gehrts,<sup>3</sup> Benjamin and Rooksby,<sup>1, 2, 3</sup> Schottky,<sup>1</sup> Heinze and Wagener<sup>1, 2</sup>). Reimann and his collaborators, who first found that emission and conductivity increase together during the activation process, developed a theory which also considered the core metal as the real source of the emission. Although the experiments of Becker and Sears refuted this theory, they did not diminish the importance of Reimann's experiments, which first established that the interior of the coating plays a definite part in the emission.

In recent years the oxide cathode has been called upon to supply emission currents of ever-increasing magnitude. The consequent

difficulties have been investigated by Coomes,<sup>1</sup> Fineman and Eisenstein,<sup>1</sup> and Wright,<sup>1, 2</sup> who found that interface layers which are formed at the boundary between core metal and oxide coating restrict the maximum current density in the coating.

As a result of the investigations since 1930 a concept of the mechanism of the oxide cathode has been established which will provide the basis of this book. Summarizing, this concept may be outlined as follows:

A metallic base which may be heated directly or indirectly supports a coating consisting of metal oxides, mostly oxides of the alkaline earth metals. This coating has a considerable thickness compared with the monatomic layers of other cathodes. The lower limit of the thickness may be given as  $10^{-5}$  cm. =  $0.1 \mu$ , equal to about 400 atom layers. As a result of an activation process excess metal is produced in the coating and to a certain degree on its surface. This excess metal, which is nearly always an alkaline

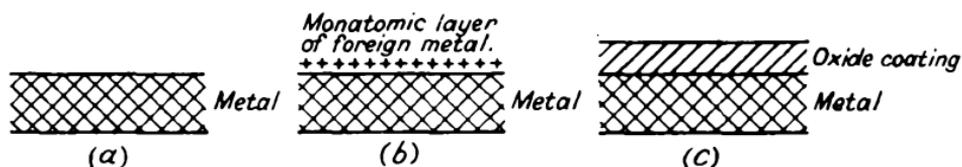


Fig. 1.—Section through (a) a Pure Metal Cathode, (b) an Atomic Film Metal Cathode, (c) an Oxide Cathode.

earth metal, makes the coating a semi-conductor. If the cathode is heated, free electrons arise in the semi-conductor which are conducted to the surface of the coating and can then be emitted into the vacuum. The form of the oxide cathode may be compared with that of the pure metal cathode and the atomic film cathode (e.g. tungsten-thorium) by reference to Fig. 1. As a result of this concept the emission state of the oxide cathode is seen to depend mainly on the constitution of the interior of the coating and to a certain degree on the constitution of the surface. The core metal, however, has only an indirect influence on the emission. These facts also have an important bearing on the practical aspects of the cathode.

While the physics of the oxide cathode was being investigated, commercial development went ahead speedily. When broadcasting was introduced, there was in particular a demand for cathodes of high efficiency which could be satisfied by using oxide cathodes. Consequently the oxide cathode has replaced all other types of cathode in radio receiving valves. The higher efficiency,

$W$ , of the oxide cathode compared with other types may be seen from the values in Table I. These values are not peak values of the emission current, but are mean values obtained from the operating emission currents of commercial receiver and transmitter valves run under such conditions as ensure adequate life. The measure of the efficiency is the emission current per watt of heater power (mA/watt). The other important measures of cathode performance, the current density (mA/cm.<sup>2</sup>) and specific heater power (watts/cm.<sup>2</sup>) will be quoted later, as also will the maximum values of the emission current which can be obtained where considerations of life are disregarded (cf. sections 11 and 13).

TABLE I

*Mean Values of Efficiency of Different Types of Cathodes in Commercial Receiver and Transmitter Valves*

Type of cathode	$W$
Pure tungsten	1.7 mA/watt
Tungsten-thorium	6     "
Oxide cathodes, indirectly heated	10    "
"            directly heated	40    "

Apart from the high efficiency, the possibility of producing a cathode which is electrically independent of the heater current has also greatly widened the application of the oxide cathode. Such a type of cathode—the indirectly heated cathode—can only be made economically by using an oxide cathode. Today these indirectly heated oxide cathodes are much more widely used than directly heated ones, since the former enable A.C. to be employed as a source of heater power, which is a great advantage.

The oxide cathode has now reached such a high state of development that striking innovations are no longer likely. Considering the many different applications of the oxide cathode, however, improvements in technical manufacture, concerning mass production, for instance, will always be possible. Such improvements will be established most readily by utilizing the knowledge obtained of the physical processes in the oxide cathode.

## 2. Applications and Different Types

Before discussing the different applications and types of oxide cathodes, the terms emission current, saturated current, space-charge current, etc., will be defined, since they will be used frequently.

The law governing the electron emission is not always the same, but is determined by the density of the electrons and by the anode voltage. This is shown by Fig. 2, in which the logarithm of the emission density of an oxide cathode is plotted as a function of anode voltage for different cathode temperatures. Such a plot of the emission current gives, at negative voltages, a steeply rising straight line, the slope of which decreases with increasing temperature. If a high positive voltage is applied, however, the emission current

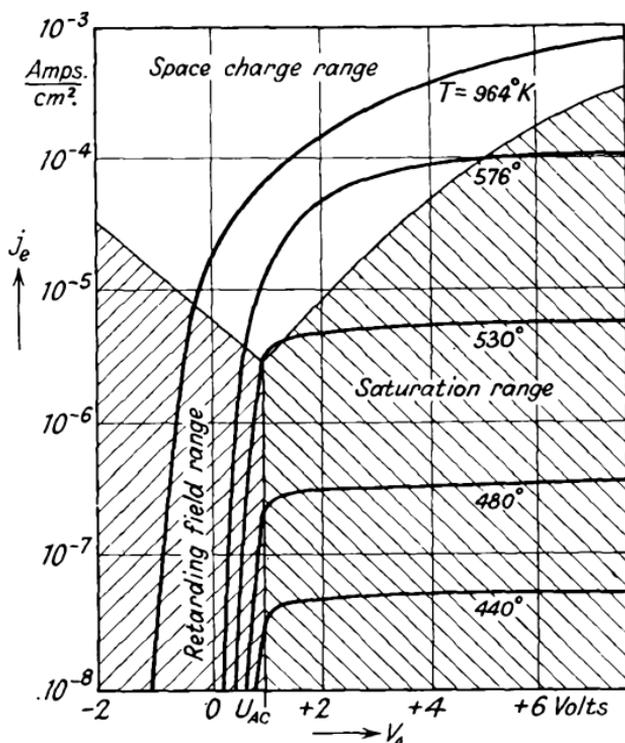


Fig. 2.—Emission Density  $j_e$  as a Function of Anode Voltage  $V_A$  for Different Cathode Temperatures.

increases very little with increasing voltage. The current is described as saturated in this range of voltages where it is virtually dependent on temperature only. The two ranges of voltage and current which are so characterized are called the retarding field range and the saturation range respectively. Between them there is a third range called the space-charge range in which the emission current likewise depends highly on anode voltage. The law for the emission current as a function of voltage in this range, however, is different from the law in the retarding field range mentioned above. As can be seen from Fig. 2 the space-charge range becomes smaller with

decreasing temperature and disappears almost completely below a current density of about  $10^{-5}$  amps./cm<sup>2</sup>. The retarding field current passes directly to the saturated current at these low temperatures.

The laws of the electron current passing to the anode in the three ranges are derived in Vol. II. Only the result of these derivations will be given here. Let  $T$  denote the absolute temperature of the cathode,  $S$  its surface area, and  $V_A$  the anode voltage (neglecting the contact potential). Then the laws required are:

$$(1) \text{ retarding field current: } I_r = I_s e^{1.16 \times 10^4 V_A / T} \quad (V_A < 0) \quad (1)$$

$$(2) \text{ space-charge current: } I_{sp} = c V_A^{3/2} \quad \dots \quad (2)$$

$$(3) \text{ saturated current: } I_s = S A_0 T^2 e^{-1.16 \times 10^4 \psi / T} \quad \dots \quad (3)$$

In these equations  $\psi$  indicates the work function of the electrons for the cathode material concerned (cf. Vol. II, Sec. 2). The value of this work function, lying between 1 and 6.5 volts for different materials, decreases with increasing emissivity of the cathode material. The value of  $A_0$  is nearly constant for all cathode materials and approximately equal to 120, while  $c$  is a constant depending on the dimensions of the electrode system used.

In order to avoid confusion the electron current emitted from the cathode will be called emission current, or in short emission, if this current is discussed in general. If, however, the electron current flowing in one of the above ranges is considered, the appropriate terms referring to these ranges will be used.

After this preparatory work the different applications of the oxide cathode will be discussed. First of all the factors will be given which limit the commercial application of the oxide cathode. These factors are:

- (1) The electrical field strength at the surface of the cathode.
- (2) The density of the emission current to be drawn from the cathode.
- (3) The temperature of the electrodes surrounding the cathode (grids, anode, etc.).

The limit of the field strength at the cathode surface is determined by the bond between the coating and the core metal, because the coating or parts of it may be torn from the core metal by electrostatic forces if the field strength is too high. An exact limit of the field strength cannot be given, as commercial oxide cathodes mostly have a very rough surface which makes an exact calculation of the

field strength impossible. If a smooth surface is produced by a special preparation of the coating, considerably higher field strengths than with normal coatings may be applied. In this manner a limit of 400 kV/cm. may be reached.

If the cathode is operated in the space-charge range the field strength calculated from the anode or grid voltage will only exist at the cathode surface during the warming-up period. When the cathode reaches the normal temperature, the field strength decreases almost to zero due to the formation of the space charge. The conditions when the heater supply is switched on are therefore of particular importance and the application of the oxide cathode may be limited by those conditions. In the case of rectifiers the field strength is especially high during the blocking phase, when the limit given above may be reached. Another important fact is that the mechanical forces on the oxide coating of rectifiers and of valves for pulsed emission are not exercised continuously but alternately. The application of the oxide cathode may be limited by these alternating forces at values of the field strength which are much lower than the limit given above.

The density of the emission current is limited, because the oxide coating is heated by the emission current flowing through the coating and this heating may destroy the coating. If modern high-power valves are considered, especially those designed for short-wave operation, it is found that they are operated with current densities between 100 and 300 mA/cm.<sup>2</sup> (average D.C.). A very high momentary current density is drawn from cathodes for pulsed operation, especially from those in magnetrons. The peak values obtained in this case are between 10 and 30 amps./cm.<sup>2</sup>.

The temperature of the electrodes surrounding the oxide cathode is of importance, as these electrodes become activated by evaporation of the oxide or of its active metal component, an effect which cannot be avoided. These electrodes can therefore also act as a cathode provided their temperature is high enough and their potential has a suitable value. The thermionic grid emission in valves with grids and the reverse current in rectifier valves are produced in this manner. For this reason the oxide cathode cannot be employed in valves which run with high electrode temperatures, as for instance in large transmitting valves.

After having considered the limitations of the oxide cathode we now turn to its various applications. Two groups of cathodes may be distinguished, namely cathodes operated in a vacuum of less

than  $10^{-4}$  mm. mercury (high-vacuum cathodes) and cathodes operated in a gas discharge of  $10^{-3}$  mm. or more (gas-discharge cathodes).

Among the high-vacuum cathodes the oxide cathode holds a predominant position at the present day. Its advantages can be utilized in this application due to the introduction of getters which enable the necessary high vacuum to be obtained under economical mass-production conditions. The high-vacuum oxide cathode is generally used in receiver, amplifier, transmitter, and rectifier valves for anode voltages up to some kilovolts. Valves used for more special applications, such as measuring and controlling, also come into this group. The limit given for the anode voltage must not be considered as final since this value is very dependent on the electrode configuration of the valve concerned. During experiments or, when using small emission densities of the order of  $10 \text{ mA/cm}^2$ , the application of 10 to 15 kV anode voltage is quite acceptable. In valves operated with pulses anode voltages up to 25 kV are reached in the intervals between the pulses (cf. Fay <sup>1</sup>).

Furthermore, the oxide cathode is an ideal point source of electrons, since it possesses a large emission density and is not very sensitive to temperature variations due to its high saturated current. Consequently the oxide cathode is used in cathode-ray tubes (oscilloscope and television tubes) almost without exception. The anode voltages generally applied in these valves are up to 5 kV in oscilloscope tubes and up to 50 kV in television tubes. The field strength at the cathode surface of these tubes is comparatively small due to the special configuration of the electrode system. For this reason the above voltages will certainly not be the attainable limit.

The gas-discharge oxide cathodes are generally used in small rectifiers and thyratrons. The type of cathode normally employed is Hull's multicellular cathode, which has a very high efficiency due to some special measures to be discussed later. The admissible operating voltages of gas-filled rectifiers depend on the gas pressure and also on the quantity of cathode material evaporating to the anode due to sputtering. If the pressures are of the order of some mm. mercury the attainable peak inverse voltages are a few hundred volts, while those rectifiers working with low pressures may be operated with voltages up to 20 kV.

The oxide cathode is, moreover, employed in gas-discharge lamps in which the positive column of a gas discharge is utilized for

obtaining light. The function of the oxide cathode in these lamps is quite different in the different ranges of pressure in which the lamps are operated. The oxide cathode is the real source of the electrons only in the low-pressure lamps, while in the high-pressure lamps the electron emission of the oxide coating is utilized for diminishing the striking voltage when switching on the discharge. The latter method is also employed in glow discharge tubes, especially in stabilizers.

From the above discussion it will be clear that oxide cathodes can be employed in cathode-ray tubes, operating with a gas filling at voltages up to 5 kV. They can also be used as a source of electrons in experimental tubes. Wehnelt<sup>3</sup> himself was the first to employ his discovery for determining  $e/m$  of the electrons. More recently the electron emission of the oxide cathode has been applied to testing chemical reactions (Jacobs<sup>1</sup>).

It should be evident that different types of cathodes will be necessary for the different purposes mentioned. Considering the commercial high-vacuum cathodes, the oxide coating always consists of oxides of the alkaline earth metals. If the less important difference between directly and indirectly heated cathodes is disregarded, the following types may be distinguished:

- (1) The uncombined oxide cathode, consisting of a coating of pure alkaline earth oxides which are generally obtained by decomposing alkaline earth compounds in vacuum.
- (2) The combined oxide cathode, whose oxide coating is heated to red or yellow heat in a gas atmosphere before being built into the valve. By this heating process chemical compounds of the oxide coating and core metal are produced which give the oxide coating a dark appearance quite different from that of the pure white uncombined cathodes.
- (3) The condensation cathode, which is prepared by a completely different method. The core metal before being built into the valve is not coated with barium compounds, but is slightly oxidized. The oxide coating is produced on the core metal by evaporating barium metal, which reacts with the core metal oxide and forms barium oxide.

Of these three types of high-vacuum cathodes the two latter ones are more of historical interest only. The description of the manufacture and the characteristics of the oxide cathode will therefore be restricted mainly to the uncombined cathode. The condensation

cathode will be discussed in a special section because of its wide usage in earlier years.

When making the gas-discharge cathodes, other oxides than those of the alkaline earth metals are sometimes used either in addition to the alkaline earth oxides or even alone. These additional oxides, which always decrease the emission, make the oxide coating more resistant to the bombardment of ions. This type of cathode will also be considered in a special section.

Concluding this chapter the question may be discussed, why the oxides of the alkaline earth metals are almost exclusively used for obtaining a highly emitting cathode. The high electron emission of these oxides cannot alone be the deciding factor, as there are other metal oxides which are good emitters, but which are not employed commercially.\* An oxide which is a good emitter may be employed for commercial cathodes, if this oxide is stable in a high vacuum at the temperatures necessary for the electron emission. The dissociation pressure of the alkaline earth oxides is so low that no dissociation can be observed in practice. The vapour pressure of these oxides is higher, but the rate of evaporation resulting from this pressure is within limits which only make the application of the alkaline earth oxides slightly more difficult in some special cases. In addition to this the oxide used must be able to contain and to bind at the operating temperature a sufficient quantity of the excess metal necessary for the emission. Furthermore, the oxide must not be too reactive chemically, as the products of reactions with the core metal or with residual gases in the valve, if occurring in sufficient quantities, will diminish the electron emission of the oxide concerned. Finally it must be possible to prepare the metal oxide in a simple manner suitable for commercial mass production. All these demands together with the high emissivity are so far sufficiently fulfilled only by the alkaline earth oxides.

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\* For instance, caesium oxide as a thick coating, which must be distinguished from the atomic film cathode caesium-oxygen (M-O-Cs).

THE OXIDE-COATED CATHODE

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## CHAPTER 2

### THE MANUFACTURE OF THE CATHODE BEFORE MOUNTING IN THE ENVELOPE

Before describing the manufacture of the cathode in detail it may be pointed out that the demands on the purity of the materials used are probably more stringent than in any other manufacturing process. Impurities of only a few hundredths of a per cent. may be decisive to the quality and serviceability of the cathode. Strict observance of the approved processes of manufacture and maintenance of the utmost cleanliness during these processes, however, guarantee a sufficient consistency of the manufactured cathode. On the other hand, when varying the processes of manufacture, it will be possible to avoid failure if the mechanism of the oxide cathode is sufficiently known.

When discussing the manufacture of the cathode it will be convenient to distinguish between the processes carried out before mounting the cathode in the valve envelope and the processes carried out afterwards. The first part comprises the making of the core metal and of the emission paste, the deposition of this paste on the core metal, and, as far as indirectly heated cathodes are concerned, the manufacture of the heater. After the cathode has been mounted in the valve envelope, the earth alkaline compounds of the emission paste are transformed into the oxides by a heat treatment and the oxide coating so obtained is finally activated, until the conditions for operating the cathode are reached.

#### 3. The Core Metal

The core metal must satisfy various demands, one or another of which may be more important for different applications and types of cathodes. The demands concerned will differ for directly heated and indirectly heated cathodes, but as there is no sharp boundary between the two cases they will be discussed together. The following properties are demanded of the core metal.

- (1) Stability at the operating temperature and at the temperatures occurring during the manufacture, in particular a low rate of evaporation and a high melting-point.

- (2) Adequate mechanical properties at the high temperatures at which the cathode is used, which means high tensile strength and low recrystallization.
- (3) A favourable influence on the emission.
- (4) Chemical stability at all temperatures towards the oxide coating and any gases or vapours possibly existing.
- (5) The ability to be readily degassed during the manufacture of the cathode.
- (6) Properties which guarantee a good heat economy such as low heat conductivity and low radiant emissivity.

Owing to these numerous demands to be made on the core metal only few metals or alloys of such metals can be used for the core. The first demand at once greatly restricts the number of metals to be employed. The rate of evaporation which has been plotted for the more important metals in Fig. 3 may be considered first. The following selection can then be made.

The amount of metal which evaporates into and through the coating during manufacture and operation must be limited in order to avoid a deterioration of the cathode emission and of the insulation between the electrodes in the valves. The admissible upper limit for this amount of metal is about 1 mg. per cm.<sup>2</sup> surface area of the cathode. The time to be considered will be some 1000 hours for the operation between 900 and 1200° K. and 1/100 to 1/10 hour for the maximum manufacturing temperature, which is between 1300 and 1500° K. Consequently the rate of evaporation admissible at the operating temperature will be 10<sup>-6</sup> to 10<sup>-5</sup> g./cm.<sup>2</sup> hour, while the appropriate value for the manufacturing temperature is 10<sup>-2</sup> g./cm.<sup>2</sup> hour. By comparing these limits with Fig. 3 it is seen that only metals whose rate of evaporation is equal to or smaller than that of iron or nickel may be used as a core metal. If a low operating temperature is chosen (about 1000° K.) copper would also satisfy these demands.

Furthermore, it is important that the melting-point of the metal, which is also seen from Fig. 3, is high enough above the maximum manufacturing temperature. As the melting-point of copper, which is 1357° K., is within the range of manufacturing temperatures, this metal is again the limiting case. Summarizing, we may state that all metals which are seen on the right-hand side of copper in Fig. 3 may be used as a core metal. The number of these metals, of course, may be increased considerably by producing suitable alloys with appropriate melting-points and rates of evaporation.

The second demand quoted, namely high tensile strength and low recrystallization, is particularly important for directly heated cathodes. A high tensile strength is required because the core wire is given a high mechanical tension in order to fix the distance between the wire and the other electrodes as precisely as possible. Variations of this distance produce the undesirable microphonic noise. Apart from this, if the distance is rather small a short-circuit between the cathode and the neighbouring electrode may occur. For these reasons the tension to be applied to the core

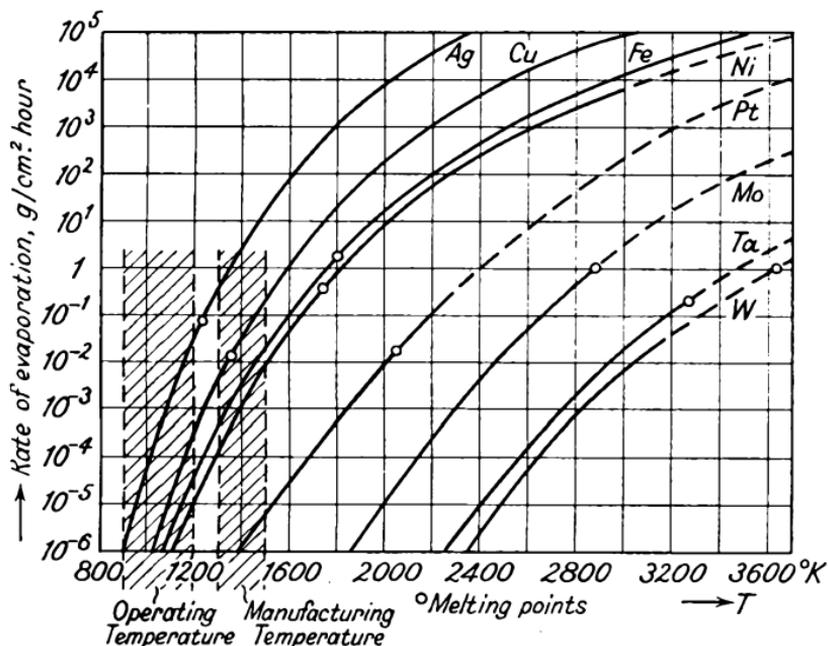


Fig. 3.—Rate of Evaporation of Different Core Metals as a Function of Temperature.

wire is taken as high as is compatible with the life of the cathode. If the core material recrystallizes too much, the cathode may become so brittle within the first few hours of operation that it may break due to a mechanical shock, even when not heated. This would be especially undesirable for valves in portable sets.

When comparing the tensile strengths of different core materials (cf. the works of Ransley and Smithells,<sup>1</sup> Peters,<sup>1</sup> and Wise<sup>1</sup>) attention must be paid to the fact that the tensile strength very much depends on the pre-treatment of the wires or ribbons; for instance, on the type of heating process carried out during the manufacture and on the degree of deformation obtained. Consequently the values given in the papers for a definite material show

a considerable spread. As an example Fig. 4 shows the tensile strength of two tungsten wires which were differently treated but not recrystallized. While tungsten, as will be seen from this figure, possesses a very high strength at the temperature necessary for the oxide cathode, the tensile strength of all other core materials is considerably smaller. This is shown in Fig. 4 by the curves for

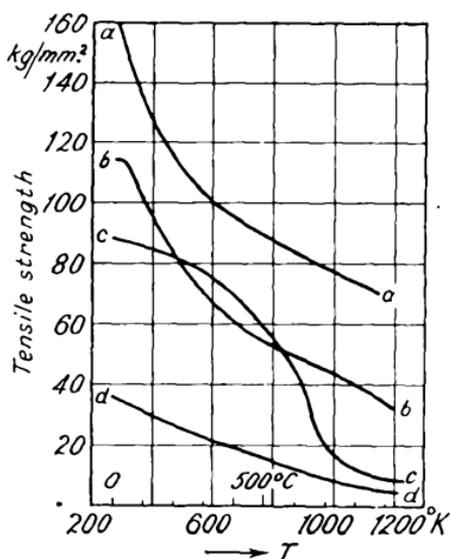


Fig. 4.—Tensile Strength of Tungsten and Nickel Wires as a Function of Temperature: (a) Tungsten 0.63 mm. diam.; Worked to 97.5% reduction of Area; (b) the Same to 56% Reduction; (c) Nickel 0.65 mm. diam., cold drawn, not annealed; (d) Nickel 0.04 mm. diam., annealed at 1275° K. (Jeffries,<sup>1</sup> Ransley and Smithells<sup>1</sup>).

nickel wires, one of which was annealed at 1275° K. before being measured.

Although tungsten seems to be the best core metal for directly heated cathodes according to the above; it could not be introduced generally. This is due to the fact that tungsten reacts with alkaline earth compounds and that it is therefore slightly inferior to nickel if the effect of the core metal on the emission is considered. (Vol. II, Sec. 32.) Efforts have been made to improve the bad tensile strength of nickel by producing suitable alloys. The most important properties of such nickel alloys are compiled in Table II according to values of Peters.<sup>1</sup> By comparing these values with Fig. 4 one sees that the tensile strength may be increased by the

formation of alloys, particularly at high temperatures, but a value comparable with that of tungsten cannot be obtained.

The third demand, namely a favourable influence on the emission of the oxide coating, is also of much importance. According to Liebold<sup>1</sup> nickel has, among the pure metals, the best influence on the emission. Lowry,<sup>1</sup> Beese,<sup>1</sup> Benjamin,<sup>3</sup> Wright,<sup>1</sup> and Violet and Riethmüller<sup>1</sup> found that, when employing alloys for the core metal, the optimum emission of the cathode much depended on the composition of those alloys. Reducing agents which are normally added to nickel in order to make it more readily workable are especially important. Some of these agents such as aluminium, magnesium, and titanium are known for their ability to speed up

the activation process of the cathode (cf. Sec. 8) and are therefore much in use. Sometimes, however, the reducing action must be kept small for special reasons to be discussed later. Special types of commercial nickel are offered for both purposes and examples for their composition, given by firms in the U.S.A., will be seen from Table III.

TABLE II

*Properties of Nickel Alloys, used as Core Metals, according to Peters<sup>1</sup>*

	Percentage composition						
	Ni	Co	Si	Mn	Fe	Ti	Al
Pure nickel	99.7	0.08	—	—	0.17	—	—
Silicon nickel	97.0	—	3.0	—	—	—	—
Hilo (similar to konel)	75.0	18.0	—	—	5.0	2.0	—
Cobanic	54.5	44.5	—	—	1.0	—	—
Tensite	98.0	—	—	—	—	—	2.0

	Melting-point (° C.)	Percent- age elonga- tion	Tensile strength kg./mm. <sup>2</sup>		Electrical resistance μ Ω cm.	
			(20° C.)	(850° C.)	(20° C.)	(800° C.)
Pure nickel	1455	39	39.6	7.4	8.3	48.0
Silicon nickel	1420	35	53.7	11.2	26.5	51.0
Hilo (similar to konel)	1450	32	74.8	18.4	42.0	114.0
Cobanic	1500	38.5	60.5	12.6	12.5	81.2
Tensite	1425	30	39.9	9.6	15.0	54.8

TABLE III

*Chemical Analyses of Different Types of Nickel for Cathode Sleeves  
(Superior Tube Company, U.S.A.)*

Name of alloy	Percentage additions of other elements						
	C max.	Cu	Fe	Mg	Mn	S	Si
Grade A	0.08	0.25	0.30	?	0.35	0.008	0.20
INCO 220	0.08	0.20	0.20	0.01-0.10	0.20	0.008	0.01-0.05
„ 225	0.08	0.20	0.20	?	0.20	0.008	0.15-0.25
Driver-							
Harris 499	0.05	0.04	0.05	0.01	0.02	0.005	0.01
„ 599	0.08	0.04	0.05-0.10	0.01	0.10	0.005	0.15-0.25
„ 699	0.08	0.04	0.05-0.10	0.05-0.15	0.10	0.005	0.05-0.15

The fourth demand, adequate chemical stability towards the oxide coating and reaction products occurring during the manufacture of the coating, eliminates quite a number of metals. If this chemical stability is not sufficient, the products of the reaction between the alkaline earth oxides and the core metal form an interface layer between the coating and the core. Such an interface layer is detrimental to the emission and to the bond between coating and core. The interface layers are also formed with some of the nickel alloys used commercially (cf. Table III), for instance with those containing higher percentages of silicon. This is particularly important if high emission currents (pulsed emission) are to be drawn from the cathode, and the core materials concerned are therefore not suitable for such applications (cf. Sec. 12, 13 and Vol. II, Sec. 32).

A metal which cannot be used as a core metal on account of its high chemical affinity to the oxide coating is iron. The application of tungsten, molybdenum, and tantalum is also made difficult by these chemical influences, which increase in the sequence given above.

As the application of tungsten is very desirable on account of its high tensile strength, attempts have been made to remove the detrimental chemical influences by suitable measures. For example, direct contact of the tungsten and the oxide coating may be avoided by electrolytically coating the tungsten with a metal not affected by the oxide. Alternatively a wire may be wound round the tungsten; this also improves the bond between the core and coating. The latter type of cathode, which may be called multi-core cathode, is therefore used particularly in gas-discharge valves where a good bond is essential. It should be pointed out that the desired effect can be inhibited by the formation of alloys between the two core metals. The mechanical or electrical properties may be altered by this formation of alloys, or the alloy formed may show the undesired chemical properties of the covered metal.

The fifth demand on the core metal, namely that it can readily be degassed, is satisfied by avoiding blowholes and porosity. This can be achieved by employing special additions for deoxidation.

The final requirement, that of good heat economy, is only important for indirectly heated cathodes. Then the low heat conduction required is not so much a property of the core metal used but may be achieved much more simply by a suitable support of the cathode in a thin material of low heat conductivity, for instance

mica. In addition to this the tape holding the cathode and leading the current to it (cf. Fig. 6) can be made of an alloy of low heat conductivity (invar). The radiation properties of the core metal influence the temperature of the cathode only in so far as the core metal radiates through the coating. The amount of this radiation through the coating, of course, depends on the thickness and density of the coating. As copper of all metals considered has the lowest radiant emissivity in the region of temperatures concerned, its application gives an exceptionally good heat economy. The

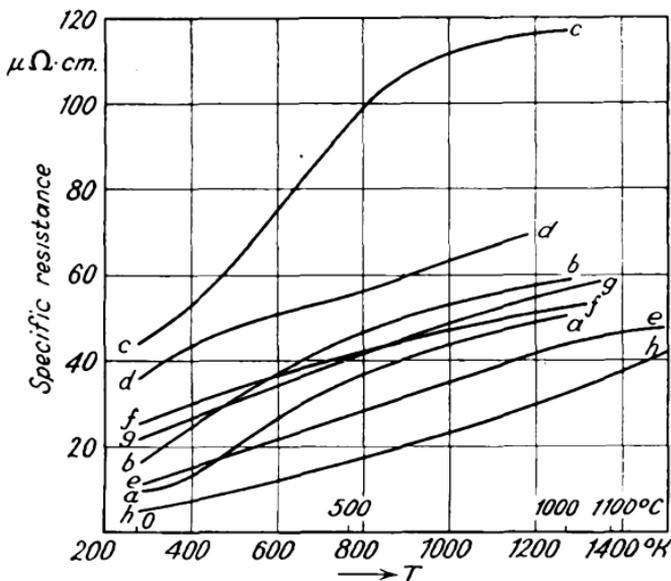


Fig. 5.—Specific Resistance of Core Metal Wires as a Function of Temperature: (a) Nickel, very pure (Espe<sup>1</sup>); (b) Tensite (Peters<sup>1</sup>); (c) Hilo (Peters<sup>1</sup>); (d) Silicon nickel (Peters<sup>1</sup>); (e) Platinum, very pure; (f) Platinum + 5% Iridium; (g) Platinum + 5% Nickel (Espe<sup>1</sup>); (h) Tungsten (Langmuir and Jones<sup>1</sup>).

details for this will be given when the thermal properties of the oxide cathode are discussed in Sec. 9 (cf. Fig. 43).

In addition to the demands compiled at the beginning of this section, a knowledge of the electrical resistance will be important for directly heated cathodes. The values of this resistance are needed, for example, for ascertaining the necessary diameter and length of the core metal wire for a given heater voltage and heater power. The conductivity of the core material can be influenced by forming alloys in the same way as is done for obtaining the necessary mechanical properties. Details of the resistance values will be seen from Fig. 5 and Table II.

It is seen from the different demands to be made on the core metal that only a few metals satisfy all these demands so far that they may be employed commercially. For directly heated cathodes either tungsten is used on account of its high tensile strength or nickel because of its favourable effect on the emission. The strength of nickel is then usually increased by forming alloys (cf. Table II). In special cases platinum alloys, which were much in use in the early years, are still employed. Nickel, which also shows a good workability, is almost exclusively used for indirectly heated cathodes. Only in special cases where a high heat economy is necessary is copper employed, the more general use of which is inhibited by the above-mentioned difficulties resulting from its high rate of evaporation and its low melting-point.

After having discussed the reasons for the application of the different core materials we may now consider the manufacture of these metals. The metal to be used for the core must be produced with the utmost care and as pure as possible. The usual metallurgical processes must be considerably refined and improved in order to give materials which are sufficiently consistent and suitable for oxide cathodes. In order to show the amount of care which is necessary for producing such a core metal a manufacturing process given by Ransley and Smithells<sup>1</sup> may be briefly outlined here. Although the authors have used this process for experimental melts only, its application to commercial processes seems to be possible.

A very pure commercial nickel (99.3%) was at first desulphurized by electrolysis in a chloride bath. This was necessary, as an amount of less than 0.01% sulphur may make the material unsuitable for the manufacture of thin wires due to the formation of envelopes of nickel sulphide at the crystal boundaries. The nickel deposited at the cathode of the chloride bath was then heated in hydrogen for one hour at 1000° C. in order to reduce the oxides possibly existing in the nickel. Subsequently the nickel was melted in hydrogen in a high-frequency furnace clad with magnesium oxide. Then it was treated with nitrogen and cast into rods. The metal so made could be drawn without applying special means for deoxidation; its purity was 99.91% according to the chemical analysis.

Further details concerning the commercial manufacture of nickel for oxide cathodes have been given by Weber,<sup>1</sup> while the testing of this nickel in mass production of valves has been described by McCormack<sup>1</sup> and by Acker.<sup>1</sup>

The method described above for nickel cannot be used for producing tungsten on account of the high melting-point of this metal. Tungsten, as is well known, is therefore made by the powder metallurgical process, by sintering the extremely pure metal powder at temperatures which are chosen as high as possible but which are lower than the melting-point of the metal concerned. After sintering, the metal is made ductile by swaging at high temperatures until it may be worked by drawing or rolling. This method, which was originally only applied to metals with very high melting-points, is nowadays successfully used also for other metals in order to produce these in high purity or as an alloy with a definite composition.

After production the metal is worked in different ways according to the type of cathode. The wires needed for the directly heated cathodes are made by drawing to the desired diameter, while the ribbons are made by rolling wires to the required cross section. The indirectly heated cathode normally consists of a metal sleeve which carries the oxide on the outside and which is heated by a special heater either by heat conduction or radiation. Another suggestion is heating by electron bombardment\* from a metal cathode inside the sleeve. But such a design, being unstable and less economic than the other types of heating, has so far only been used for experiments (Wehnelt and Bley<sup>1</sup>), and not for commercial cathodes.

The sleeves, which normally consist of nickel, are made by extruding nickel tubes or by rolling and folding nickel sheet. The folded sleeves (lockseam-sleeves) compared with the seamless extruded sleeves have the advantage of being cheaper. But their disadvantage according to Michael<sup>1</sup> is that the coating on these sleeves tends to flake off due to impurities remaining in the fold. The wall thickness of the sleeve depends on its diameter and length, as these three values together determine the stability and tolerance limits of the sleeve necessary for complying with the electrical characteristics of the valve. Apart from this the wall thickness has a considerable influence on the temperature distribution along the cathode and on its warming-up time (cf. Sec. 6). Cathode sleeves for receiver valves normally have a wall thickness between 0.05 and 0.1 mm.

The further treatment of the sleeve depends very much on the final shape of the cathode, and some general indications will therefore be sufficient. The necessary processes will be seen from Fig. 6

\* German Patent 358420.

showing different types of indirectly heated cathodes. These processes, for instance, are pressing of a collar (see top of Fig. 6 (a)), pressing of pips (bottom of (b) and (c)), reducing the sleeve to a locating pin (see top of (b)), cutting a tail (bottom of (d)), and welding of an invar tape (bottom of (b)). The purpose of all these procedures is to fix the position of the cathode in the supporting parts of the valve and to prevent variations of this position during operation. Fig. 6 (d) shows a cathode sleeve for cathode-ray tubes and television valves which carries the coating on its end face.

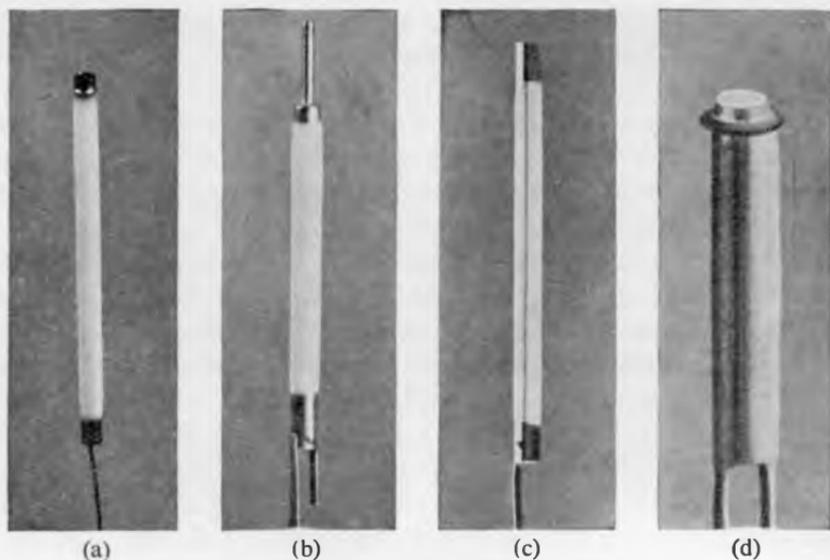


Fig. 6.—Types of Indirectly Heated Cathodes  
(Telefunken, Berlin).

A variety of the multi-core cathodes mentioned above was recently employed for indirectly heated cathodes which have to supply high-pulsed currents. Pomerantz<sup>1</sup> and Fisk, Hagstrum, and Hartmann<sup>1</sup> give details for the manufacture of such cathodes made by covering the nickel sleeve either with nickel gauze (0.15 mm. wire diam. and 0.3 mm. mesh) or with nickel powder (about 50  $\mu$  grain-size) which is sintered on the sleeve (Fig. 7). These cathodes are employed in magnetrons, where a particularly good bond between coating and core is needed because of the high current densities and of the additional heating of the cathode due to bombarding electrons and ions.

Before use the sleeves, wires or ribbons are cleaned by the processes

normally employed in high-vacuum technique. A typical sequence of such processes is, washing in a degreasing liquid, etching in a dilute weak acid (e.g. acetic acid), and heating in a reducing atmosphere. These processes are described by Wagner,<sup>1</sup> who points out that they are also necessary for obtaining a good bond between core and coating. Sometimes the surface of the sleeve is electrolytically polished in order to decrease the heat radiation of the sleeve.

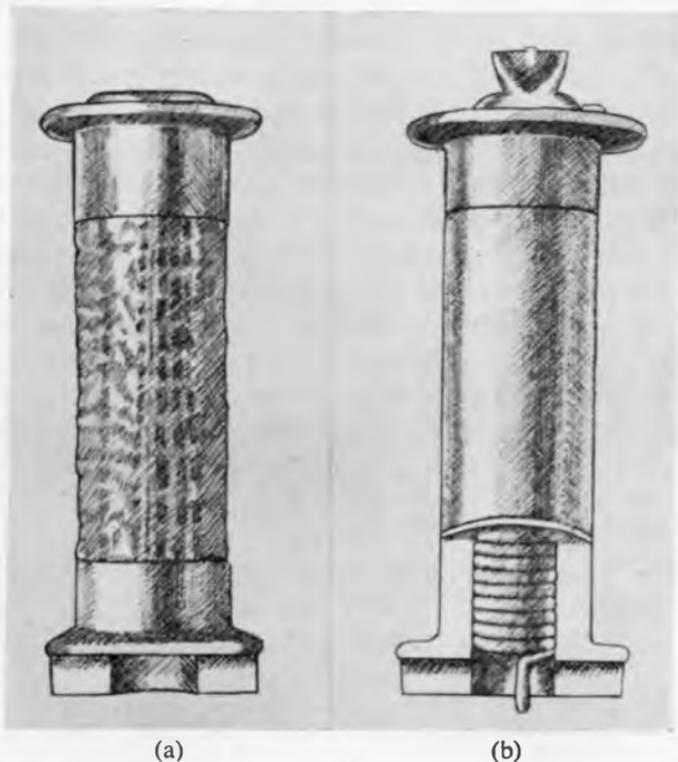


Fig. 7.—Cathode Sleeves for Magnetrons, covered with (a) Nickel Gauze, (b) Sintered Nickel Powder (Fisk, Hagstrum, and Hartman<sup>1</sup>).

#### 4. Preparation of the Emission Paste used for the Oxide Coating

When discussing the manufacture of the emission paste the necessity of using pure materials and clean processes cannot be emphasized too strongly. As shown later, very small additions of foreign materials to the emission paste may influence the emission decisively, giving rise to a deterioration of emission in nearly all cases (cf. Vol. II, Sec. 26.2).

The paste to be deposited on the core metal is a suspension of alkaline earth compounds in an organic liquid, or water to which

organic binders are added for improving the bond. Disregarding the influence of solvents and binder at first, we may distinguish two methods of making commercial emission pastes. The first method, much employed in the early years, uses a paste consisting of pure alkaline earth oxides. The second method, however, which is normally used in mass production nowadays, employs alkaline earth compounds which are decomposed into the oxides concerned during the further manufacture of the valve. The first method has been displaced by the second one owing to the fact that the alkaline earth oxides are quite unstable and are easily converted into hydroxides or carbonates by the quantities of water vapour and carbon dioxide normally existing in air. These hydroxides and carbonates affect the bond between core and coating and may cause the coating to flake off during storage. In addition to this a hydroxide content is undesirable, as the water vapour developed during the degassing of the valve is detrimental to the cathode. For these reasons the methods using oxides have lost their importance and it may be sufficient to point out that oxides of a commercial purity are taken for these pastes. Columns I (BaO), and II (SrO) of Table IV give the composition of the respective oxides.

TABLE IV

*Purity of Alkaline Earth Oxides or Carbonates for Manufacture of Oxide Cathodes*

	I (%)	II (%)	III (%)
BaO	77.17	1.53	—
BaO <sub>2</sub>	4.52	—	—
SrO	—	93.03	—
BaCO <sub>3</sub>	17.24	—	99.2
SrCO <sub>3</sub>	—	4.56	
Al <sub>2</sub> O <sub>3</sub>	0.18	0.21	<0.001
Fe <sub>2</sub> O <sub>3</sub>	0.24	0.28	<0.01
SiO <sub>2</sub>	0.56	0.41	<0.01
Cl			<0.001
SO <sub>4</sub>			<0.001
NH <sub>3</sub>			<0.05
NO <sub>2</sub> , NO <sub>3</sub>			<0.05

The second method normally uses carbonates which are decomposed into oxides during the further manufacture of the valve. The carbonates are preferred because the product of their decomposition, carbon dioxide, reacts very little with the electrodes of the valve and removes the carbon of the binder by forming carbon monoxide.

Soon after introducing the oxide cathode into commercial valves, it was found that mixtures of two or more alkaline earth carbonates (e.g. BaO and SrO) give better results than the single carbonates. Firstly, a paste of mixed carbonates gives a better bond to the core than a paste consisting of barium carbonate only, provided solvents and binder are the same. This may be explained by the lower tendency of strontium oxide to react with the core metal. More important, however, is the fact that the emission obtained from mixed oxides may be higher than the emission from barium oxide only, if certain conditions are satisfied. This was first recognized by Spanner<sup>1</sup> and Simon,<sup>1</sup> and the necessary conditions were investigated in detail by Benjamin and Rooksby,<sup>1, 2</sup> Burgers,<sup>1</sup> Huber and Wagener,<sup>1</sup> and Eisenstein.<sup>1</sup> It was found that there is a definite relation between emission and crystallographical structure of such mixtures of alkaline earth oxides. The summarized results of these investigations are as follows. The carbonates and oxides of barium and strontium form a continuous series of mixed crystals, and crystals of mixed carbonates, when being decomposed, are converted into crystals of mixed oxides. The emission of an oxide coating consisting of such mixed crystals is higher than the emission of a mechanical mixture of the appropriate oxides. The details of these phenomena will be considered when discussing the physics of the oxide cathode (cf. Vol. II, Sec. 26.1). When manufacturing cathodes it is important to know that the carbonates should be supplied as mixed crystals. When using only barium and strontium carbonate, a mixture of nearly equal parts of these gives the optimum emission,\* but this emission can be increased further if about 10% calcium carbonate is added to the mixture (Violet and Riethmüller<sup>1</sup>).

In order to avoid the detrimental influence of impurities the firms producing valves with oxide cathodes normally make their own carbonates by a suitable method of chemical precipitation. This precipitation is carried out by using a solution of alkaline earth nitrates or hydroxides, etc., in water. The alkaline earth carbonates required are precipitated by adding a solution of an alkali carbonate or by passing carbon dioxide. Various precipitation methods and their influence on the emission were described in two publications of Benjamin<sup>4, 5</sup> and collaborators. These workers examined their carbonates by taking light microscopical and electron

\* A coating consisting of mixed crystals of BaO and SrO will be denoted by [BaSr]O.

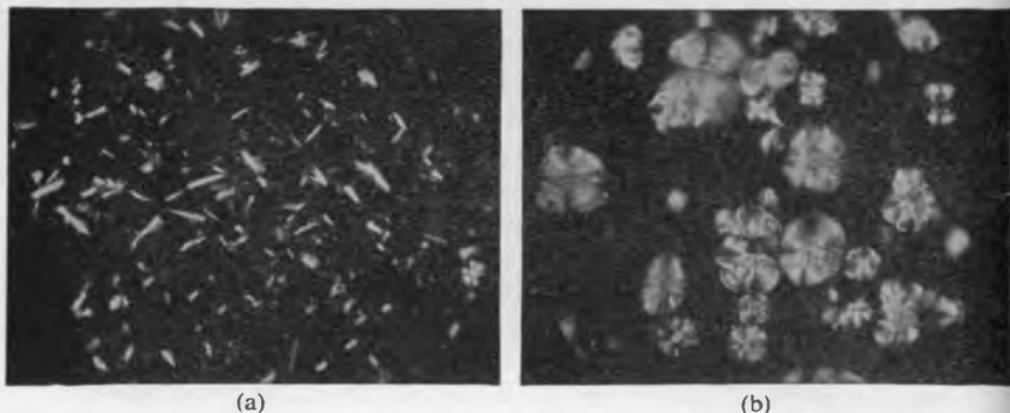


Fig. 8.—Microphotographs of Alkaline Earth Carbonates precipitated by Different Methods (made with Polarized Light in Dark Field, mag.  $\times 700$ ): (a) Needles, (b) Spherulites.

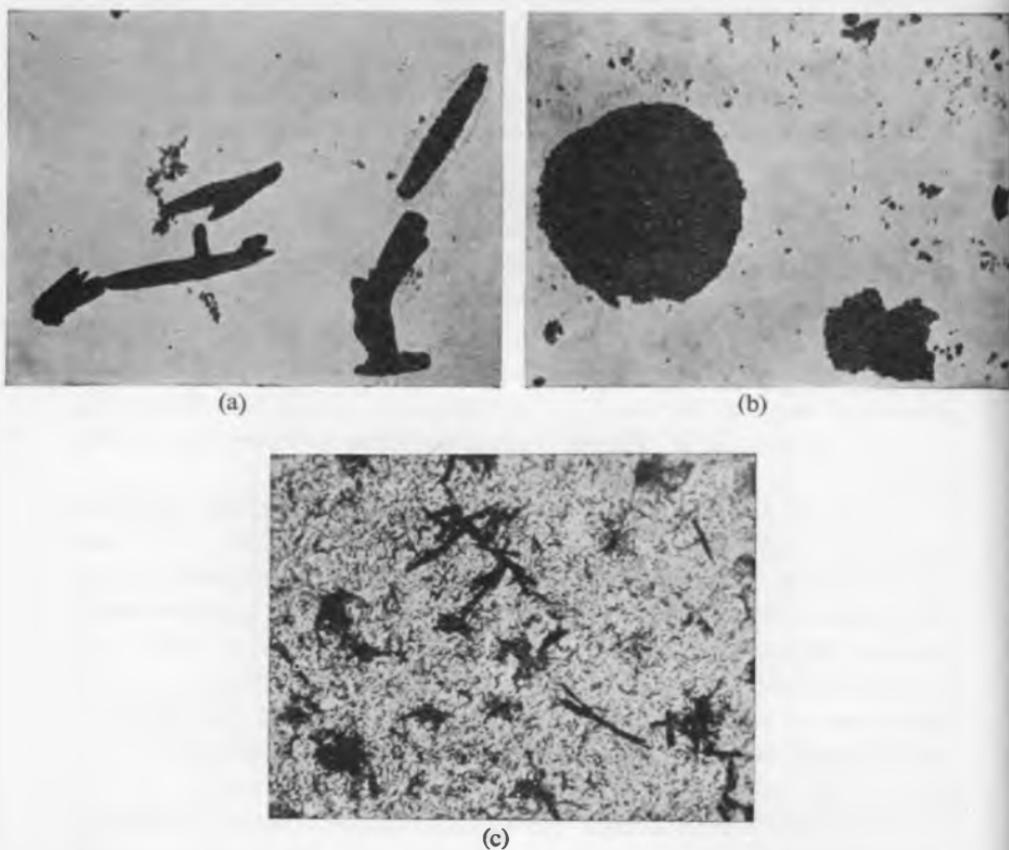


Fig. 9.—Electron Microscopical Images of Alkaline Earth Carbonates precipitated by Different Methods (mag.  $\times 4000$ ): (a) Needles, (b) Spherulites, (c) Colloidal Carbonates (mag.  $\times 5000$ ).

microscopical images as well as X-ray patterns. As is seen from their results given in Table V, the carbonates may be made as needles or spherulites, and either mixed crystals or two different phases may be obtained by the different methods of precipitation. Figs. 8 and 9 show light and electron microphotographs of such carbonates. It may be pointed out in this context that the individual carbonate crystals and the carbonate particles consisting of such crystals must be well distinguished. The precipitated particles generally consist of a certain number of crystals; further details of

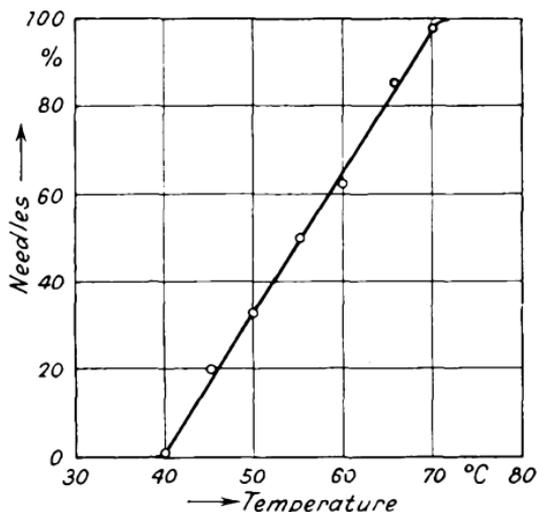


Fig. 10.—Proportion of Needles to Spherulites in Barium, Strontium Carbonates as a Function of Precipitation Temperature (Biguenet and Mano<sup>1</sup>).

this will be given when discussing the decomposition of the carbonates (cf. Sec. 7).

Biguenet and Mano<sup>1</sup> examined how temperature and concentration of the solutions used for the precipitation, influence the shape of the particles. The precipitation methods investigated were those given in the first four rows of Table V, the concentration of the solution of alkaline earth nitrates being 10%. Spherulites of 1 to 3  $\mu$  diameter were found below a precipitation temperature of 40° C., while needles of 10 to 20  $\mu$  length and 1  $\mu$  diameter were obtained above 80° C., this result being nearly independent of the speed of precipitation. The proportion of needles to spherulites increased linearly with temperature in the range between the two above temperatures (cf. Fig. 10).

The ratio between the two shapes of particles varies with the

TABLE V

*Influence of Precipitation Method on the Formation of Mixed Crystals, Size and Shape of Particles, and Emission Current (Benjamin, Huck, and Jenkins <sup>5</sup>)*

Composition	Method of preparation	Speed of precipitation (cm. <sup>3</sup> /min.)	Constitution	Particle-size before milling ( $\mu$ )	Particle-shape after milling	Emission at 1 watt/cm. <sup>2</sup> (mA)
Ba, Sr, 50 : 50 mol. %	(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> , added to nitrates solution. Made alkaline with NH <sub>2</sub> OH.	350 750	Homogeneous double carbonate.	50	Large aggregates, mainly spherulites.	70
Ba, Sr, 50 : 50 mol. %	Na <sub>2</sub> CO <sub>3</sub> added to nitrates solution.	350 750	Homogeneous double carbonate.	3	Fair number of prismatic needles.	130
Ba, Sr, 50 : 50 mol. %	CO <sub>2</sub> passed into nitrates solution. Made alkaline with NH <sub>4</sub> OH.	1000	Generally two phases very close together.	15	Mainly spherulites	Not tested.
Ba, Sr, 50 : 50 mol. %	CO <sub>2</sub> passed into nitrates solution. Made alkaline with NaOH.	1000	Generally two phases close together.	Less than 1/2.	Large number of needles.	40
Ba, Sr, Ca, 56 : 31 : 13 % by weight.	(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> added to solution of nitrates. Made alkaline with NH <sub>4</sub> OH.	350 750	Homogeneous triple carbonate.	100	Large crystalline aggregates.	50
Ba, Sr, Ca, 56 : 31 : 13 % by weight.	Na <sub>2</sub> CO <sub>3</sub> added to nitrates solution. Made alkaline with NaOH.	350 750	Homogeneous triple carbonate.	7	Fair number of needles.	140

concentration of the nitrate solution. Fig. 11 shows this relationship for the precipitation method quoted third in Table V and for a temperature of 50° C. The process of stirring and mixing during precipitation had no influence on the ratio between the two shapes of particles, even if ultrasonics were used, provided the temperature of the solutions was not varied. Finally the experiments showed that the size of the needles increases with decreasing concentration, needles of 100  $\mu$  length being obtained with the smallest concentration of only 2.5%.

Carbonate particles of colloidal dimensions are obtained by the method of Patai and Tomashek <sup>1,2</sup> and Buzagh <sup>1</sup> by passing CO<sub>2</sub>

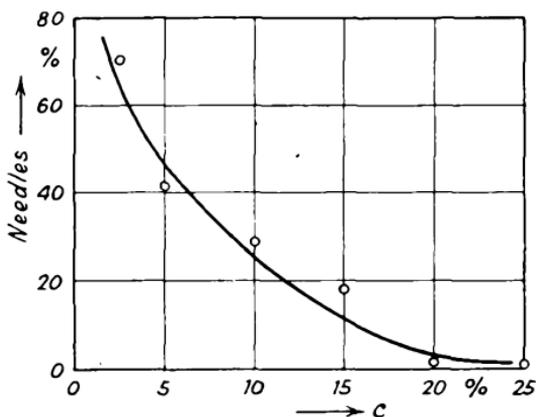


Fig. 11.—Proportion of Needles to Spherulites in Barium, Strontium Carbonates as a Function of the Concentration  $c$  of the Nitrate Solution used for Precipitation (Biguenet and Mano<sup>1</sup>).

into a solution of alkaline earth hydroxides in glycerine. The size of these carbonate particles depends on the viscosity of the glycerine solution and therefore on its concentration. If the concentration is increased, the particle-size decreases. In this manner particles of different sizes down to 0.03  $\mu$  can easily be obtained. Fig. 9 (c) shows an electron image of carbonate particles made in this way.

The relationship between the size of the carbonate particles and the emission of an oxide coating made of those carbonates will also be seen from Table V. Within the range between 100 and 3  $\mu$  the emission increases with decreasing size of particles. In addition to this the emission is also influenced by the surface roughness of the oxide coating, which depends on the process of depositing the emission paste on the core metal and which will be discussed in the next section. The suitability of a precipitation method can only be

assessed in connection with the deposition process and with the methods of pumping and activating to be dealt with later. Fig. 12 shows a modern precipitation unit in which 20 kg. of carbonates can be produced in one process with the necessary consistency. The purity of the carbonates so produced, which is much higher than that of the normal oxides, will be seen from the third column



Fig. 12.—A Precipitation Unit for Mass Production of Alkaline Earth Carbonates (Telefunken, Berlin).

of Table IV. For analysing the purity, the spectrographic analysis as described by Organ and Parsons<sup>1</sup> is preferably used. This type of analysis can also be employed for determining the percentages of the individual alkaline earth metals in a given carbonate mixture (cf. Hartmann and Prescott<sup>1</sup>).

After being precipitated the carbonates are dried, mixed with solvents and binders to a paste, and ballmilled for several hours or days in order to break up conglomerations. For obtaining an

adequate consistency of the paste it is necessary to keep constant the number and size of balls, the quantity of paste, and the speed and time of milling. The composition of the solvents and binders may be varied within wide limits and is not as important as is sometimes assumed. This composition mainly depends on the method of depositing the emission paste on the core metal and on the conditions during the depositing process. The solvents and binders influence the emission of the cathode only if they contain components or impurities which produce poisoning. If an organic binder is not desired, the carbonates are suspended in alcohol or distilled water. Then up to 10% alkaline earth nitrates are usually added to the carbonates in order to improve the bond between core and coating. Some examples of the composition of emission pastes are given in Table VI.

TABLE VI  
*Composition of Emission Pastes*

	I	II	III	IV	V
Carbonates	1000 g.				
Nitrates	—	—	—	—	10 g.
Acetone	—	—	1000 cm. <sup>3</sup>	5000 cm. <sup>3</sup>	—
Amyl acetate	—	1800 cm. <sup>3</sup>	6500 cm. <sup>3</sup>	—	—
Ether	—	—	—	—	} 1300 cm. <sup>3</sup>
Methyl alcohol	—	900 cm. <sup>3</sup>	—	—	
Diethyl carbonate	1200 cm. <sup>3</sup>	—	—	—	—
Diethyl oxalate	400 cm. <sup>3</sup>	150 cm. <sup>3</sup>	—	—	—
Triethanol amine	—	—	—	50 cm. <sup>3</sup>	—
Nitrocellulose	25 g.	25 g.	150 g.	25 g.	50 g.
Application	Spraying	Spraying	Spraying	Electro-phoresis *	Dragging

\* Deposition on anode, British Patent 587039.

## 5. Deposition of the Emission Paste on the Core Metal

When the emission paste has been deposited on the core metal, the solvents evaporate and leave a coating of alkaline earth compounds containing more or less binder-material. The thickness required for this coating depends on the type of cathode. In all cases, however, this thickness must be as consistent and uniform as possible, because the characteristics of the valve containing the cathode depend on the distance between the electrodes and the coating surface and therefore on the thickness of the coating. Furthermore, parts of the cathode having a thickness which is much different from the mean value may give rise to excessive heating and

possibly to destruction of the coating. Since the beginning of the development of oxide cathodes it has therefore been tried to find methods which give a definite and uniform thickness of the coating and which—for economical reasons—make a quick depositing process possible. Four different methods may be used:

- (1) The painting method.
- (2) The dipping method and its technical improvement, the dragging process.
- (3) The spraying by means of a spraying gun.
- (4) The electrophoresis.

The first two methods, which are very similar, will be described together. These methods are mainly applied to directly heated cathodes, while the spraying method is preferably used for indirectly heated ones.

In the earliest methods of deposition, which were described, for example, by Statz,<sup>1</sup> the emission paste was painted on the core metal and dried subsequently. This process was repeated several times until the coating had the necessary thickness. The painting can be replaced by dipping the core wire into the emission paste once or several times, this dipping again being followed by drying. The drying is preferably carried out at higher temperatures, which are produced either by passing current through the core wire or in a suitable furnace, the atmosphere being either air or carbon dioxide depending on the type of core metal and emission paste. If the temperature is high enough the so-called "combined cathodes" may be obtained in which the emission paste reacts with the core metal and forms compounds like platinates or nickelates at the interface. As these reaction products diminish the emission, the core wire was sometimes covered first with a thin coating of an emission paste containing no barium or only a small amount of it. The real coating for emission, being rich in barium, was then deposited on top of the primary coating.\*

These individual methods, which are not suited for mass production of oxide cathodes, very often give non-uniform cathode surfaces (Fig. 13 (a)). Apart from this the combining process is undesirable, as the reaction products formed during this process increase the radiant emissivity of the oxide coating and therefore make the cathode less economical. Attempts have therefore been made very early to develop methods for preparing coated wires and

\* German Patent 565052.

ribbons of any length and to avoid the combining effect by choosing a lower furnace temperature. A continuous coating process was obtained by the dragging method, in which the core wire or ribbon runs through a container with paste and subsequently through a furnace, the total process being repeated several times until the necessary thickness is obtained. Such a method guaranteeing adequate uniformity of thickness and giving a wire which may be bent after being coated was described by Statz<sup>1</sup> in 1927 (cf. Fig. 13 (b)). 80 to 100 metres coated wire per hour could be supplied in this way.

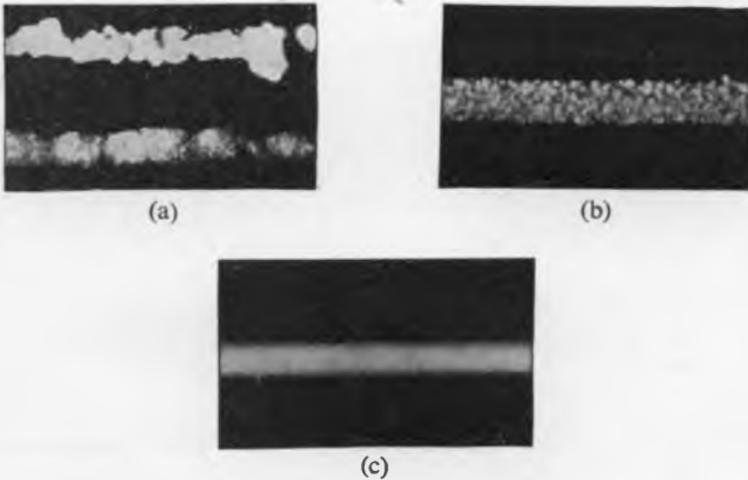


Fig. 13.—Wires Coated by Different Methods: (a) Early Individual Method; (b) Dragging Process of the Early Time; (c) Modern Dragging Process.

The further development of this method was directed not so much towards increasing the capacity, but more towards extending its application to all types of paste and core materials. The number of furnaces was decreased and the method modified in such a way that the total depositing process could be carried out in air.\* By installing suitable devices for controlling furnace temperatures and for measuring the thickness it was made possible for the wires and ribbons to be prepared with the necessary uniformity by less skilled workers. Such an improved coating unit is shown in Fig. 14, while Fig. 13 (c) shows a cathode made in this unit. The temperatures of the furnaces and the speed of dragging, of course, depend on the type of solvents and binders, and values for these which are generally valid can therefore not be given. After having deposited the emission paste and perhaps a protective layer of

organic lacquer on top, the paste is stripped either by hand or machine from the coated wires or ribbons at intervals equal to the length of the cathode. The wires are then cut into pieces and may be built into the valve.

The two methods described may also be applied to indirectly heated cathodes in a slightly modified manner. Coatings which have to be smooth and strong, as for instance those for rectifiers, can be made satisfactorily by such a combined dipping and painting method (cf. Figs. 16 (c), 17 (c), 18 (c), 19 (c)). Usually the indirectly heated cathodes, however, are coated by the spraying method, as is used for instance in painting technique.

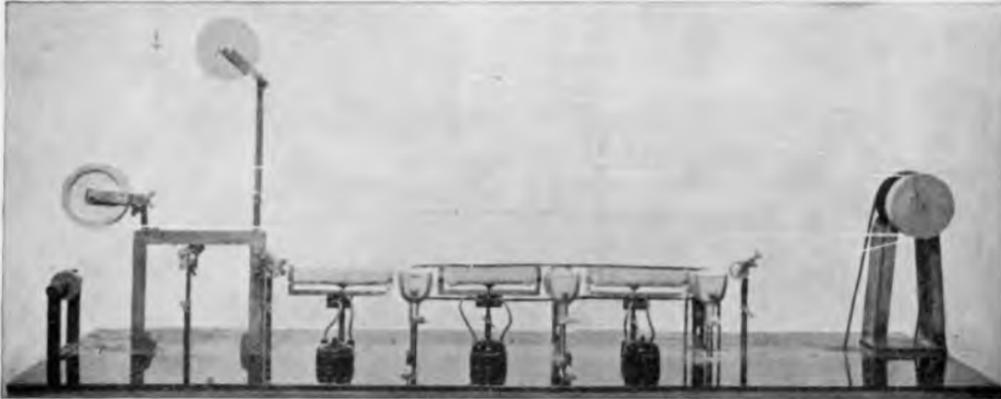


Fig. 14.—Unit for Coating Wires by the Dragging Method (Telefunken, Berlin).

This spraying is carried out in the simplest way by attaching the cathode sleeves to a revolving frame and by passing the spraying gun across the sleeves by hand several times at a constant distance. Such a method, however, is not suitable for obtaining the thickness with the necessary consistency, and the spraying process had therefore to be mechanized considerably. In a method frequently used, the sleeves, fixed in frames, pass between several spraying guns, the spraying beams being directed in such a way that a uniform thickness is obtained. In another method the sleeves are fixed on the edge of a disc where, when revolving, they pass between two spraying guns. In a third method the sleeves arranged in a frame rotate while the spraying gun passes across several times at a constant distance.

A spraying unit for mass production designed for the method

described last is shown in Fig. 15. In addition to the mechanical equipment an exhausting fan for sucking off the solvent vapours must be supplied, because these vapours form explosive mixtures with air. The gases employed for spraying must be dry and must not affect the carbonates chemically. The pressures used are between 15 and 50 lbs./sq. in. The remaining solvents which have not evaporated but have condensed on the sleeve are removed by

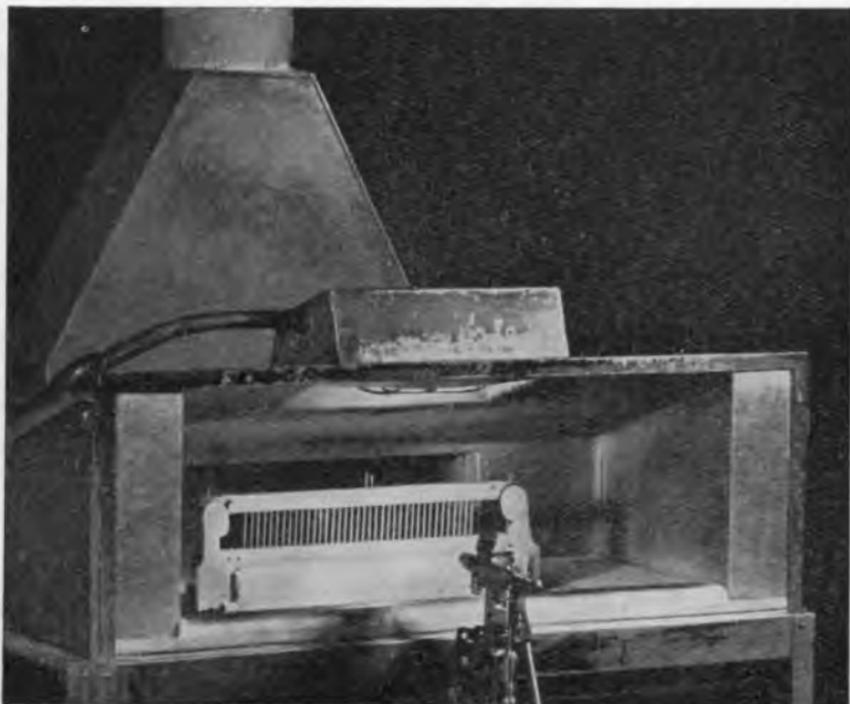


Fig. 15.—Unit for Spraying Indirectly Heated Cathodes (Telefunken, Berlin).

drying either in air or, for solvents with high boiling-point, in an oven.

Both the thickness and the density of the sprayed carbonate coating are important for the practical use of the cathode. The density, which is determined by the volume  $V_p$  of the pores is either measured in  $\text{g./cm.}^3$  (absolute density  $\delta_a$ ) or in  $\text{mg./cm.}^2$  (relative density  $\delta_r = \text{mg. coating weight per } 1 \text{ cm.}^2 \text{ surface area}$ ). The latter value only makes sense if the thickness  $d_c$  of the coating is given simultaneously (normally in  $\mu$ ). The density of normal equimolar carbonates without pores is  $\delta_a \simeq 4$ , and the relations between the

different densities, the thickness and the volume of the pores therefore are:

$$\delta_a = 10 \frac{\delta_r}{d_c}$$

$$\frac{V_p}{V_t} = \left(1 - \frac{\delta_a}{4}\right) 100 = \left(1 - 2.5 \frac{\delta_r}{d_c}\right) 100\%$$

$V_t$  denoting the total volume of the coating.

Volume of pores and density may be influenced considerably by the type of solvents used for the paste. Solvents with high boiling-point evaporate rapidly on the way to the cathode sleeve and therefore produce a very loose coating of carbonates, while solvents with low boiling-point arrive in larger quantity on the sleeve and leave a rather dense coating there. Apart from this the atmospheric conditions (humidity and temperature) existing during the spraying are of importance. Low humidity and high temperature increase the rate of evaporation of the solvents and therefore make the coating looser. Normally solvents with different volatility are used in order to adapt the emission paste to different atmospheric conditions (cf. Table VI). Finally the distance between spraying gun and sleeve and the pressure of the gases employed for spraying must also be taken into account, as these two values together determine the time which the paste needs for passing from the spraying gun to the sleeve.

The volume of the pores of very loose coatings may have values up to 85% ( $\delta_a = 0.6$ ), while in very dense coatings the value may be about 65% ( $\delta_a = 1.4$ ). The differences between the structures of such loose and dense coatings will be seen from Figs. 16 to 18. Fig. 16 shows microphotographs of low magnification, made of carbonate coatings which were sprayed loosely or densely on flat sleeves. The differences in density between these coatings will be seen better still by comparing the stereoscopical shadow images of Fig. 17. These stereoscopical images were obtained by illuminating carbonate coatings sprayed on aluminium foil by X-rays at two different angles of incidence. The images concerned, when viewed by a stereoscope, clearly show the distribution of pores in the interior of the coating, the dark areas in the images representing the regions in which only few carbonate crystals, i.e. many pores, are found.

When manufacturing cathodes commercially the normal density of the coating lies in between the two extreme values shown in

the figures ( $\delta$ , between 3 and 8 mg./cm.<sup>2</sup> for 40 to 100  $\mu$  thickness). Experience shows that a coating packed too densely is inferior in emission to a loose coating, while on the other hand the carbonate or oxide particles of a coating, being too loose, may fall from the cathode and give rise to many faults. If a water paste is used for spraying, the density of the coating is generally chosen slightly larger than when employing a paste of equal particle-size containing a binder.

The thickness of the carbonate coating can be produced within a

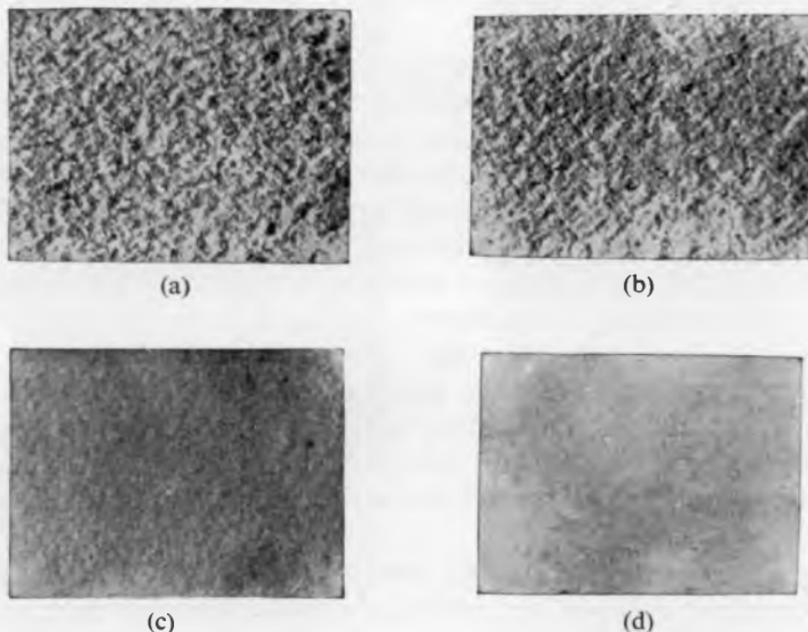


Fig. 16.—Microphotographs of Carbonate Coatings Deposited in Different Ways (mag.  $\times 15$ ): (a) Loosely Sprayed; (b) Densely Sprayed; (c) Deposited by Dipping; (d) Colloidal Carbonates Deposited by Cataphoresis.

few per cent if the composition of solvents and binder, the spraying pressure and the relative movement of sleeves and spraying gun are reproduced with sufficient consistency and if due account is taken of the atmospheric conditions. It may be pointed out that the final thickness of the oxide coating made from the carbonates is smaller, because the coating sinters to a certain degree during the decomposition of the carbonates into the oxides (cf. Sec. 7). Apart from thickness and density of the coating the roughness of its surface sometimes is also of importance. This roughness may be seen from Figs. 18 and 19. The microphotographs of the carbonate

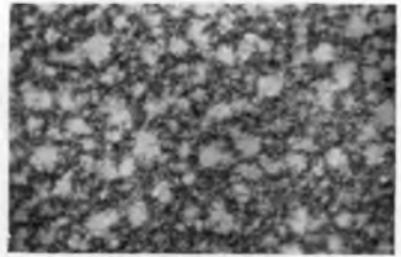
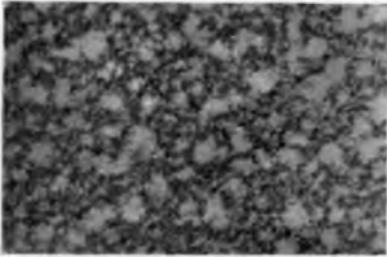
coatings shown in Figs. 18 (a) to (d) (upper images) are made with considerably higher magnification than before ( $\times 100$ ). These photographs are stereoscopical and, if viewed in a stereoscope, give a good picture of the composition of the coating surface. The photographs shown in Fig. 19 were obtained by projecting a narrow slit of light towards the cathode surface, the angle of incidence being  $45^\circ$ . The image so produced was magnified 75 times by a microscope (method of Schmaltz\*). One sees from the two figures, 19 (a) and (b), that the roughness is considerable with all sprayed coatings and is only slightly varied by the type of the spraying method.

A main disadvantage of the spraying method is the large consumption of emission paste resulting from the small ratio between cathode area to be sprayed and cross-section of the spraying beam. This disadvantage does not exist either with the dragging method or with the electrophoretic deposition to be discussed now. The electrophoretic deposition is obtained by immersing the core metal and a second electrode into an emission paste of suitable composition and by applying between these two electrodes a potential which normally is about 10 to 100 volts. The carbonates of the paste are then deposited on one of the electrodes by the electric field, the direction of deposition depending on the composition of the paste. Usually a deposition on the cathode (of the bath) is preferred, so that a negative potential must be applied to the core metal to be coated.

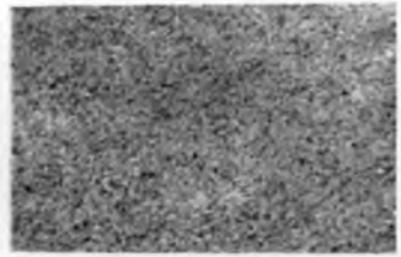
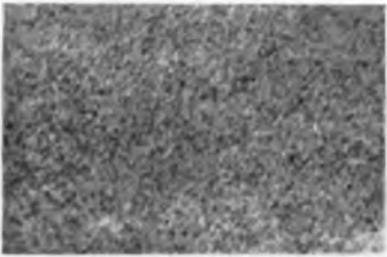
The electrophoresis was first used by Patai and Tomaschek<sup>1,2</sup> for depositing colloidal carbonates; its application, however, is not restricted to colloidal carbonates but may also be extended to emission pastes with normal particle-sizes. The electrophoretic method is especially suitable for coating wires and ribbons in appropriate lengths, because the deposition can easily be stopped by switching off the current. Furthermore, this method makes it possible to produce the thickness of the coating within very small tolerances. This is especially important if very thin coatings are to be made. When using colloidal carbonates with a particle-size of a few hundredths of a micron, coatings of 0.5 to 1  $\mu$  thickness can be produced.

The dependence of the electrophoretic deposition on the type of

\* G. Schmaltz, *Technische Oberflächenkunde*, 1936, p. 73 (Technique of Surfaces).



(a) Loosely Sprayed



(b) Densely Sprayed



(c) Prepared by Dipping

Fig. 17.—Stereoscopic X-ray Shadow Images of Carbonate Coatings Prepared in Different Ways.



Carbonate

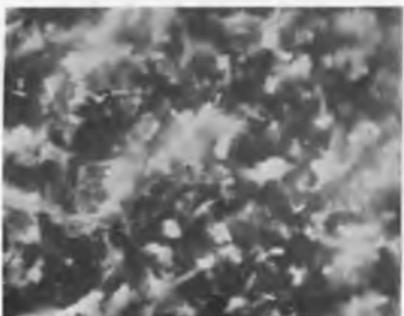


Oxide

(a) Loosely Sprayed



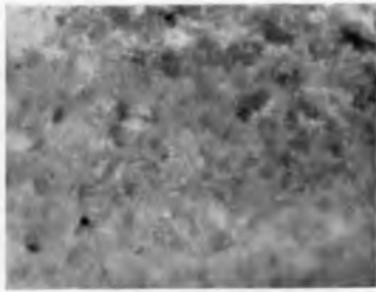
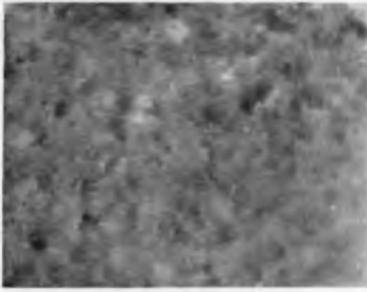
Carbonate



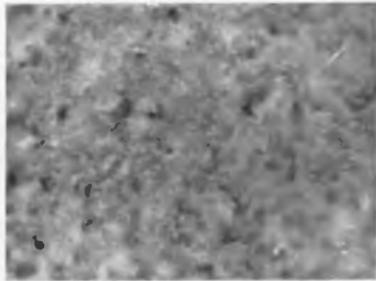
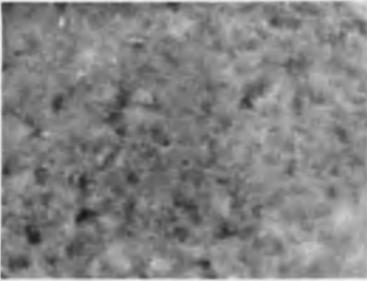
Oxide

(b) Densely Sprayed

Fig. 18 (a) and (b).—Stereoscopical Microphotographs of Carbonate and Oxide Coatings before and after Decomposition (mag.  $\times 100$ ).

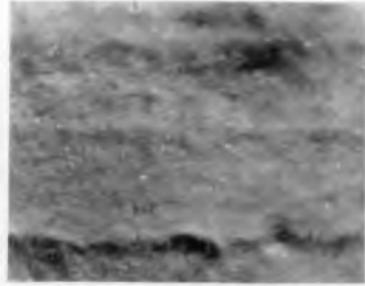
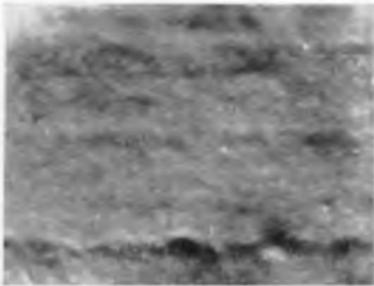


Carbonate

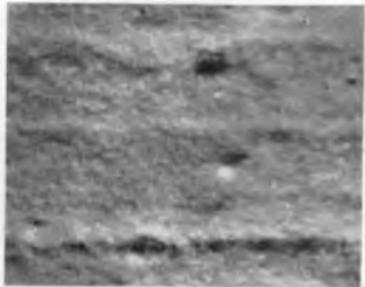


Oxide

(c) Deposited by Dipping



Carbonate



Oxide

(d) Colloidal Carbonates, Deposited by Electrophoresis

Fig. 18 (c) and (d). Stereoscopic Microphotographs of Carbonate and Oxide Coatings before and after Decomposition (mag.  $\times 100$ ).

solvents used for the paste, on the concentration of this paste, and on the voltage applied has been investigated by Hamaker,<sup>1</sup> Benjamin and Osborn,<sup>6</sup> Biguenet and Mano,<sup>2</sup> and Hill, Lovering, and Rees.<sup>1</sup> According to these workers the quantity deposited is proportional to concentration, applied voltage, and time. The accuracy within which this proportionality is obtained may be seen from Fig. 20. As Biguenet and Mano found, the electrophoretic yield (weight deposited per unit of electric charge) decreases with increasing

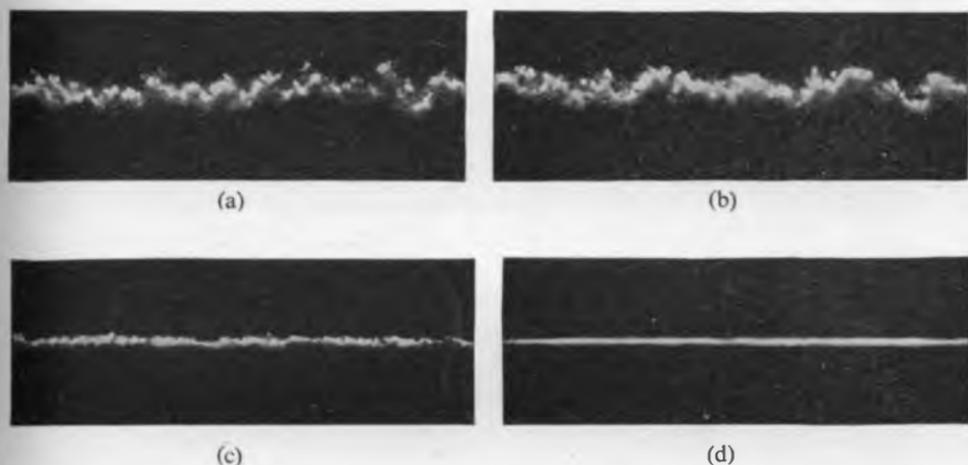


Fig. 19.—Images of Carbonate Coatings Deposited in Different Ways. Obtained by the Method of Schmaltz (mag.  $\times 75$ ): (a) Loosely Sprayed, (b) Densely Sprayed. (c) Deposited by Dipping, (d) Colloidal Carbonates Deposited by Electrophoresis.

temperature of the paste. The organic liquids used for the paste have considerable influence on the yield, amyl alcohol, for example, giving 15 times as much deposit as ethyl alcohol. The bond between the deposited coating and the core metal also greatly depends on the type of liquid. Coatings obtained from methyl alcohol show a very poor bond, while those obtained from acetone or amyl alcohol adhere very well. Impurities in the electrophoretic bath alter the concentration of ions and the conductivity of the bath and so produce considerable differences in the electrophoretic yield which may lead to a change in the direction of deposition. If a binder is added to the bath similar effects are produced (Hill, Lovering, and Rees). Of the different particle-shapes the needles are deposited with a slightly higher yield than the spherulites, but when they are mixed, none of them is deposited preferably. The density of the coatings

obtained by electrophoresis is high and is not very much influenced by the concentration of the carbonates and by the applied voltage.

As the dragging method, the painting method, and the electrophoresis all give a high coating density (cf. Figs. 16 (c) and 17 (c)), the thickness of the coatings so produced is normally chosen smaller than the thickness of the sprayed coatings. Moreover, the methods mentioned give a surface which is considerably smoother than that by the spraying method (cf. Figs. 18 (c) and 19 (c)). The surface becomes especially smooth if colloidal carbonates are used

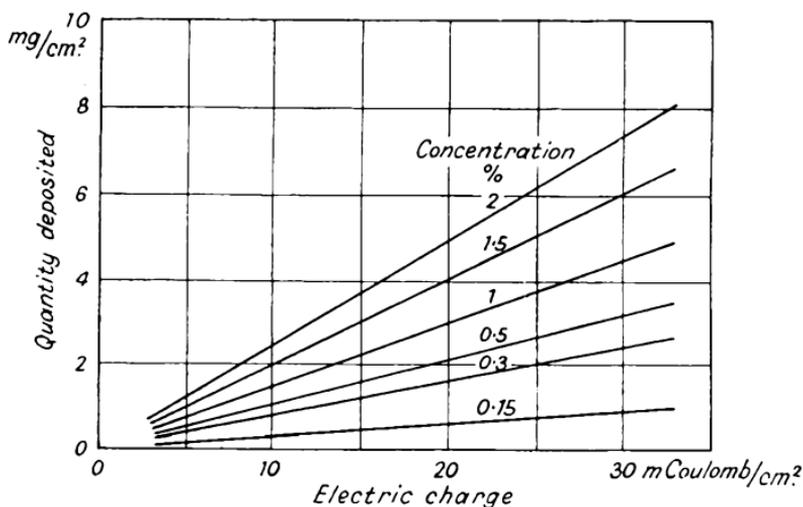


Fig. 20.—Quantity of Carbonates Deposited by Electrophoresis as a Function of Electric Charge supplied ( $V=50$  volts) (Biguenet and Mano 2).

for the electrophoretic process, the surfaces so produced being shown in Figs. 16 (d), 18 (d), and 19 (d).

All methods for deposition described so far, however, give coatings with a pore volume of more than 55% ( $\delta_a \leq 1.8$ ). For some special applications coatings are desired which are more closely packed, and it has therefore been suggested to increase the density of the coating by carrying out the deposition in a centrifuge \*).

The manufacture of the directly heated cathodes, as far as the processes outside the valve are concerned, is finished when the emission paste is deposited. The indirectly heated cathodes, however, must be supplied with the heater, and possibly with some additional insulating parts, before they may be built into the valve.

\* U.S.A. Patent 2433821.

The manufacture and properties of the heater and of the insulation between heater and sleeve will be discussed in the next section.

### 6. Preparation and Characteristics of the Heater of an Indirectly Heated Cathode

The idea of an indirectly heated cathode arose only ten years after the discovery of the oxide cathode.\* The commercial development of this type of cathode, however, only began when mains receivers were first made in larger numbers (Freeman<sup>1</sup>). The emitters in the valves of these receivers had to be separated from the heater circuit in order to avoid influencing the emitted electrons by the electromagnetic field of the alternating heater current. The first indirectly heated cathodes consisted of a nickel sleeve, an insulating twin-bored tube which fitted into the sleeve, and a V-shaped tungsten wire inserted into this tube. The nickel sleeve was sometimes replaced by nickel powder sintered on the insulating tube, the sintered powder being used as core metal for the oxide cathode. Such a "sintered nickel cathode" supplied with a V-shaped or "hairpin" heater is shown in Fig. 21. These types of cathodes had a high heat capacity and therefore had to be heated for the rather long time of one minute or more before reaching their operating temperature. As it was very desirable to shorten this warming-up time the heat capacity had to be reduced by dispensing with the insulating tube and a special type of heater without such a tube had to be developed. Furthermore, the manufacture of sintered nickel cathodes was discontinued because these cathodes could not be made with sufficient accuracy.

The heaters with the desired low warming-up time are made by depositing the insulating material directly on the heater wire; they usually consist of a non-inductively wound helix (reverse helix). If the heater is to be used for higher heater voltages a large quantity of wire must be accommodated within the sleeve. The simple wire used for winding the reverse helix is then replaced by a wire previously formed into a closely wound helix. A reverse double helix is thus obtained, which is manufactured by the same method as the

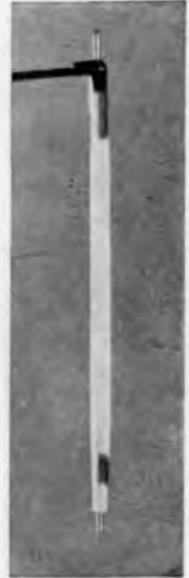


Fig. 21. — Sintered Nickel Cathode with Hairpin Heater.

\* British Patent 6476/1915, German Patent 312044.

double helices used in incandescent lamps, the heater wire being wound on two mandrel wires which are later pulled out or etched out

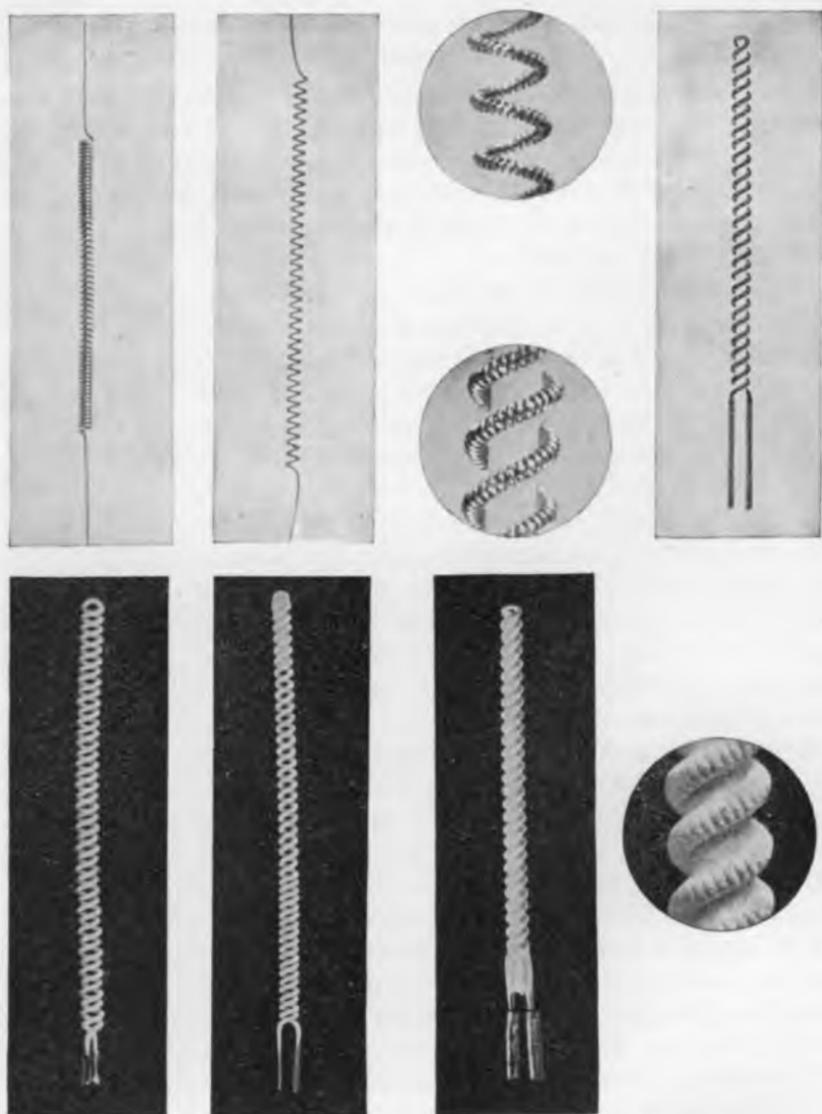


Fig. 22.—Different Types of Heaters (mag.  $\times 3$  in general,  $\times 12$  in the circles).

by acids. In this way heaters for voltages up to 100 volts can be made which fit into sleeves of 1 to 2 mm. diameter and 15 to 30 mm. length.

As the commercial manufacture of such heaters consisting of thin tungsten wires is a difficult process it has been suggested repeatedly that the heater might be made of a massive body of low electrical conductivity, e.g. carbon or sintered corundum.\* The application of semi-conductors for heating cathodes indirectly has also been suggested.†

Fig. 22 shows examples of different heater spirals, some of them uninsulated and some of them after being insulated. Some of these spirals have a variable pitch which gives a more even temperature distribution along the sleeve (cf. Fig. 23). The mechanical strength of the double helices is not sufficiently high to make them self-supporting in the sleeve at the operating temperature. Before coating these heaters with alumina, therefore, an alumina rod is passed down the centre of the helix. This rod, after being attached to the helix by depositing the coating on it, provides support along the entire length.

Another type of heater used is the folded heater, the most simple type of which, the hairpin heater, has been mentioned above. This type of heater is normally made

by first coating the heater wire with insulating material and by subsequently folding this wire once or several times. If larger quantities of wire are to be accommodated a helix instead of a wire can also be used for making this heater. Fig. 24 shows different types of folded heaters. The question whether spirals (helices) or folded heaters are to be used is decided by economical considerations and by the required characteristics of the valve. The folded heater has a larger magnetic field than the spiral and is more prone to insulation and short-circuit faults. As shown by Michael<sup>1</sup> the folded heater also develops more faults during long

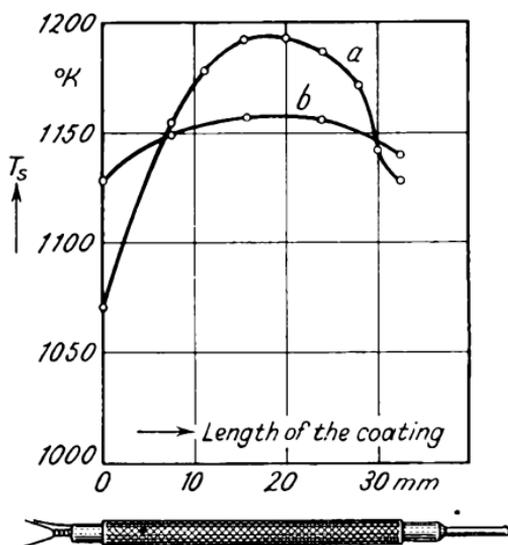


Fig. 23. — Temperature Distribution of a Cathode Sleeve when using (a) Normal Heater Spiral, (b) a Spiral with Variable Pitch.

\* U.S.A. Patent 905119, German Patent 608696, British Patent 346050.

† German Patent 666833.

operation. Moreover, the insulating coating of the folded heater is more exposed to being scraped off by the sleeve than the coating of a spiral. The advantage of the folded heater is its more simple and therefore more economical process of manufacture.

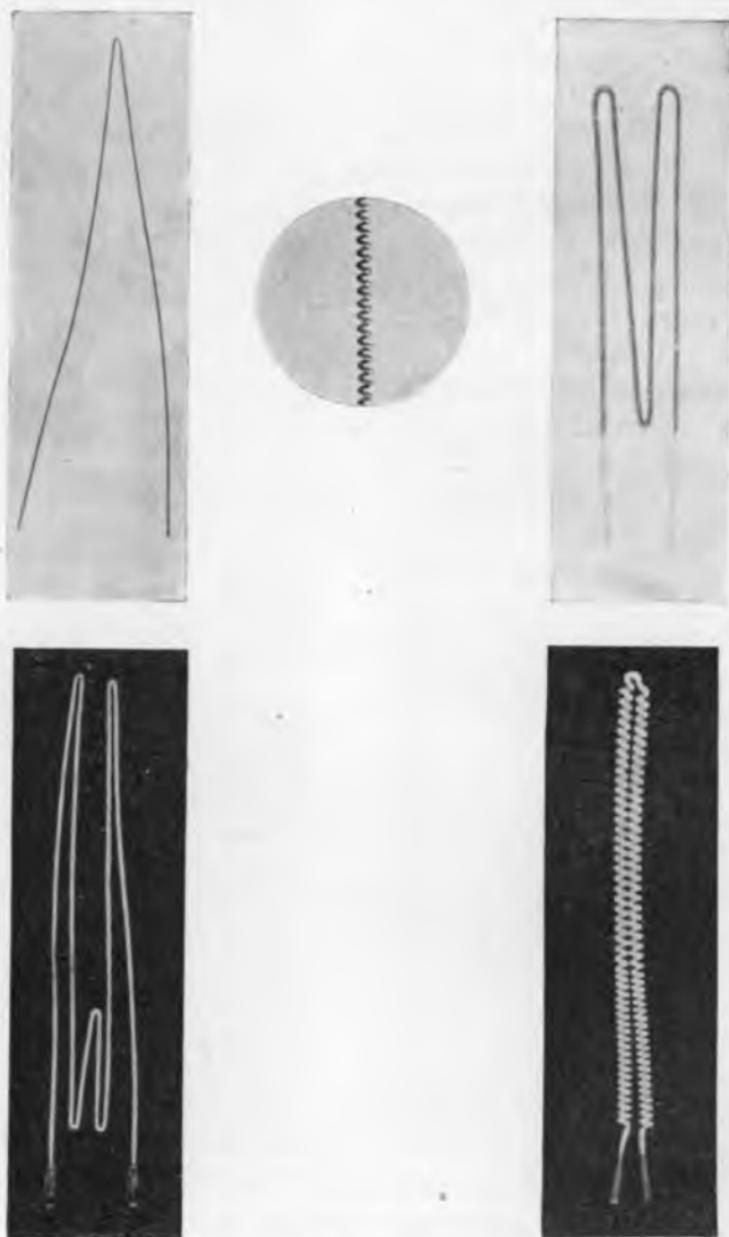


Fig. 24.—Different Types of Folded Heaters (mag.  $\times 2$  to  $\times 4$  in general,  $\times 12$  in the circle).

The material used for the heater wire is mainly tungsten, but alloys of tungsten and molybdenum are also used. These alloys combine a melting-point which is considerably higher than that of pure molybdenum with a ductility which is nearly the same as that of molybdenum; they are therefore easier to be worked than tungsten. The recrystallization properties of tungsten may be improved by adding alumina, silica, or thoria, a well-known technique in the production of electric lamps.

The insulating coating must be made of a material which guarantees a high insulation between heater wire and sleeve at the operating temperature, this high insulation being necessary for circuit reasons. In the U.S.A. the insulating tubes of the early time were made of porcellaneous materials (Allen <sup>1</sup>). The insulation of these materials, however, was insufficient and they were therefore replaced by pure magnesia or sometimes silica. In Germany tubes of pure magnesia were used from the beginning. As magnesium oxide is reduced by the hot tungsten wire, magnesium metal evaporates from such insulating tubes and produces faulty valves. In order to avoid this the heater wire was coated with alumina before being inserted into the magnesia tube. It was known at that time that the insulation of alumina is better than that of magnesia, but tubes of alumina could not be made commercially. On the other hand, methods were found for depositing alumina directly on the tungsten wire and it was thus possible to omit the insulating tube and to make the modern heaters with considerably smaller warming-up time. Today alumina is used almost exclusively, but beryllium oxide may be added for further improving the insulation (cf. Fig. 25).

The quality of the insulation between heater and sleeve (heater-cathode insulation) depends on purity and particle-size of the alumina. As described by Benjamin, Cosgrove, and Warren,<sup>4</sup> impurities such as alkali, alkaline earth, iron, and manganese oxides impair the insulation considerably. The alumina for the heaters is therefore purified carefully, as was for instance described by Bidgood and Kent.<sup>1</sup> These latter authors also examined the influence of particle-size on the mechanical properties of the insulating coating. They find that coarse particles give soft coatings which may be scraped off easily, but yield if the wires are bent. Fine particles, on the other hand, produce a brittle enamel-like coating which may cause breaking of the wire, when this is bent. The optimum particle-size is given as 15  $\mu$  on the average.

Before being deposited on the heater, the insulating material is

mixed to a paste in the same way as the emission carbonates. For improving the adherence to the heater either organic binders or aluminium nitrate are added. The solvents used for the paste depend very much on the method of deposition and on the type of heater (cf. Table VII). Helical heaters are coated either by spraying or by electrophoresis. The coated heaters are then fired in hydrogen at temperatures between 1800° and 2000° K., the insulating coating being sintered on the heater in this way.

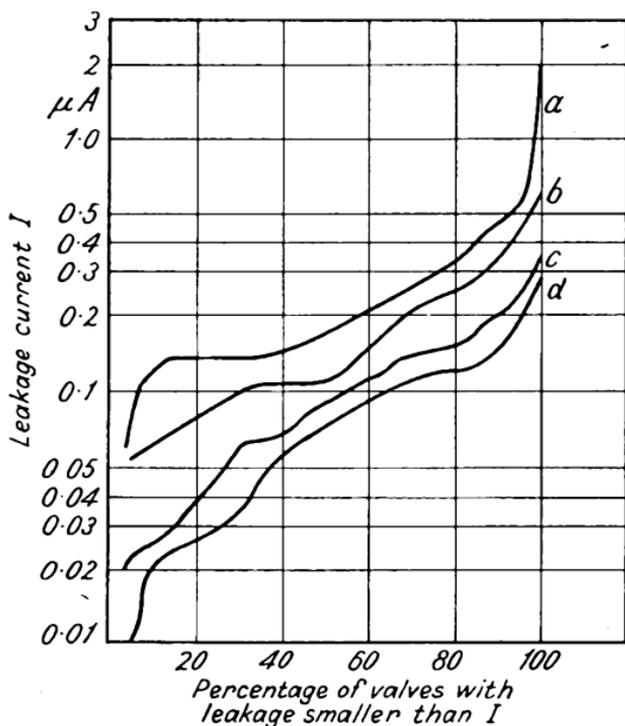


Fig. 25.—The Influence of Different Insulation Materials on Heater-Cathode Insulation: (a) Alumina, (b) Purified Alumina, (c) Alumina Pre-sintered at 2025° K., (d) Alumina with 1% Beryllium Oxide (Benjamin, Cosgrove, and Warren<sup>4</sup>).

When making folded heaters, the heater wire may be coated either before or after being folded into the final shape (cf. O'Neill<sup>1</sup>). In the first case the coating can be done continuously either by a dragging method or by an electrophoretic process, the details of the two methods being described by Bidgood and Kent.<sup>1</sup> If the dragging method is used, the equipment is very similar to that for directly heated cathodes; it consists of several sub-units, each of them having a container for deposition and an adjacent small furnace. Modern devices use reversing spools, by means of which

TABLE VII

*Insulating Pastes*(According to Biguenet,\* Bidgood and Kent,<sup>†</sup> Brit. Pat. 587039.)

	I	II	III	IV
Alumina	1000 g.	1000 g.	1000 g.	1000 g.
Aluminium nitrate	—	—	—	300 g.
Silica	—	30 g.	—	—
Amyl acetate	1800 cm. <sup>3</sup>	—	170 cm. <sup>3</sup>	—
Methyl alcohol	1250 cm. <sup>3</sup>	—	3100 cm. <sup>3</sup>	—
Acetone	—	10000 cm. <sup>3</sup>	—	—
Triethanolamine	—	140 cm. <sup>3</sup>	—	—
Nitrocellulose	50 g.	70 g.	25 g.	—
Distilled water	—	—	—	1000 cm. <sup>3</sup>
Application	Spraying	Electro- phoresis. †	Electro- phoresis.	Dragging

\* Ch. Biguenet, *Les Cathodes Chaudes*, Paris, 1947.

† Deposition on anode.

the wire is passed through the same containers and an appropriate furnace up to 18 times. The temperature during the coating process must be controlled very accurately, as too high a temperature makes the tungsten wire brittle or produces a very hard coating which causes breaking of the wire when this is bent. On the other hand, too low a temperature produces a coating which is too soft and which may be scraped off when the heater is inserted into the sleeve.

After being coated in this manner, the wire is preformed by means of suitable devices, and the insulation paste is stripped from those places where the ends of the heaters will be located. Finally the wire is cut to the required length. The properties of the insulating coating are especially important during these processes. A very hard coating, as mentioned above, may cause breaking of the wire, while too soft a coating may be rubbed off during forming. Furthermore, the soft coating is difficult to remove completely from the heater ends.

The formed and cut heaters are fired in hydrogen at about 1100° K. before being folded by hand into their final sharply bent shape. During the latter process the coating breaks off at the kinks. For removing these faults each heater is dipped into a bath of insulating paste and the faulty spot is made good by electrophoretic deposition. The insulating paste is automatically deposited only at those spots at which an adequate current can flow. The heater is finally protected by coating it with an organic lacquer.

It will be convenient now to describe the characteristics of the indirectly heated cathode as far as they are related to the heater. The heater-cathode insulation of the processed valve depends on:

- (1) the type and purity of the insulating material;
- (2) the temperature of heater and sleeve;
- (3) the kind and value of the voltages applied between cathode and heater during decomposition (Sec. 7) and activation (Sec. 8);
- (4) the polarity and magnitude of the voltages applied between heater and sleeve during operation of the cathode.

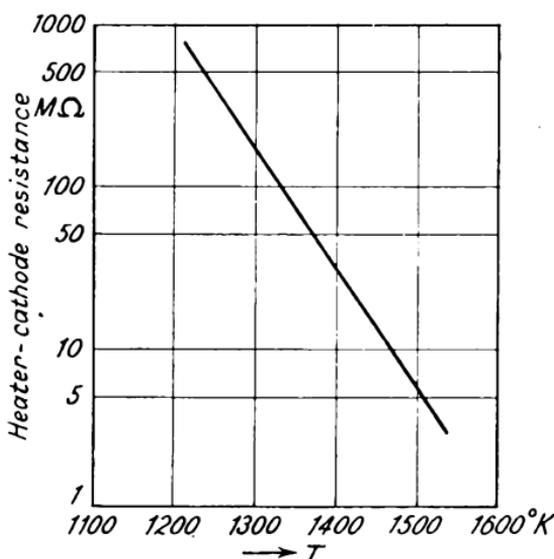


Fig. 26.—Heater-Cathode Resistance as a Function of Heater Temperature (Benjamin, Cosgrove, and Warren <sup>4</sup>).

The influence of type and purity of the insulating material will be seen from Fig. 25, which gives a distribution curve for the leakage current of commercial valves.

Due to the negative temperature coefficient of the insulating resistance, the insulation is the better the lower the temperature of the heater (cf. Fig. 26). For this reason the modern cathodes having no special insulating tube show a better insulation than the older ones which were supplied with such tubes.

During the further manufacture the choice of D.C. or A.C. voltages applied between heater and sleeve influences the final value of the insulation differently. For obtaining an optimum heater cathode insulation, a suitable selection of these voltages is of considerable importance.

Fig. 27 shows how the insulation current depends on polarity and value of the voltage if different heater voltages are used. The

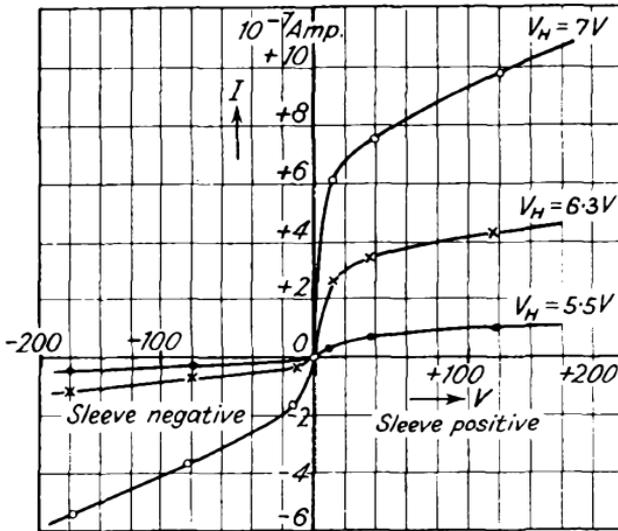


Fig. 27.—Current Voltage Characteristic of the Heater-Cathode Insulation at Different Heater Voltages.

saturation of the insulation current, as seen from this figure, is due either to an electron emission from the sleeve or the heater, or to polarization phenomena. Graffunder<sup>1</sup> examined by means of a

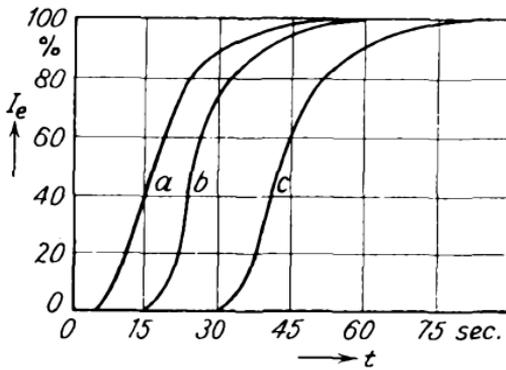


Fig. 28.—Warming-up Time of Different Types of Indirectly Heated Cathodes ( $P_h=2.5$  watts): (a) Simple Reverse Helix, (b) Reverse Helix on Insulating Rod, (c) Reverse Helix with Insulating Rod and Insulating Tube.

cathode-ray tube the connection between low insulation faults and their effects in the valve (e.g. insulation hum). It may be concluded from the polarization phenomena found by him that the current through the insulating coating is partly electrolytic.

The time between switching on the cathode and reaching full emission is, of course, much longer for an indirectly heated cathode than for a directly heated one, due to the much larger heat capacity of the former cathode. The warming-up time is mostly defined as the time between switching on the cathode and reaching half the final emission current. This time depends very much on the type of heater, as will be seen from Fig. 28. The warming-up time can be shortened by an initial overheating of the heater, which is released after a certain time or after reaching a certain emission current.

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## CHAPTER 3

### FURTHER PROCESSING OF THE CATHODE AFTER MOUNTING IN THE ENVELOPE

After having finished the processes described above, the oxide cathode is built into a valve assembly together with the other electrodes. When this assembly has been sealed into a glass bulb or welded into a steel envelope the valve so obtained is ready for pumping. During the pumping process the valve envelope and the electrodes must be degassed by heating them at temperatures which are higher than those of normal operation. At the same time the alkaline earth carbonates must be converted into the respective oxides by heating the cathode. Various names have been given to the heat processing of the cathode which is necessary for achieving this: the process will be called decomposition in this book. This process, as will be shown later, is normally followed by a second one necessary for producing the final operating state of the cathode. This second process will be called activation.

In almost all cases the decomposition is carried out during pumping, because the carbon dioxide resulting from the decomposition of the carbonate must be removed. The activation may also be undertaken on the pump, but it is normally done in the sealed-off valve because the better vacuum which exists after sealing off is more favourable to this process.

#### **7. The Decomposition of the Alkaline Earth Carbonates into the Oxides**

In considering the decomposition process the chemical equilibrium between the alkaline earth carbonates, the corresponding oxides, and the resulting carbon dioxide as given by the formula



must be examined. Such an equilibrium, as is well known, is determined by the dissociation pressure, that is, the pressure at which the resulting carbon dioxide is in equilibrium with the carbonate and the oxide. This dissociation pressure as a function of temperature has been plotted in Fig. 29 for the three alkaline earth

carbonates which are commercially important. It will be seen from these curves that for constant temperature the dissociation pressure of barium carbonate is always lowest and that this pressure is therefore decisive for selecting the dissociation temperature of commercial oxide coatings.

The carbon dioxide pressure existing in the valve during decomposition does not depend on size and temperature of the cathode only, but also on the exhausting speed of the vacuum pump employed, on the diameter of the pumping tubes, and on the volume of

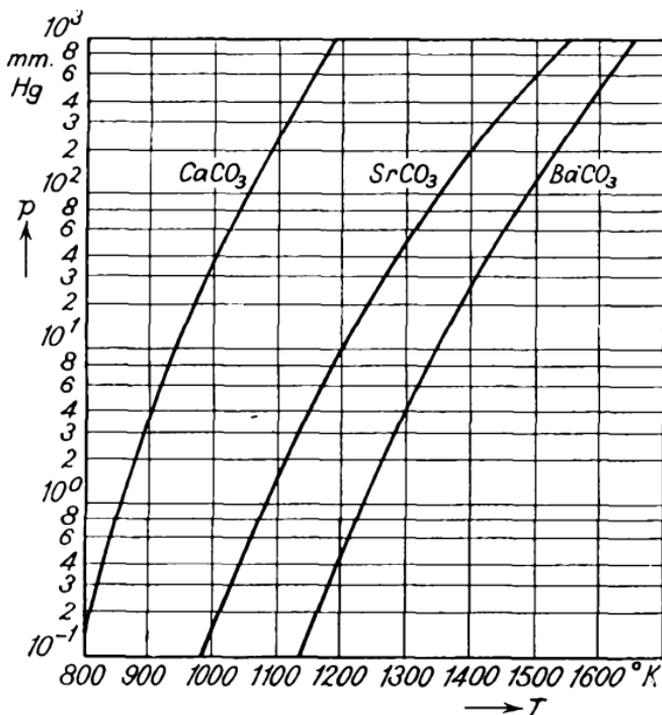


Fig. 29.—Dissociation Pressure  $p$  of Alkaline Earth Carbonates as a Function of Temperature (Finkelstein,<sup>1</sup> Smith and Adams,<sup>1</sup> Tamaru and Siomi.<sup>1</sup>)

the valve. In mass production the valves are mainly pumped by means of pumping machines consisting of a rotating disc on which the valves are automatically moved from the initial pumping stages to the final stages supplying the necessary good vacuum. The necessary processes, such as heating the cathode, degassing the glass bulb and the electrodes, and evaporating the getter, are also carried out automatically on these machines. The vacuum during the decomposition of the carbonates, as measured on these pumping machines, is between  $10^{-1}$  and  $10^{-3}$  mm. A temperature of  $1150^{\circ}\text{K}$ . would therefore be adequate for decomposing the barium carbonate.

For practical pumping, however, it will be important that the pumping time is as short as possible and that the total amount of carbon dioxide is given off as quickly as possible. The decomposition time which is necessary for converting all the carbonate into oxide will not only depend on the temperature of the cathode but also on the properties of the pumping unit. In addition to this, this time depends on the particle-size of the carbonates, on the type of binder in the paste, and, to a certain extent, on the method of deposition.

The decomposition time may be measured by two different methods. If the first method is used, the gas pressure during decomposition is measured directly in the bulb containing the cathode

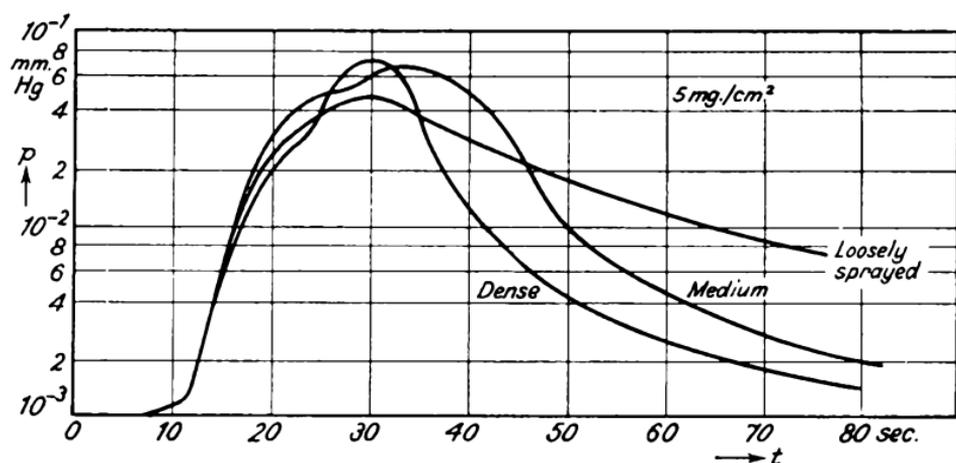


Fig. 30.—Curves showing the Decomposition of Carbonate Coatings of Different Density, obtained by Measuring the Pressure  $p$  of Carbon Dioxide as a Function of Time.

by means of a quickly responding gauge (e.g. Pirani). On the other hand, the carbon dioxide given off may be pumped by means of a diffusion pump into a container which was previously evacuated. The increase in pressure measured in this container then gives a measure for the quantity of carbon dioxide. Only relative values of the decomposition time are obtained by the two methods due to the influence of the properties of the pumping unit. It may be pointed out in this context that the pumping stem of the valve must also be taken into account, as it influences the pumping speed considerably. The measurement of the decomposition time must therefore be carried out with the same stem diameter as is used in practice.

Fig. 30 shows some decomposition curves obtained by the first

method for cathodes with different coating densities. When taking these curves the heater current was kept constant, this procedure being nearest to the conditions in practical pumping. The thickness of the carbonate coating was varied in such a way that the weights of all the coatings were the same. As seen from the curves the decomposition time increases with decreasing coating density. This means that in spite of their closer packing the particles of carbonate in a dense coating give off their carbon dioxide easier than the agglomerations in a loose coating. This may be explained by the fact that the heat conduction from the core metal to the outer parts of the coating is lower in the second case (cf. the X-ray photographs of Fig. 17 (a) and (b)).

While the decomposition time as shown above depends considerably on the method of deposition which determines the density of the coating, the particle-size and the type and quantity of binder in the emission paste have less influence. The influence of particle-size will be seen from Table VIII, giving measurements by Benjamin, Huck, and Jenkins <sup>5</sup> for three different carbonate compositions.

TABLE VIII

*Decomposition Time of Alkaline Earth Carbonates of Different Particle-size (Benjamin, Huck, and Jenkins <sup>5</sup>).*

Composition of carbonates	Particle-size ( $\mu$ )	Decomposition time (arbitrary units)
Ba, Sr, 50 : 50 mol. %	3	94
	50	100
Ba, Sr, Ca, 56 : 31 : 13 % by weight	7	86
	100	94
Ba, Ca, 50 : 50 mol. %	3	81
	10	81

The desired short decomposition time can only be obtained by heating the cathode to a rather high temperature. On the other hand, there are many reasons against applying too high a temperature during decomposition. One will therefore expect that there is an optimum temperature for decomposition and that a minimum decomposition time per mg. of carbonates is determined by this temperature. The reasons against raising the temperature too high during decomposition are as follows:

(1) The melting-point of the core metal must not be approached too closely.

(2) Evaporation of the core metal may produce faults by contaminating the coating or the insulating parts of the valve.

(3) The more volatile barium oxide evaporates preferentially from the mixture of barium and strontium oxides which is normally used. The concentration of barium oxide in the coating is thus diminished, the composition of the coating approaches more and more that of pure strontium oxide which emits much less efficiently, and the emission current of the cathode decreases correspondingly. Fig. 31 shows the decrease in emission obtained in this way by Benjamin and Rooksby.<sup>1</sup> One sees from this curve that a considerable decrease in emission due to preferential evaporation of barium oxide is obtained if the cathode is heated at a temperature of

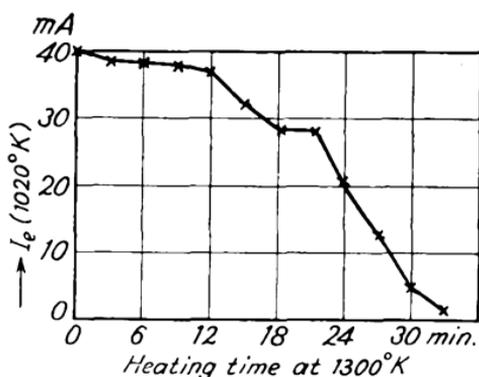


Fig. 31.—Decrease of the Emission Current of a [BaSr]O Cathode during Heating at 1300° K. (Benjamin and Rooksby).

1300° K. for about half an hour. The detrimental effect of heating the cathode to a higher temperature than absolutely necessary is thus demonstrated. In addition to this the barium oxide evaporating from the coating activates the electrodes surrounding the cathode and gives rise to an undesirable thermal grid emission (cf. Sec. 8).

(4) The crystal structure of the oxide crystals arising during decomposition is unfavourably influenced by too high a decomposition temperature and the production of excess barium is thus rendered more difficult.

(5) If directly heated cathodes are used the danger of burning out the filament is increased.

(6) With indirectly heated cathodes too high a decomposition temperature may impair the insulation between heater and cathode sleeve.

The decrease in decomposition time with increasing cathode

temperature can be seen from Fig. 32, which shows the carbon dioxide pressure measured for different temperatures in the manner described above. Theoretically a minimum decomposition time must be expected, given by the properties of the pumping unit, especially by the diameter of the pumping stem. This theoretical value, however, is difficult to obtain experimentally, because it is of the same order as the time which is necessary for heating an indirectly heated cathode up to the decomposition temperature.

The decomposition temperatures used in practice are between  $1350^{\circ}$  and  $1500^{\circ}$  K., the decomposition times for 1 mg. of carbonates, deposited by spraying, ranging from 20 to 50 seconds. One can

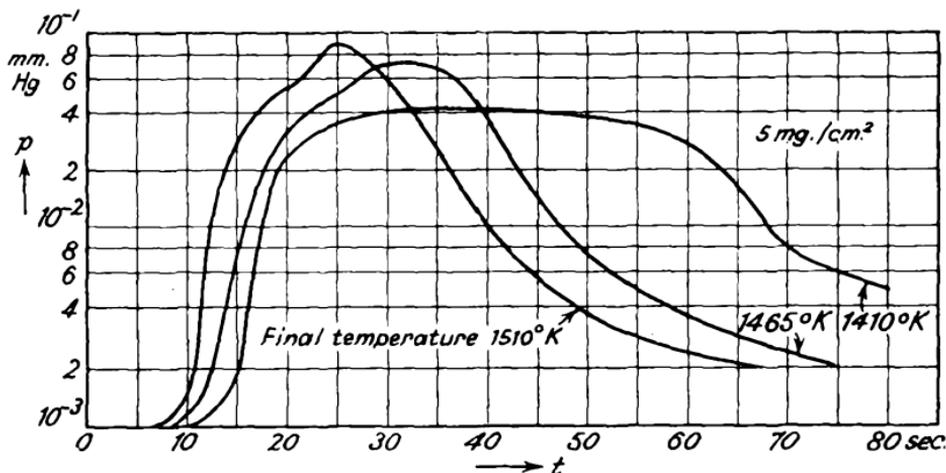


Fig. 32.—Decomposition of Carbonate Coatings at Different Cathode Temperatures (curves obtained as in Fig. 30).

give the rough rule that the maximum heater voltage applied during the decomposition should be between 200 and 225% of the normal operating voltage.

When estimating the necessary pumping time resulting from these values, it must be borne in mind that the cathode must not be heated up to the decomposition temperature at once. Such a procedure, producing considerable temperature differences along the cathode, may cause a cracking of the coating. The cathode therefore is normally heated up in several stages to the highest temperature needed. The total decomposition times thus obtained are between 1 and 5 minutes for the indirectly heated cathodes of receiver valves, while they may be up to 15 minutes for larger cathodes as used in transmitting valves.

Before considering the further treatment of the cathode it seems

to be desirable to discuss in detail the crystallographical processes occurring during the decomposition. These processes have been investigated by means of X-ray patterns and by the emanation method introduced by Hahn.

Investigations by X-rays were undertaken by Eisenstein,<sup>1</sup> who examined pure barium carbonate, pure strontium carbonate, and the mixed carbonates. The crystal-size of these carbonates as obtained from the X-ray patterns was  $0.03 \mu$ , while the average particle-size measured under the microscope was about  $3 \mu$ . When heating these carbonates at  $775^\circ \text{K}$ . Eisenstein observed a growth of both crystals and particles. After several hours' heating time some crystals had grown to more than  $10 \mu$ , while the average particle-size had simultaneously increased to twice the original value, the increase being highest for the particles consisting of mixed carbonates. It follows from this result that the particles which initially consist of a large number of crystals are mostly composed of only one crystal after being heated. When heating at  $875^\circ \text{K}$ . the time necessary for the growth of the crystals and particles was only about 15 minutes.

TABLE IX

*Crystallographic Processes during the Decomposition of Mixed Barium-Strontium Carbonates (Eisenstein<sup>1</sup>).*

Time of treatment (min.)	Maximum temperature (brightness)		Pressure (mm.)	Results	Crystal-size ( $\text{\AA}$ , $10^{-8} \text{cm}$ .)
	( $^\circ \text{C}$ .)	( $^\circ \text{K}$ .)			
60	450	720	$10^{-7}$	No physical or chemical change in carbonate coating.	250
1	600	870	$10^{-5}$	No change	—
3	700	1010	$5 \times 10^{-4}$	Growth in carbonate crystal size.	—
2	740	1010	$>10^{-3}$	Crystal growth, first SrO lines present.	—
2	795	1065	$>10^{-3}$	BaCO <sub>3</sub> and SrO	—
4	810	1080	$<10^{-6}$	BaO and SrO	135-180
30	800	1070	$10^{-7}$	[BaSr]O	180
120	800	1070	$10^{-7}$	"	190
5	850	1120	$10^{-7}$	"	—
5	890	1160	$10^{-7}$	"	—
5	940	1210	$10^{-7}$	"	220
5	1000	1270	$10^{-7}$	[BaSr]O (large crystals).	—
5	1050	1320	$10^{-7}$	[BaSr]O (very large crystals).	up to 100,000.

The decomposition of mixed barium-strontium carbonates ( $[\text{BaSr}]\text{CO}_3$  in equimolar proportions sprayed on a nickel sleeve with  $10 \text{ mg./cm.}^2$ ) was examined according to the scheme shown in Table IX giving the results of the investigation. It was found that at first the strontium carbonate existing within the mixed carbonates is converted into the corresponding oxide, while the barium carbonate remains unchanged and is only converted some time later. When the decomposition is finished, the two oxides ( $\text{BaO}$  and  $\text{SrO}$ ) exist in separate phases in spite of the fact that mixed crystals of carbonates have existed before. The mixed oxide crystals  $[\text{BaSr}]\text{O}$  are only obtained by further heating.

If a mechanical mixture of the two carbonates is used instead of the mixed crystals, much higher temperatures and longer times must be employed after finishing the decomposition in order to obtain the mixed crystals. This was first shown by Burgers<sup>1</sup> and Benjamin and Rooksby<sup>2</sup> and their results are given in Table X. One sees from this table that very high temperatures would be necessary if mixed crystals were to be produced from a mechanical mixture in a reasonable time.

TABLE X

*Times Necessary for Forming Mixed Crystals by Heating the Cathode at Different Temperatures (Burgers<sup>1</sup>)*

Temperature		Time
(° C.)	(° K.)	(min.)
930	1200	195
1130	1400	20
1230	1500	5

The size of the oxide crystals depends on the type of carbonates used. The mixed carbonates give smaller oxide crystals ( $135\text{--}180 \text{ \AA.}$ ) than the single carbonates ( $240\text{--}325 \text{ \AA.}$ ). The oxide crystals only grow when heated to higher temperatures. The largest dimensions observed were up to  $10 \mu$ , which means that an oxide particle consisted of one crystal only.

Eisenstein tried to influence the size of the oxide crystals by a pretreatment of the carbonates or by suitable variations in his decomposition schedule, but without any success. It may be concluded from this that the size of the oxide crystals is independent of the size of the carbonate crystals and particles. The final size of the oxide crystals seems to depend only on the maximum

temperature which the cathode reaches during manufacture or during life.

The second possibility for observing crystallographical processes, the emanation method, was used for alkaline earth carbonates by Zimens<sup>1</sup> and Kallweit.<sup>1</sup> When employing this method, radioactive atoms which give off emanation are built into the crystals to be examined. Only a certain fraction of the emanation given off by those radioactive atoms can diffuse to the outside of the crystals. The magnitude of this fraction, which is called the emanation strength, depends on the size of the crystals and on the degree of disorder in the structure of the crystals. The emanation strength can be measured by the usual radioactive methods, and such a measurement may give evidence of the amount of irregularities in the crystals concerned. An especially high increase in emanation strength is observed when the structure of the crystals changes from one type to another, as the emanation can diffuse to the outside at an exceptionally high rate during such a conversion process. If the emanation strength of alkaline earth carbonates is measured as a function of temperature, such changes in structure may be detected and the decomposition into the oxides may be checked in the same way.

Thorium X, which is an isotope of radium and the carbonate of which is isomorphic with the alkaline earth carbonates, was used as radioactive material in the investigations of Zimens and Kallweit. This thorium X may be built into the alkaline earth carbonates during the precipitation without difficulty. The results obtained by the emanation method agree with those found by the X-ray examinations. The details of the crystal structure of alkaline earth carbonates and their mixtures are given in Vol. II, Sec. 18.

When the coating is made of pure  $\text{BaCO}_3$  the decomposition must be carried out more slowly than when using the usual mixtures with  $\text{SrCO}_3$ . This is necessary, as during the decomposition of pure  $\text{BaCO}_3$  an intermediate compound is formed which has a relatively low melting-point. If the melting-point of this compound is exceeded before most of it is converted into the real oxide, the compound concerned falls from the cathode in drops. Probably this intermediate compound is identical with a basic carbonate  $\text{BaO} \cdot \text{BaCO}_3$  which is formed during the decomposition of pure  $\text{BaCO}_3$ , according to Boeke<sup>1</sup> and Finkelstein,<sup>1</sup> and which has a melting-point of about  $1175^\circ \text{K}$ . This undesirable property of pure barium carbonate brought about the introduction of mixtures

of barium and strontium carbonates in the early years, while their better emission properties were only found later.

When decomposing the cathode, the carbon existing in the organic binder of the emission paste must be removed from the coating. The binder decomposes at some hundreds of degrees centigrade, and the remaining carbon then gives a grey colour to the carbonates of the coating. This carbon is normally removed by the carbon dioxide, which oxidizes the carbon by forming carbon monoxide. The oxidation process is determined by the chemical equilibrium between  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{C}$ . It can be calculated from the equilibrium constant that the equilibrium pressure of  $\text{CO}$  is more than  $10^4$  times larger than that of  $\text{CO}_2$ , if the total pressure is about  $10^{-1}$  mm. and if the temperature is higher than  $1000^\circ \text{K}$ . The equilibrium therefore favours the oxidation of the carbon, which is normally complete due to the excess of carbon dioxide. When the removal is completed the radiant emissivity of the coating decreases considerably, and if the heater power remains constant, a visible increase

in temperature is thus produced. A further increase in temperature is obtained at the end of the decomposition owing to the cessation of heat convection through the carbon dioxide. Fig. 33 shows the variation of temperature and pressure during the decomposition of an indirectly heated cathode. The first increase in temperature occurs during the warming-up of the cathode and is therefore not seen in the figure, while the increase which is produced by the cessation of heat convection definitely coincides with the decrease in pressure due to the end of decomposition.

Another point to be mentioned is the sintering of the carbonates occurring during the decomposition. The degree of sintering determines the final thickness of the oxide coating, the knowledge of which is necessary for determining the characteristics of valves using oxide cathodes. The degree of sintering depends on the decomposition temperature, the crystal-size of the carbonates (precipitation

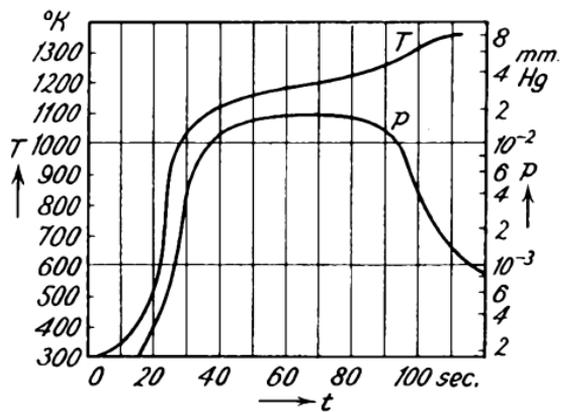


Fig. 33.—Variation of Cathode Temperature  $T$  and Gas Pressure  $p$  during Decomposition.

method), and on the original density of the coating (deposition method). Under normal conditions the degree of sintering is between 15% and 30%. The structure of the cathode surface is not changed by the sintering process, as will be seen by comparing the upper and lower images of the image groups in Fig. 18 referring to different methods of deposition. Consequently the roughness of the surface also remains unchanged during decomposition. Changes in the structure of the surface are only observed if the oxide coating cracks, but this is always due to faults in the method of manufacture.

When working with oxide cathodes experimentally, one may observe that the colour of the oxide coating turns grey, especially if greased ground-joints or stop-cocks are used in the pumping equipment. This grey colour originates from a deposit of carbon which is produced by the dissociation of hydrocarbons. As the radiation and emission properties of such cathodes are entirely different from normal ones, these cathodes are not suitable for the investigation of properties of the normal cathodes. This fact may be mentioned, as it has sometimes not been accounted for (cf. Vol. II, Sec. 31.3).

### 8. The Activation of the Cathode

After decomposition and sealing off the valve, the cathode normally gives a reasonable emission current at the operating temperature. This current, however, varies from valve to valve and is not stable during the operation of any one valve. Consequently a further treatment of the sealed-off valve is necessary in order to produce an emission current which is invariable and sufficiently high. This treatment will be called activation of the cathode (the name "ageing" is also used for this process).

Two processes which are fundamentally different must be distinguished in considering the activation of commercial valves:

- (1) The production of an adequate quantity of excess barium built into the oxide coating, enabling the coating to emit at a given heater power an electron current which is as high as possible.
- (2) The removal of residual gases from the electrodes surrounding the cathode, especially gases which might impair the cathode and diminish its emission during operation.

The early investigators thought that for the first process, the production of excess barium, an electrolytical treatment of the oxide

coating was absolutely necessary. Their opinion is valid for the combined cathodes used at that time. If these cathodes were heated to a high temperature and an anode voltage was applied, an emission current was measured which was very small initially but which increased slowly. This increase may be explained by the assumption that the emission current flowing through the oxide coating dissociates the alkaline earth oxides electrolytically into barium and oxygen. Oxygen then escapes and excess barium is so produced. This treatment, which is called activation by drawing current or forming, is no longer absolutely necessary with the uncombined cathodes which are used now. A high emission current can be obtained from these cathodes by only heating them to a high temperature without drawing any current. According to the present concept the excess barium during this process is produced by a reduction of barium oxide, and this type of activation is therefore called activation by reduction. The reducing agent may be either the carbon originating from the dissociation of the binder, or the carbon monoxide obtained by the dissociation of carbon dioxide, or the core metal itself (cf. Vol. II, Sec. 29). All these reduction phenomena, of course, are possible only with uncombined cathodes. In the combined cathodes all reducing agents are oxidized during the combining process, and activation by drawing current is therefore absolutely necessary. This shows why the early investigators thought that activation by electrolysis was the only possible process.

As pointed out by Benjamin, Cosgrove, and Warren,<sup>4</sup> the reduction of barium oxide to barium is improved if the core metal contains metallic additions which act as good reducing agents. By employing these additions, which have been discussed in Sec. 3, the activation process may be speeded up (cf. Vol. II, Sec. 29). With commercial cathodes means are thus provided for producing at any rate an adequate quantity of excess barium by simply heating the cathode.

Since a reduction will occur during the decomposition, the cathode, as mentioned above, gives an emission current immediately after decomposition. For two reasons, however, it is generally necessary to activate after sealing off the valve. Firstly the optimum excess of barium cannot be produced under the vacuum conditions existing during commercial pumping. Secondly the quantity of excess barium produced is highly influenced by the degassing of the other electrodes, which is normally carried out in the sealed-off valve.

At first only the formation of the optimum excess of barium in the coating will be considered. The processes determining this formation are the reduction of barium oxide to barium, the diffusion of this barium, and its evaporation. The diffusion is as necessary as the reduction because the excess barium which, for instance, may be produced at the boundary between oxide coating and core metal must be transferred into the interior of the coating and must be built into the crystal lattice there. While these two processes influence the activation favourably, the third one, the evaporation of excess barium, acts against them. All the three phenomena, reduction, diffusion, and evaporation, increase with increasing temperature, and an optimum range of temperatures will therefore exist in which reduction and diffusion are large enough but the

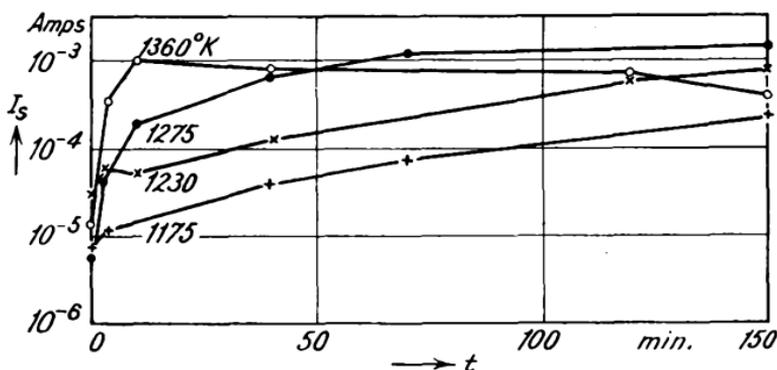


Fig. 34.—Saturated Current  $I_s$  of a BaO Cathode during an Activation by Reduction carried out at Different Temperatures (H. Huber, unpublished).

evaporation not too large. In order to find this optimum range the activation must be investigated by measuring the emission current as a function of activation temperature and time.

The result of such measurements undertaken by Huber<sup>1</sup> with pure barium oxide is seen from Fig. 34, which shows for different activation temperatures the saturated current measured during activation. As a very low temperature is necessary for obtaining the saturated current (cf. Sec. 10), the temperature of the cathode was decreased from the value used for activation to 750° K. during each measurement. Fig. 34 shows that the saturated current increases to a maximum during activation. The time necessary for reaching this maximum increases with temperature, while the value of the current, measured at the maximum, is smaller at high temperatures than at medium and low temperatures. If very high temperatures are applied, a falling current is observed

immediately, as the deactivation by evaporation then supervenes. According to these results the activation temperature should be chosen in a medium range in which the time necessary for reaching the maximum is not too long and in which an immediate deactivation does not occur.

Fig. 35 is obtained from Fig. 34 by taking the saturated currents for a constant time of 150 minutes and plotting these currents as a function of the appropriate activation temperature. The optimum activation temperature,  $T_{optim}$ , resulting from this plot is about 1275° K. On the right-hand side of this temperature ordinate is

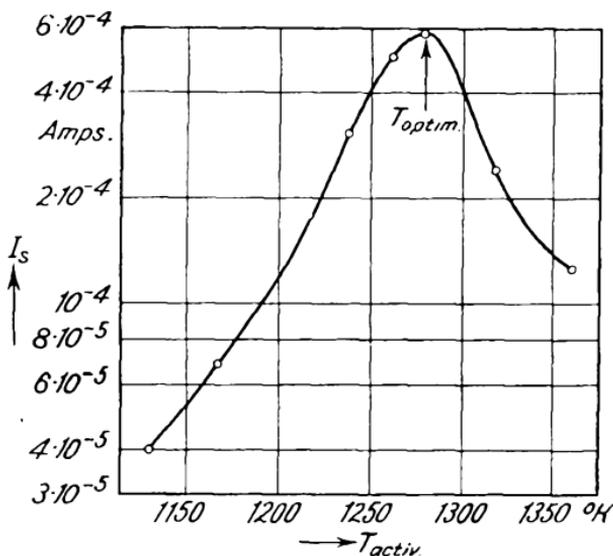


Fig. 35.—Saturated Current  $I_s$  of a BaO Cathode as a Function of Activation Temperature  $T_{activ}$  (activation time 150 min.) (Huber<sup>1</sup>).

the range in which the maximum value of the emission has been passed, while on the left-hand side the activation has not yet been finished.

In the above example the time of 150 minutes, which is rather long, has only been taken in order to emphasize the influence of the two parameters, temperature and time. In reality the activation temperatures used are higher than the above value and the necessary times therefore considerably shorter.

As shown by many experiments, the emission of normal commercial cathodes, which are activated by reduction, cannot be improved by an activation by current.

The second part of the activation process, namely the removal of residual gases from the electrodes adjacent to the cathode, may be

considered now. Strictly speaking, this degassing process is not part of the activation, but as the two processes run in parallel and cannot be separated from each other, the degassing of the electrodes will be discussed together with the activation. The fact that residual gases are present in spite of the heating of the electrodes during pumping is due to different causes which may be noted here. Firstly the vacuum in the normal pumping machines is not as good as the final vacuum in the valve, which is improved by the getter. Secondly some gas is evolved during the evaporation of the getter and whilst sealing off. Furthermore, if a metal has been degassed even by an intense eddy current heating, additional gases are always set free by subsequent electron bombardment. Finally certain

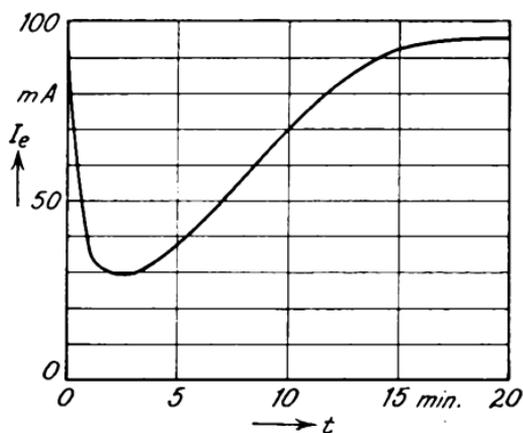


Fig. 36.—Variation of the Emission Current during the Activation of a Commercial Valve.

chemical compounds, e.g. oxides of the electrode metals, if not removed previously, may be decomposed by bombarding electrons, and gases may be set free in this way (Jacobs<sup>1</sup>). These residual gases must be removed eventually, because they would otherwise travel to the cathode during operation of the valve and would impair the emissivity of the cathode, a phenomenon which is called

poisoning of the cathode (cf. Sec. 12.5). The only practical way for removing the residual gas from the electrodes is by applying a positive potential to the electrodes and by bombarding them with electrons from the cathode. The electrodes concerned are heated in this way and the gases which are given off may then be adsorbed by the getter.

During such a treatment the emission current at first decreases as the cathode is poisoned by the gases which are set free. The emission current then passes a minimum and subsequently increases to its old value due to an activation which is partly produced by reduction and partly by the current. The phenomenon described will be seen from Fig. 36 showing the variation of the emission current during the activation of the cathode of a commercial valve. The curve does not represent a saturated but a space-charge

limited current. When plotting this curve the cathode temperature was taken somewhat lower than during the commercial activation process in order to produce a more definite fall and subsequent rise than is normally observed.

The transient poisoning occurring during the activation was examined in detail by Huber.\* The variation of the emission current measured by him for a diode is shown by Fig. 37 in which the ratio between the saturated current at 700° K. and the corresponding current at zero time has been plotted. As the preceding activation by reduction had not been finished, a further

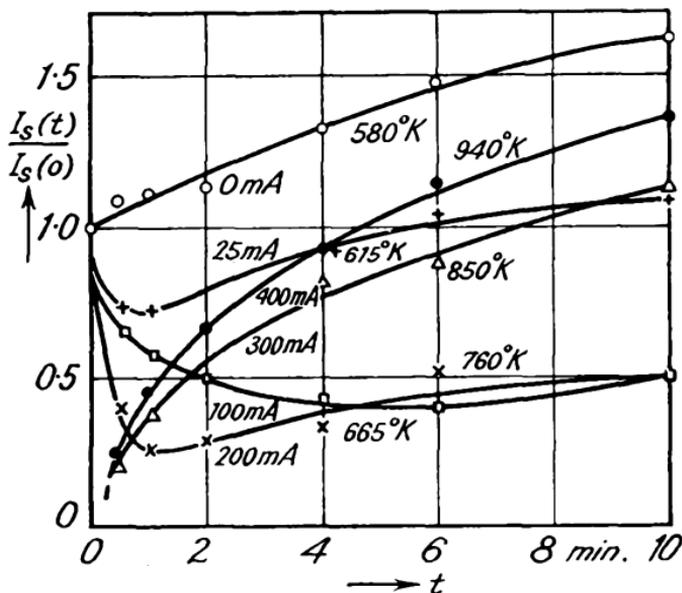


Fig. 37.—Proportional Variation of the Saturated Current during an Activation by Drawing Emission Currents of Different Magnitudes (H. Huber, unpublished).

increase in the saturated current was also observed when heating the cathode without drawing emission current. The emission currents used during the activation have been marked on the curves concerned. As will be seen from the figure, the minimum obtained during the activation by current becomes deeper and more marked if the emission current, and consequently the temperature of the anode, is increased. This anode temperature was simultaneously measured by means of a thermocouple and is also given beside the curves in the plot.

The variation of the emission current during an activation by

\* H. Huber, unpublished measurements.

current, as characterized by Fig. 37, may be explained in the following manner. If the anode temperature is increased the anode gives off more gas and the emission current will consequently fall more rapidly. The evolution of gas from the anode is compensated by the getter, which adsorbs the gas. With the anode temperature high, the residual gases are given off quickly. The adsorption by the getter may therefore take full effect after a short time, and the emission current, after having fallen rapidly before, will rise quickly. If, however, the anode temperature is low, the residual gases are only given off slowly and the getter cannot adsorb them as quickly as in the case considered first. Consequently a slow fall and a subsequent slow rise of the emission current is observed.

The activation process may be accelerated and carried out more completely by evaporating during the activation a getter which is located on one of the bombarded electrodes.\* The gases given off by the electrodes are then made ineffective more rapidly.

In the course of the years the times necessary for activation were shortened more and more by improving the electrode materials and the methods of manufacture. While in the early years the cathodes, especially the combined cathodes, were activated many hours or even days, such long activation processes are now only used in special cases. The normal activation times are between 15 minutes and one or two hours.

Details of the activation process cannot readily be given, because the size and configuration of the electrodes, the properties of their materials, the type and position of the getter, and the method of pumping, which all vary greatly between different groups of valves, must be accounted for. The dissipation of the electrodes should be taken as high as possible, but on the other hand an unnecessary overloading of the cathode and the other electrodes must be avoided. Normally the electrodes are connected together in groups to which the same voltage is applied through a common load resistor. The load resistors, usually electrical lamps, then protect the electrodes concerned from being overloaded. When working out an activation schedule some technical requirements, such as an easy way of changing over from one load circuit to another and facility in interchanging of the load resistors, must also be taken into account. As an example three different activation schedules are given in Table XI together with the appropriate dissipations of the electrodes and the operating conditions of the valves concerned.

\* German Patent 589763.

TABLE XI

*Examples of the Activation of Oxide Cathodes*

No.	Time (min.)	Heater voltage (volts)	Cathode- current (mA)	Grid dissipation (watts)		Anode dissipation (watts)
				control grid	screen grid	
I	10	8.0	150	0.9	—	5.6
	10	7.0	80	0.2	—	4.7
IA	—	4.0	8	0	—	2.0
II	5	6.5	120	—	—	22
	10	5.5	235	0.9	—	17
IIA	10	5.0	230	0.9	—	17
	—	4.0	40	—	—	10
III	6	11.0	230	1.1	6.5	5
	10	9.0	76	—	1.4	15
IIIA	—	6.3	40	—	1.2	9.0

I	Low-power valve (indirectly heated cathode)	IA	} operating values.
II	Output valve (directly heated cathode)	IIA	
III	„ „ (indirectly heated cathode)	IIIA	

The activation methods discussed so far employ direct current. If, however, large alternating currents must be taken from the valves during operation, as for instance with rectifier valves and valves used in class C amplifiers, corresponding A.C. voltages as during operation are often used during the activation. Valves operated with high power pulses are usually activated with the same or similar peak values as are applied later.

When working out an activation process it must be borne in mind that the composition of the surface of the grids, especially of the control grid, is changed by this process. These changes in surface composition produce variations of the work function of the grids. As will be shown in Vol. II, Sec. 4, every variation of the grid work function by a certain amount displaces the total characteristic curve of the valve by the same amount. A decrease in work function produces a displacement to negative, and an increase a displacement to positive, values of grid voltage. If the characteristic is displaced, the working point and the cut-off points of the valve concerned are also displaced. On the other hand, the position of these points is laid down by the specification of the valve, and the work function of the grid must therefore be given a definite value within appropriate tolerances.

The work function of the control grid is greatly influenced by gases adsorbed at the surface of the grid (cf. Vol. II, Sec. 5) and by barium and barium oxide evaporated on this surface from the cathode. The latter point is especially important, because barium oxide evaporates readily at the high temperatures applied during decomposition and activation (cf. Sec. 12.1). The barium oxide accumulated on the grid forms a second oxide cathode there, the work function of which determines the work function of the grid. This cathode on the control grid is activated during the activation of the primary cathode by the electrons bombarding the grid. Consequently the characteristic of the valve is considerably displaced to negative grid voltages, if the grid dissipation is high during the activation.

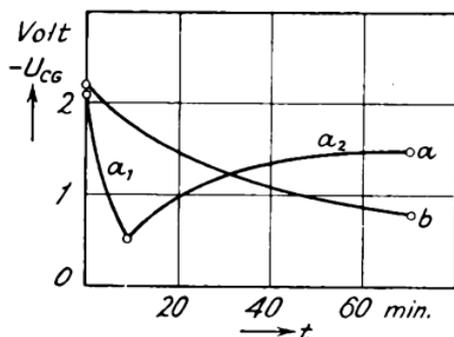


Fig. 38.—Variation of the Contact Potential  $U_{cg}$  between Cathode and Control Grid during Activation of a Commercial Valve: (a) 1. High Cathode Temperature, High Grid, but Low Anode Dissipation; 2. Low Cathode Temperature, Low Grid, but High Anode Dissipation. (b) Medium Cathode Temperature, Grid and Anode Dissipation Medium.

If the dissipation of the other electrodes (anode, screen grid) is increased during activation and the cathode temperature is decreased simultaneously, those electrodes will give off additional gas, while less barium oxide will evaporate. Then the highly activated state of the grid cannot be maintained because the cathode on the grid is poisoned by the gases concerned. The work function of the grid will therefore increase and the characteristic will now be displaced to positive grid voltages. The variation of the grid work function described above can also be detected by measurements of the contact potential as shown by curve (a) in Fig. 38. The variation of work function and contact potential, of course, depends considerably on the details of the activation schedule applied, as may be seen from curve (b) in Fig. 38.

As the control grid is heated either by radiation or by electron bombardment from the cathode, it may emit electrons if its work function is sufficiently low. This phenomenon, which is called thermal grid emission, is very undesirable, because it brings about a power consumption in the grid circuit and a displacement of the working point of the valve characteristic. Too low a work function of the grid must therefore be avoided when drawing up the

activation schedule. The same may be said for rectifier valves, which show a tendency to backfire if the work function of the anode is too low.

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## CHAPTER 4

# THE CHARACTERISTICS OF THE OXIDE CATHODE

The most important characteristics of an oxide cathode which determine its size and its electrical values are the electron emissivity, the efficiency, and the life of the cathode. As all these characteristics depend very largely on temperature, the methods of measuring the temperature and the appropriate thermal properties of the cathode will be discussed first (Sec. 9). The methods for measuring the emission will be dealt with in Sec. 10, while the values of electron emissivity and efficiency which may be obtained will be given in Sec. 11. The pulsed emission values of oxide cathodes, which have become important of late, will then also be discussed. Sec. 12 will give a compilation of the undesirable features of the oxide cathode which limit its application, and finally Sec. 13 will deal with the influence of these undesirable features on the life of the cathode.

### 9. Measurement of Temperature and Thermal Properties

An exact measurement of the cathode temperature is usually not possible with commercial valves owing to the non-uniform distribution of temperature (cf. Fig. 23) and to the interference of the surrounding electrodes of the valve. In general it will therefore be necessary to use special experimental valves which are as similar as possible to the commercial valves whose cathode temperature is to be ascertained.

Four different methods for determining temperature will be discussed: the resistance measurement, the thermoelectrical measurement, the pyrometrical method, and the measurement by means of the retarding field current. The fundamentals of the three first methods are assumed to be known, and only the particulars of the application of these methods to the oxide cathode will therefore be discussed.

#### 9.1 Resistance measurements

This method is used in a simple way for directly heated cathodes, the temperature of which may be ascertained from the known

temperature dependence of the resistance of the core material (cf. Fig. 5). The main disadvantage of this method is that the value obtained must be corrected in order to account for the lower temperature of the ends of the cathode, this correction being difficult to calculate. If experimental valves are used this disadvantage may be removed by connecting probe leads to the core wire, by which means the potential drop along the cathode is measured. The method has two further disadvantages. Firstly, another correction must be applied to allow for the fact that, when measuring, the actual resistance is reduced by the shunt resistance of the oxide coating, and secondly, due to heat conduction, the desired temperature of the coating surface is slightly less than the measured temperature of the core wire.

If indirectly heated cathodes are used, the temperature of the cathode sleeve and of the oxide coating can be determined from the variation of the resistance of the heater. This method utilizes the empirical fact that (cf. Fig. 39) a linear relation exists between the resistance of the heater and the temperature of the sleeve, as, for instance, measured by a thermocouple. If therefore the cold resistance of the heater is measured at room temperature and the hot resistance determined at one higher temperature by one of the other methods, for instance pyrometrically, each temperature in the intermediate range can be ascertained from a curve like that of Fig. 39 by measuring only the heater resistance. This method is especially suitable for temperatures between the room and operating temperatures which cannot be measured pyrometrically. The method has an accuracy which is sufficient for most practical purposes.

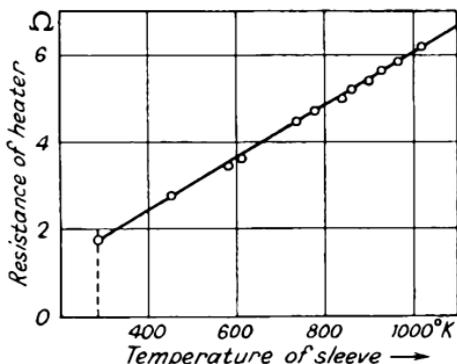


Fig. 39.—The Resistance of the Heater of an Indirectly Heated Cathode as a Function of the Temperature of the Sleeve.

## 9.2 Thermoelectrical measurements

This method is normally not applied to directly heated cathodes, because their temperature would be influenced too much by the heat conduction of the thermocouple wires. When measuring indirectly heated cathodes, the heat conduction must also be kept

small by using very thin wires for the thermocouple (less than 0.1 mm. diameter). The best type of thermocouple to use is platinum and platinum-rhodium. These materials have the least influence on the emission; they can, furthermore, be sealed into the glass of the valve and can therefore be taken to the outside where the temperature of the cold junction can be controlled or measured. The temperature of the part of the cathode sleeve to which the thermocouple is welded can be determined very accurately in this way. This method also gives, of course, the temperature of the core metal, and the surface temperature of the coating can only be calculated from the core metal temperature by using a value for the heat conductivity of the coating which is somewhat uncertain (p. 84).

### 9.3 Radiation measurements (pyrometrical method)

This method has the advantage that it allows measurements of the temperature of the cathode to be made without appreciable modification of the valve. Normally it is only necessary to provide the anode of the valve with one or more holes through which the cathode can be seen. The only condition which must be taken into account is that no essential part of the radiation used for the measurement is cut off by the rim of the holes or by other electrodes. A hole diameter of about 1 mm. is adequate with normal receiver valves. Both the total radiation and the radiation at a definite wavelength (spectral radiation) may be used for the measurement. The disadvantage in both cases is that only the brightness temperature  $T_b$  of the cathode is thus obtained, from which the actual temperature  $T_a$  must be calculated using the respective radiant emissivities. The measurement of the total radiation is closely connected with the thermal constants of the cathode and will therefore be discussed later together with these constants.

If the spectral radiation is used the actual temperature  $T_a$  is calculated from the formula:

$$1/T_a - 1/T_b = 1.61 \times 10^{-4} \lambda \log e_\lambda \quad . . . . \quad (4)$$

where  $e_\lambda$  denotes the spectral radiant emissivity measured at the wavelength  $\lambda$  of the pyrometer (normally  $\lambda = 0.65 \mu$ ). The spectral emissivity of oxide cathodes has not a universal value, but depends on various properties of the oxide coating, namely on the temperature, on the type of core metal, and on particle-size, thickness, and density of the coating. The temperature measurement by the

pyrometer is therefore not very accurate if the value of the spectral emissivity is not determined for each series of measurements.

As the knowledge of the spectral emissivity is so important for the pyrometrical measurement, the methods of measuring this emissivity will be discussed in detail. In so far as other figures are not given, the discussion will be confined to [BaSr]O cathodes of normal thickness ( $\simeq 50 \mu$ ) made by spraying carbonates of medium particle-size (1 to 10  $\mu$ ). A simple method for determining the spectral emissivity  $e_\lambda$  is obtained by depositing on the coating surface a small patch of a material having a known constant emissivity. The spectral emissivity of the coating can then be evaluated by comparing the brightness temperatures of the normal coating and of the patch. Herrman<sup>1</sup> used  $\text{Cr}_2\text{O}_3$  for this purpose, for which  $e_\lambda = 0.8$ . Allowance must be made for the fact that with this method the areas of the coating surrounding the patch will be cooled due to the increased radiation from the patch. Accurate values of the emissivity can therefore only be obtained by measuring patches of different diameters and extrapolating to zero diameter. The values of  $e_\lambda$  measured by this method are between 0.18 and 0.30.

If this simple method is not accurate enough, the proper method for measuring the spectral emissivity may be used by building a hollow body of core metal which is supplied with a hole and then coated with the alkaline earth oxide. The actual temperature is then measured by focussing the pyrometer on the hole while the brightness temperature is obtained by focussing on the oxide coating beside the hole. Moore and Allison<sup>1</sup> used this method and obtained, for indirectly heated cathodes with nickel cores, values of the spectral emissivity which were, on the average, between 0.28 and 0.32.

When using the hollow body an error will arise because the actual temperature of the core metal, which is measured in the hole, is different from the actual temperature of the coating surface owing to the low heat conduction in the coating. This difficulty was removed by Clausing and Ludwig<sup>1</sup> by accommodating a coated nickel sleeve in a quartz tube heated by a flame. The temperature differences across the coating were thus eliminated. Another method suitable for directly heated cathodes was given by Patai and Tomaschek.<sup>2</sup> The temperature of the core metal was determined by measuring its resistance. This was done first in vacuum and then in a gas atmosphere, while the brightness

temperature of the cathode surface was kept constant by means of a pyrometer. The heater power which had to be supplied to the cathode in the two cases was also determined. Using all the measured values, two equations for the flow of heat through the oxide coating could be formed, and both the actual temperature of the cathode surface and the heat conductivity of the coating could be calculated from these equations. A similar method was employed by Champeix<sup>2</sup> who measured the heater powers at two different temperatures of the cathode and calculated the spectral emissivity from these two heater powers and from the brightness temperatures which were measured simultaneously.

Another possible method of determining the spectral emissivity is obtained by comparing the temperature measured by a pyrometer

with temperatures measured for the same cathode by one of the other methods. In this way Heinze and Hass<sup>2</sup> and Liebold<sup>1</sup> found values of  $e_\lambda = 0.25$  using the retarding field current method for comparison. Finally Prescott and Morrison<sup>1</sup> measured the coefficient of reflection and calculated the spectral emissivity from this coefficient. The valve containing the oxide cathode was brought into a cylinder the inside of which was covered with white cotton velvet and which was illuminated from inside. By using a hole in the cylinder, the reflection co-

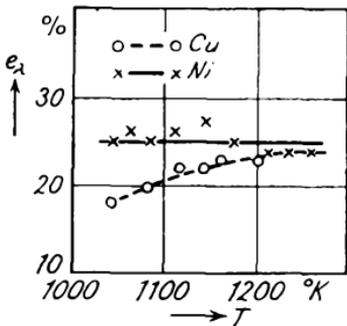


Fig. 40. — Spectral Radiant Emissivity  $e_\lambda$  ( $\lambda = 0.65 \mu$ ) of Oxide Cathodes with Nickel and Copper Cores as a Function of Temperature (W. Liebold, unpublished).

efficient of the coating could then be measured and by subtracting the obtained value from 1 the emissivity was derived. Moore and Allison<sup>1</sup> compared this method with the results of their measurements described above and found a good correspondence.

The influence of temperature and core metal was also examined by Liebold, the result being given in Fig. 40. He showed that the spectral emissivity differs between cathodes with different core metals, but that this difference decreases with increasing temperature. It follows therefore that the radiation of the core metal is more and more absorbed by the oxide coating if the temperature is raised. The dependence on the thickness of the coating was examined by Clausing and Ludwig,<sup>1</sup> and Champeix,<sup>3, 4</sup> who found a decrease in spectral emissivity with increasing thickness. Champeix's values,

for instance, vary from 0.27 at 30 to 0.09 at 105  $\mu$  thickness. The dependence on particle-size and on the method of depositing the emission paste has not yet been investigated to any great extent. Patai and Tomaschek<sup>1</sup> gave the spectral emissivity for colloidal coatings of high density, deposited by electrophoresis. They are of the same order as the values given above. Champeix<sup>3,4</sup> likewise found no difference between coatings obtained by spraying and those prepared by electrophoresis. Moore and Allison,<sup>1</sup> when studying commercial nickel cathodes deposited by a dragging method, obtained a mean value of the spectral emissivity  $e_\lambda=0.46$ .

Summarizing the results of the spectral emissivity measurements which have been published so far, a value  $e_\lambda=0.25-0.30$  can be taken for oxide coatings of a thickness between 40 and 100  $\mu$  prepared by the normal spraying method. Fig. 41 gives the relation between actual temperatures and brightness temperatures for cathodes with nickel cores prepared by spraying or by dragging ( $e_\lambda=0.45$ ). It may be emphasized again that in order to obtain accurate values of the temperature, the spectral emissivity must be determined for the particular cathode used in the experiments.

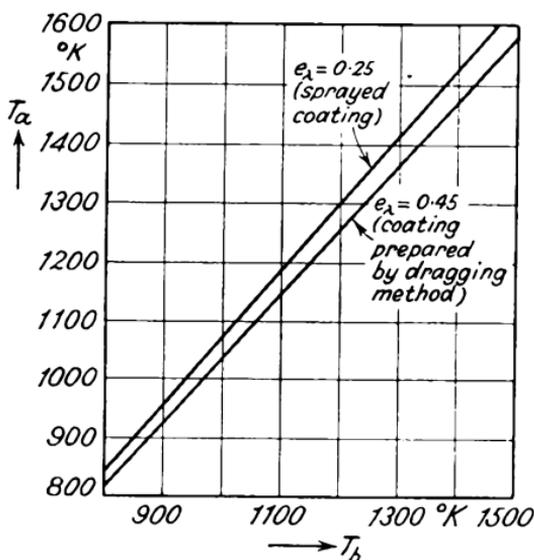


Fig. 41.—Relation between Actual Temperature  $T_a$  and Brightness Temperature  $T_b$  for Oxide Cathodes of Commercial Design.

#### 9.4 Measurement of the retarding field current

This method utilizes the fact evident from equation (1) that a plot of the logarithm of the retarding field current  $I_r$  against voltage gives a straight line whose slope is determined only by the temperature of the cathode. This temperature can then be calculated from the slope of the straight line using the formula

$$T = 5040 \frac{dV_A}{d \log I_r} \quad \dots \quad (5)$$

This method, when first used for oxide cathodes by Koller <sup>1</sup> and Rothe, <sup>1</sup> gave values which were about 60% too high. Later Heinze and Hass <sup>2</sup> found that the method had only a limited application. It cannot be applied to valves with grids owing to the distortion of the potential field produced by these grids. For diodes, however, accurate results can be obtained by this method, especially if experimental valves of special design are used. If the configuration of the electrodes is cylindrical a correction must be applied to equation (5), and if directly heated cathodes are used a special circuit shown by Fig. 47 (Vol. II) must be employed in order to eliminate the potential drop along the cathode.

This method was modified by Macdonald and Fürth <sup>1</sup> using the following relation derived from equation (1). Let  $R_p$  denote the plate resistance of the diode under observation; then from (1):

$$R_p = \frac{1}{\partial I / \partial U} = \frac{T}{1.16 \times 10^4 I_r}$$

or

$$T = 1.16 \times 10^4 R_p I_r \quad . . . . . (6)$$

If  $R_p$  is measured in the region of the retarding field current by means of an A.C. method, the temperature  $T$  can be ascertained from the above equation using for  $I_r$  the (D.C.) mean value of the retarding field current.

Finally another method for measuring the temperature may be mentioned which was given by Schlesinger <sup>1</sup> for directly heated cathodes. In this method use is made of the fact that the resonant frequency of the core wire depends on its temperature. The application of this method to commercial valves seems to be difficult, as the components necessary for supporting the filament, such as springs and insulating parts, will influence the resonant frequency of the filament more than the variation of its temperature.

## 9.5 Thermal properties of the cathode

Consideration will now be given to the question of how much heater power must be supplied in order to heat the cathode to the correct operating temperature. The heater power  $P_H$  which must be supplied per cm.<sup>2</sup> of the total cathode surface  $S_t$  will be called the specific heater power. This is normally given in watts/cm.<sup>2</sup>. The heater power  $P_H$  is equal to the sum of the heat radiation  $P_{rad}$  from the cathode and the heat conduction  $P_{cond}$  through the cathode supports. Losses by convection will not, of course, occur with

cathodes operated in a high vacuum. The most economical cathode will be that which has the smallest total radiant emissivity and the lowest heat conduction. The total radiant emissivity, which will be discussed first, depends on various properties of the cathode, such as density and particle-size of the coating, kind and surface of the core metal, as does the spectral emissivity discussed earlier. Universal values of the total emissivity cannot therefore be given.

The measurement of the total radiant emissivity  $e_t$  is best undertaken by using the centre part of a long cathode sleeve which is heated by direct flow of current. The voltage drop along the centre part is measured by using suitable probe wires welded to the sleeve. The power supplied to the centre part of the cathode and radiated from it can then be calculated from the measured values of current and voltage. The result of such measurements undertaken by Clausing and Ludwig<sup>1</sup> for SrO-coatings sprayed on a nickel core is shown in Fig. 42.

By comparing these values with those of a black body which are also shown in the figure the total emissivity can be derived. The mean value  $e_t = 0.3$  which is so obtained for coatings

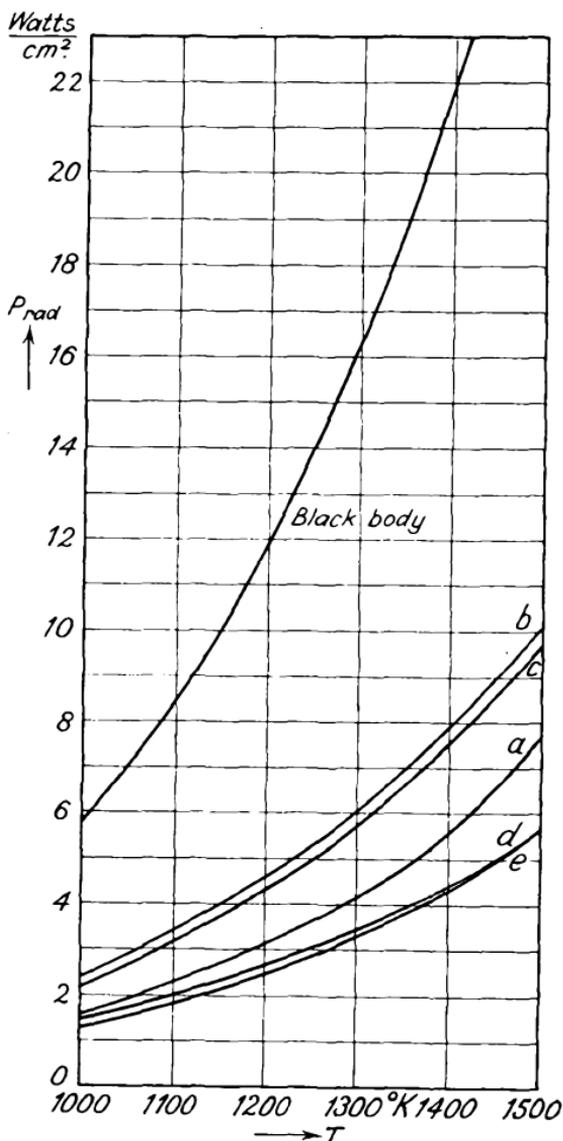


Fig. 42.—Power  $P_{rad}$  Radiated from Sprayed SrO-coatings of Different Thicknesses, as a Function of Temperature (Nickel Cores) Coating Thickness: (a) 0, (b) 39  $\mu$ , (c) 33  $\mu$ , (d) 126  $\mu$ , (e) 188  $\mu$  (Clausing and Ludwig<sup>1</sup>).

of normal thickness sprayed on nickel cores was confirmed by

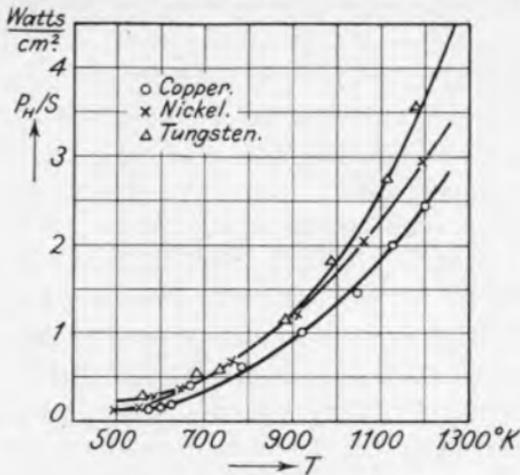


Fig. 43.—Specific Heater Power  $P_H/S$  of Oxide Cathodes with Different Core Metals, as a Function of Temperature (W. Liebold, unpublished).

Moore and Allison,<sup>1</sup> who examined commercial coatings 36  $\mu$  thick. The influence of the core metal on the radiation from the cathode can be seen from Fig. 43, showing the specific heater power as a function of temperature for different core metals. The values given in this figure were obtained with indirectly heated cathodes, and they were not corrected for the heat conduction at the ends of the cathode.

Details of the losses by heat conduction cannot be given. These losses are kept as small as possible, not only for economical reasons but also to obtain a uniform temperature distribution along the cathode. This is achieved by supporting the cathode in thin materials of low heat conduction, such as mica or ceramic materials, the latter ones being less suitable for small cathode dimensions. Furthermore, the lead necessary for making a connection to the cathode (the tail) is made of an alloy of low heat conduction (invar). The reduction of the heat conduction through the cathode support is limited by the demand for an adequate mechanical strength of this support. It depends on the particular design of the valve which of the two demands will prevail. Another phenomenon which must be taken into account when designing the cathode support is the variation of the length of the cathode due to thermal expansion. A value

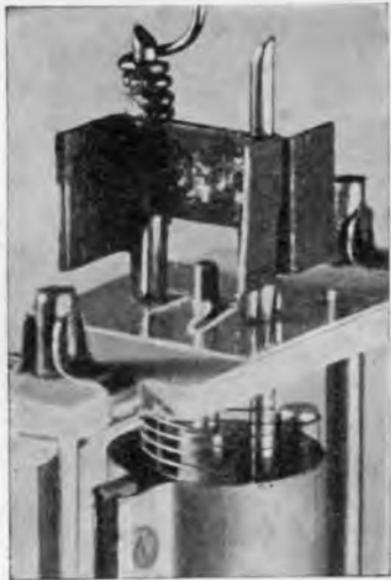


Fig. 44.—Cathode Support with Low Heat Conduction (Telefunken AC2).

of 0.5% to 1% of the total length is normally assumed for this expansion. If directly heated cathodes are used a spring takes up the expansion. With indirectly heated cathodes a suitable design of one of the supports, as shown, for instance, by Fig. 44, will guarantee that the expansion may take place whilst the heat conduction remains low and the cathode accurately centred.

It can be seen from these considerations that the specific heater power may be reduced by suitable design of the supports only to a limited extent. Attempts have therefore been made to reduce the radiation of indirectly heated cathodes by using a sleeve of copper.\* Table XII shows that the heater power may thus be reduced to one-half of the value obtained with nickel sleeves. Owing to the low melting-point and the inadequate mechanical strength of copper, however, cathodes with copper sleeves are difficult to manufacture and have not been made in large numbers. The same efficiency has now been achieved with nickel cathodes by improving their electron emissivity.

TABLE XII

*Specific Heater Powers  $P_H/S_t$  and Average Operating Temperatures of Different Types of Cathodes*

Type of cathode	Type of valve	$P_H/S_t$ (watts/cm. <sup>2</sup> )	Average operating temperature
Indirectly heated nickel cathodes.	Low-power valves: early valves	2.7-3.2	1100° K. and higher.
	modern valves	2.0-2.7	950-1050° K.
	Output and trans- mitting valves	2.0-2.3	1050-1150° K.
	Rectifiers	2.2-3.5	1100-1200° K.
	Miniature valves	2.5-4.0	
Indirectly heated copper cathodes.	Generally	0.9-1.1	≈ 1020° K.
Directly heated cathodes with tungsten or nickel core.	Low-power valves	1.5-2.3	950-1100° K.
	Output valves	2.0-2.5	1100-1200° K.
	Rectifiers	2.7-3.3	1100-1200° K.

Table XII gives the specific heater powers and the operating temperatures for different types of cathodes.

When discussing the methods of measuring the temperature it was mentioned that differences in temperature exist between the core metal and the surface of the coating which are due to the low heat

\* British Patents 408185, 413950.

conductivity of the coating. This heat conductivity can be determined by the method of Patai and Tomaschek <sup>1</sup> discussed on page 77. Another method, given by Clausing and Ludwig,<sup>1</sup> is derived from their method of measuring the spectral emissivity discussed above. The measurement in the quartz tube heated by flames was supplemented by another measurement in vacuum, the cathode sleeve being heated by direct flow of current. The temperature of the core metal was measured by focussing the pyrometer on a hole in the cathode sleeve. The heat conductivity can then be ascertained using this temperature of the cathode sleeve, the temperature of the coating surface, and the heater power required. The values obtained by those two methods show a considerable spread between  $5 \times 10^{-4}$  and  $5 \times 10^{-3}$  watt/degree cm. The temperature differences between core metal and coating surface may be estimated from those values of heat conductivity. They are between 2° and 20° for normal thicknesses and for a temperature of about 1000° K. The influence of the structure and density and of the chemical composition of the coating on the heat conductivity is not as yet known.

## 10. Methods of Measurement and Comparison of Emission Values

In scientific work, comparisons between the emissivity of different cathodes are normally made by measuring their work function. In commercial manufacture, however, these methods of measurement are too complicated, and simpler ways for testing cathodes must be used. The simplest method would be the static measurement of the saturated current at the operating temperature, but this method cannot be applied to an oxide cathode owing to the difficulties produced by the high magnitude of its saturated current. As shown in detail in Sec. 12, the emission current, by flowing through the oxide coating, produces in this coating a quantity of heat which increases the temperature of the cathode, when the emission current is switched on. The amount of heat produced by the saturated current at the operating temperature is normally of the same order or even higher than the heater power supplied to the cathode. A steady saturated current cannot therefore be measured at the operating temperature without increasing the temperature of the coating unduly and thus impairing or destroying its emissivity.

Another difficulty occurring when measuring such high densities of saturated current is the overloading of the electrodes in the valve. The evolution of gas and the rise in temperature of the cathode

produced in this way will highly influence the emissivity of the cathode and may even destroy it. If directly heated cathodes are measured, the saturated current will be of the same order or higher than the heater current, and unstable conditions will thus arise which likewise may give rise to the destruction of the cathode. Another fact to be accounted for is that the saturated current depends greatly on the field strength at the cathode surface and therefore on the voltages applied to the electrodes of the valve (cf. Vol. II, Sec. 21.1). When comparing the saturated currents of different cathodes by one of the methods to be described below, it will therefore be necessary to do this in valves of the same geometry and with the same voltages.

Owing to the difficulties resulting from the high density of the saturated current this current can only be measured at the operating temperature by using special methods which apply the anode voltage to the valve during a very short time. On the other hand, it is, of course, possible to drop the temperature of the cathode to such a value that the current density becomes small enough to be measured accurately ( $\leq 1$  mA/cm.<sup>2</sup>). With fully activated cathodes a temperature of 700° K. is sufficiently low for this purpose. Finally it will be possible to ascertain the value of the saturated current at the operating temperature from measurements of the retarding field current, either graphically or by a calculation.

### 10.1 Short time measurements

The first attempts to shorten the time of measuring the saturated current were made by using special contactors which closed the anode circuit for a very short time. The emission current was then measured by means of a ballistic galvanometer. In this way Thomson<sup>1</sup> obtained emission currents from 3 to 6 amps./cm.<sup>2</sup> at the operating temperature with measuring times of about  $10^{-3}$  sec. Maddock<sup>1</sup> examined variations of the emission current of oxide cathodes by the same method.

The contactors have the disadvantage that arcs at the contacts are produced if the current density becomes high. Other workers therefore used a condenser discharge for obtaining short current impulses. The emission current itself was then measured either by means of a cathode-ray tube (Heinze<sup>1</sup>) or by displacing the characteristic of an electrometer valve by means of an auxiliary condenser (Patai and Frank<sup>1</sup>). The cathode-ray tube method has the advantage that the total emission characteristic (emission current

against voltage) may be produced on the screen of the tube. The result of such a measurement undertaken with a commercial triode containing an oxide cathode is shown by Fig. 45 (a). It will be seen that no saturation is obtained at the operating temperature up to a current of at least 3 amps./cm.<sup>2</sup>, while the same method gives a definite saturated current if a pure tungsten cathode is used (Fig. 45 (b)). In spite of the short measuring times of about  $10^{-3}$  sec. achieved by this method, a heating-up of the coating produced by the emission current will still be observed in many cases, especially if directly heated cathodes with thin core wires are examined. Furthermore, the application of the method is limited by the fact

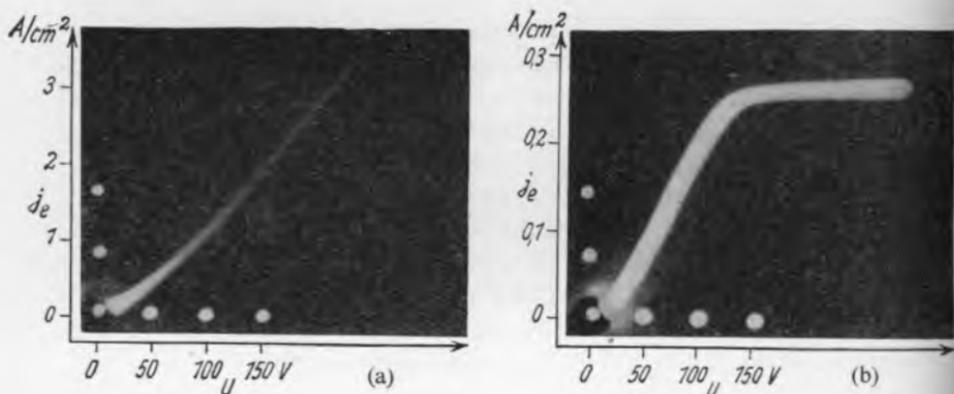


Fig. 45.—Short Time Measurements of the Emission Currents: (a) of an Oxide Cathode at the Operating Temperature ( $T \approx 1030^\circ \text{K.}$ ); (b) of a Tungsten Cathode ( $T \approx 2500^\circ \text{K.}$ ).

that the maximum field strength is suddenly applied to the cathode at the beginning of the measuring time.

These difficulties may be removed by employing pulsed anode voltages produced by one of the methods known in radar and television practice. The application of these methods for measuring emission currents was first described by Graffunder,<sup>1</sup> who used gas-filled valves for producing the pulses and so obtained measuring times of  $10^{-4}$  sec. By employing high-vacuum valves instead, the measuring time can be further reduced to about  $10^{-6}$  sec. These short pulses are not only important for measuring the saturated current but are of general interest for the practical use of cathodes in radar and television. The fundamental characteristics of pulsed voltages and currents will therefore be given here.

The pulses applied may be square or may have any other shape;

their width taken at the base will be denoted by  $w$  (measured in seconds). If the pulses are repeated  $\nu_r$  times per second,  $\nu_r$  is called the pulse recurrence frequency. The product of pulse width and pulse recurrence frequency is named the duty cycle. Fig. 46 shows the conditions for square pulses applied to the cathode. It is seen that the mean direct current  $\bar{I}$  drawn from the cathode is equal to the product of peak current  $I^*$  and duty cycle  $w\nu_r$ :

$$\bar{I} = I^* w \nu_r \quad \dots \dots \dots (7)$$

As discussed in Sec. 12, the heating of the cathode coating pro-

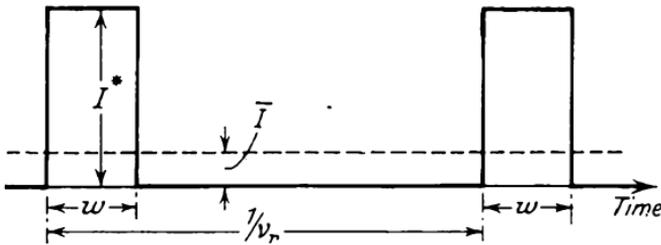


Fig. 46.—The Characteristics when Drawing a Pulsed Emission Current from an Oxide Cathode.

duced by the emission current is determined by the root mean square of the current, which is:

$$\sqrt{\bar{I}^2} = I^* \sqrt{w \nu_r} \quad \dots \dots \dots (8)$$

If pulse shapes other than squares are used, the values corresponding to equations (7) and (8) will be obtained by the appropriate integrals for the arithmetic mean and the mean square; these values will always be smaller than those obtained from the above equations.

Details of the circuits for producing the pulses, such as the well-known multivibrator circuit, have been given by Sproull<sup>1</sup> and Riethmüller.<sup>1</sup> For measuring the saturated current the pulse width used should be smaller than 1  $\mu$ -sec. and the pulse recurrence frequency should also be small ( $\leq 1000$  per sec., Coomes<sup>1</sup>). The peak anode voltage applied must, of course, be high enough to ensure that the current pulse obtained is really a saturated and not a space-charge current. The magnitude of the saturated current is generally measured by applying the appropriate pulses to a cathode-ray tube. The saturated currents obtained with such pulses are between 5 and 25 amps./cm.<sup>2</sup> as measured by Wright<sup>1</sup> and Champeix<sup>1</sup> with normal cathodes at the operating temperature. Coomes<sup>1</sup> gives values up to 130 amps./cm.<sup>2</sup> measured at 1075° K.

### 10.2 Measurements at low temperatures

Another way of comparing the emissivity of different oxide cathodes is by decreasing the temperature of the cathode to such a value that the measured saturated current has a negligible influence on the temperature of the coating. A current density of a few mA/cm.<sup>2</sup> will normally be low enough for this purpose. For comparison the saturated currents measured at the appropriate low heater voltages must be referred to the same heater power. Another

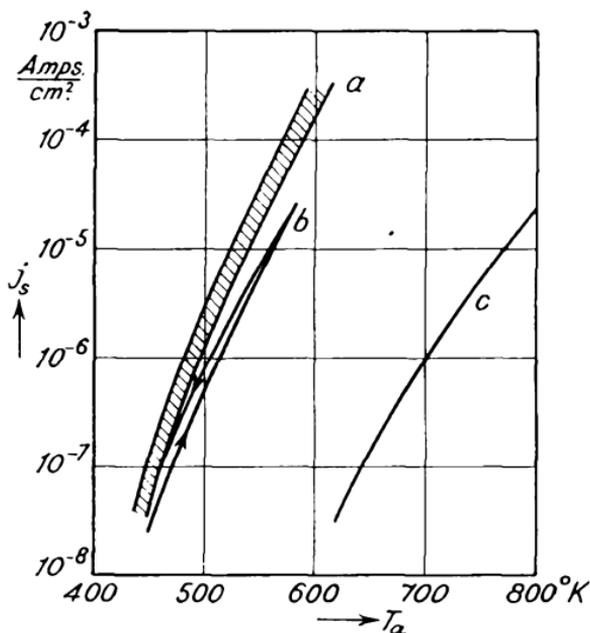


Fig. 47.—Density  $j_s$  of the Saturated Current of Indirectly Heated Oxide Cathodes at Low Temperatures: (a) Highly Activated Cathode, Temperature Measurement by a Thermocouple; (b) Activated Cathode Heated by Baking the Valve in a Thermostatically Controlled Oven; (c) Poisoned Cathode, Temperature Measurement as with (a).

possibility is to determine the heater power which is necessary for obtaining a certain value of the saturated current and to use this heater power as a measure for the emissivity. As the saturated current depends on field strength (anode voltage) at these low temperatures as well as at high temperatures, the same voltages and the same electrode configurations must be used for comparing different cathodes. The anode voltage used should be kept low ( $\leq 5$  volts if possible) in order to avoid impairing the cathode by ionizing residual gases or by decomposing thin films on the electrodes (cf. McCormack<sup>1</sup>).

Fig. 2 shows the result of such a low-temperature measurement

carried out with a commercial valve at different cathode temperatures. The density of the saturated current measured in this way and extrapolated to zero anode voltage is given in Fig. 47 as a function of cathode temperature. The current density shown by these curves was calculated by using the total surface area of the coating. For obtaining accurate densities, however, allowance must be made for the fact that most of the emission of a commercial cathode is taken from a smaller area which has the highest temperature, usually the centre part of the cathode. The actual current densities will therefore be slightly higher. This is especially important if the work function is calculated from the measured current densities (cf. Vol. II, Sec. 21).

### 10.3 Ascertaining the saturated current from the retarding field current

The retarding field current at the operating temperature as given by equation (1) can be used for ascertaining the saturated current at the same temperature. The contact potential  $U_{CA}$  between cathode and anode (or control grid) must then be added to the anode voltage  $V_A$  in equation (1) (cf. Vol. II, Sec. 4.2).

A graphical method for ascertaining the saturated current is shown by Fig. 48 (Hinsch<sup>1</sup>). The straight line, representing the retarding field current in the logarithmic plot, is extrapolated to higher emission values to intersect the ordinate  $V_A = U_{CA}$ . The emission current corresponding to the intersection point is then equal to the saturated current at the temperature used for the measurement.

As the contact potential is normally measured at low temperatures (cf. Vol. II, Sec. 10), attention must be paid to the fact that this contact

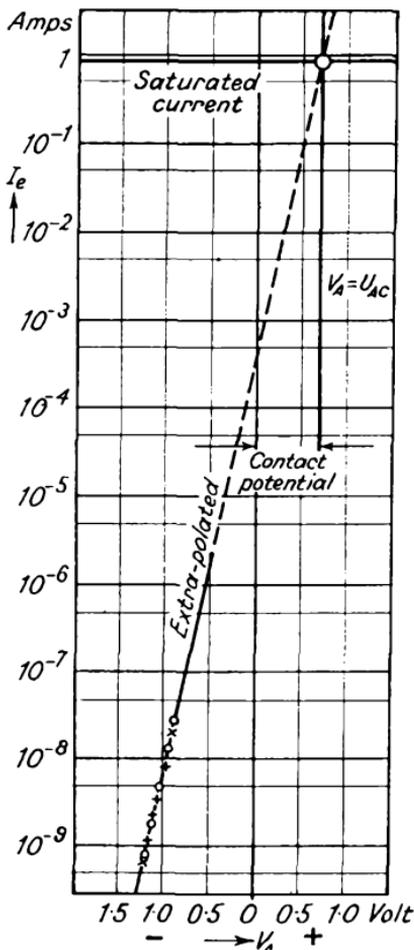


Fig. 48.—Ascertaining the Saturated Current by the Extrapolation Method of Hinsch.<sup>1</sup>

potential is temperature dependent and that this dependence will influence the value obtained for the saturated current.

As outlined by Rothe,<sup>2</sup> the saturated current may also be calculated from the retarding field current by using the exact equation which contains the contact potential. By taking the logarithm of equation (54) (Vol. II), combining with equation (53) (Vol. II), and solving for  $\log I_s$ , the following relation is obtained:

$$\log I_s = \log I_r - \frac{5040}{T}(V_A + U_{CA}) \quad . . . \quad (9)$$

If a value of the retarding field current  $I_r$  and the corresponding anode voltage is given and if the contact potential and temperature are known, the saturated current can be calculated from equation (9). The accuracy of this method is not very high due to the exponential relation between emission current and anode voltage. Thus an error of  $\pm 0.1$  volt in anode voltage alters the calculated value of the saturated current by a factor 2. For this reason the method concerned is only used for estimating the magnitude of the saturated current.

The results obtained agree with those of the short time measurements, if the latter values are extrapolated to zero anode voltage, the calculated saturated current being of the order of 1 to 10 amps./cm.<sup>2</sup> at the operating temperature. Finally it may be pointed out that such measurements may only be undertaken with directly heated cathodes, if a special circuit for eliminating the potential differences along the cathode is used (cf. Vol. II, Fig. 47).

#### 10.4 Measurement of the operating emission current as a function of cathode temperature (sensitivity to underheating)

The methods discussed so far are suitable for checking individual cathodes, but not convenient enough for the routine measurement of cathodes in mass production. On the other hand, it will not be adequate to measure only the normal emission current under operating conditions of the valve concerned, because this operating emission current is a space-charge current and therefore dependent on various other properties of the valve. If the space-charge current differs from the required value this may be due to a deviation in the dimensions of the valve, for instance in the clearance between control grid and cathode, and not to an insufficient emissivity of the cathode.

A suitable method for checking the emissivity of cathodes in mass

production is by measuring the operating emission current at two or more different temperatures of the cathode or, in other words, at different heater powers. A curve representing the operating current as a function of heater power will be called an underheating characteristic, and three such characteristics of different valves are shown in Fig. 49. If curve (a) is considered first, two parts of this may be clearly distinguished, a steeply rising part ( $a_1$ ) at low temperatures, passing at higher temperatures to the second part ( $a_2$ ) which is nearly independent of temperature. This shape of the underheating characteristic may be explained in the following way.

The cathode current at low temperatures ( $a_1$ ) is nearly a saturated current which increases rapidly with temperature. If the temperature is increased, the saturated current, however, passes gradually into the space-charge current which is nearly temperature independent ( $a_2$ ), the cooler ends of the cathode being affected last.

An underheating characteristic as represented by curve (a) will be obtained for a fully activated cathode. If the cathode is an inferior emitter, the saturated current, measured at the same heater power, will be smaller and the initial rise of the curve will therefore be less steep. The passage from the saturated region into the space-charge region will then occur at a higher heater power and will be less marked (see curve (b)). The steepness of the initial rise and the position and markedness of the bend into the nearly horizontal part of the curve may therefore be taken as a measure for the emissivity of the cathode. Deviations in the geometry of the valve, for instance a variation in the clearance between control grid and cathode, will produce a parallel shift of the horizontal part of the curve (c) and can therefore be distinguished easily from a variation in emission.

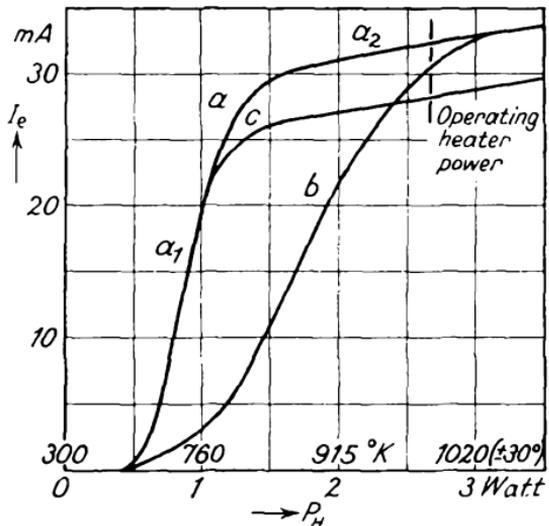


Fig. 49.—Underheating Characteristics of Commercial Triodes: (a) Fully Activated Cathode; (b) Poisoned Cathode; (c) Fully Activated Cathode, but with a Larger Clearance between Grid and Cathode than with (a).

The application of underheating characteristics for testing and comparing the quality of different types of core nickel in mass production of valves has been described by Acker<sup>1</sup> and McCormack.<sup>1</sup> During such tests the current density must not be taken too high at the low temperatures in order to avoid impairing the cathode (cf. Mie<sup>1</sup>).

The small variation of the operating emission current with heater power, as seen from curve (a<sub>1</sub>), in Fig. 49, is one of the advantages of the application of oxide cathodes and another reason for the fact that oxide cathodes are normally preferred to the other types of cathodes. It is normally possible to vary the heater power of an oxide cathode by 15%, or sometimes even by 30%, without exceeding the tolerance limit in the variation of the operating current.

The sensitivity to underheating also depends on the current density drawn from the cathode and on the geometry of the valve. The slope of the part of the underheating characteristic, representing the space-charge current, decreases with decreasing current density and with increasing clearance between control grid and cathode. The latter fact can be proved from equation (69) (Vol. II), according to which the temperature coefficient of the space-charge current decreases with decreasing conductance of the valve system. If the grid-cathode clearance is increased the conductance decreases, and therefore the slope of the high-temperature part of the underheating characteristic will also decrease.

The insensitivity to underheating is improved by the resistor in the cathode lead normally used for producing the control grid bias in commercial receivers, etc. This is especially advantageous for cathodes operated with high current densities, because these cathodes, as shown above, are more sensitive to underheating.

The rise of the initial part of the underheating characteristic, representing the saturated current, depends on the temperature distribution of the cathode to a great extent. If it is possible to make the temperature distribution more uniform, the slope of the initial part can be increased and the bend into the space-charge part can be made more marked in this way.

Finally another method for comparing the emission of oxide cathodes, described by Fox and Bailey,<sup>1</sup> may be mentioned here. These workers used an electron microscope in which they produced an electron image of an oxide cathode having two coatings of different composition. The emission of these two coatings could

then be compared by determining the brightness of the two respective images by photographic means.

### 11. Actual Values of Emission and Efficiency Obtainable

The emission values obtainable with oxide cathodes will now be compiled. In this context two characteristic values must be distinguished, namely the emission density and the efficiency of the cathode. The emission density, which is also called specific emission or electron emissivity, is related to the surface area  $S_c$  of the oxide coating and is given in mA/cm.<sup>2</sup> or amps./cm.<sup>2</sup>. The efficiency  $W$  of an emitter is defined as the ratio between the emission current obtained and the heater power supplied. The normal unit for the efficiency is mA/watt. The efficiency can also be ascertained from the ratio between specific heater power and emissivity if account is taken of the difference between the coating surface  $S_c$  and the total surface  $S_t$ .

First of all we shall survey the values of the emission currents as they occur in the practical use of the oxide cathode. The densities of the operating emission currents of different types of cathodes as measured with a D.C. meter under normal conditions, are quoted in Table XIII.

TABLE XIII

*Densities  $j_{op}$  of the Operating Emission Currents of Different Types of Oxide Cathodes*

Type of cathode	Type of valve	$j_{op}$ (mA/cm. <sup>2</sup> )
Indirectly heated nickel cathodes.	Low-power valves:	
	Early valves	3-4
	Modern valves	5-10
	Miniature valves	10-20
	Output valves	20-30
	Transmitting valves	25-150
	UHF transmitting valves	100-200
	Magnetrons *	100-500
Mains rectifiers	50-90	
Directly heated cathodes with tungsten or nickel core.	Low-power valves	20-100
	Output and transmitting valves	60-200
	Magnetrons *	100-600
	Mains rectifiers	50-90

\* No peak values are taken from this type of cathode.

These current densities were obtained by using numerous European and American types of valves. The classification into



and a high-duty cycle are required for a high transmitting power, and a compromise must therefore be made. If the usual commercial oxide cathodes are employed peak currents between 1 and 10 amps./cm.<sup>2</sup> are used with pulse widths between 1 and 10  $\mu$ -secs. and with pulse recurrence frequencies between 100 and 1000 cycles. A duty cycle of 1/1000 is normally not exceeded. If special cathodes with low coating resistances are employed (cf. Fig. 7), pulsed currents between 10 and 30 amps./cm.<sup>2</sup> can be drawn during continuous operation (Fisk, Hagstrum, and Hartmann.<sup>1</sup>) While the average direct current from such cathodes as calculated from equation (7) will be lower than some of the values in Table XIII the peak currents are very near to the attainable saturated currents, and the values of employment factor and emission reserve referred to the peak current are therefore nearly unity.

The high peak currents from cathodes operated by pulses can only be obtained consistently if every cathode is activated to the optimum condition. As outlined by Coomes<sup>1</sup> a good cathode for pulsed operation will also be a good cathode for normal D.C. operation, while a cathode which gives a sufficient direct current will not always be adequate for supplying pulsed emission currents. Coomes also found that cathodes for pulsed operation should have thicker coatings than the normal cathodes and that by employing a core metal which is purer than the Grade A nickel normally used in the U.S.A. (cf. Table III), pulsed emission currents can be doubled.

If we consider again cathodes supplying steady currents (in low-power valves and output valves of class A amplifiers), a further increase in the density of the operating current seems to be possible on account of the low employment factor. In other words, these cathodes could be diminished in size without decreasing the current taken from them, and the heater power could thus be reduced. This will be possible to a certain extent, but on the other hand the reduction in size of the valve assembly is limited by commercial and economical aspects.

Before considering the efficiency of the oxide cathode, the saturated currents obtained from this cathode will be compared with the saturated currents from other types of cathodes. Fig. 50 shows as a function of temperature the densities of the saturated currents from cathodes which are in commercial use. The values plotted were taken from the quoted papers or were calculated by means of the Richardson law (equation (3)) from the work functions given in Vol. II, Tables V and VII. The heavy part of some of the

curves shows the range in which the values were measured, while the other part of these curves was obtained by an extrapolation using Richardson's law. The operating temperatures of the different cathodes are also marked in Fig. 50.

The maximum efficiency of a cathode can be calculated from the

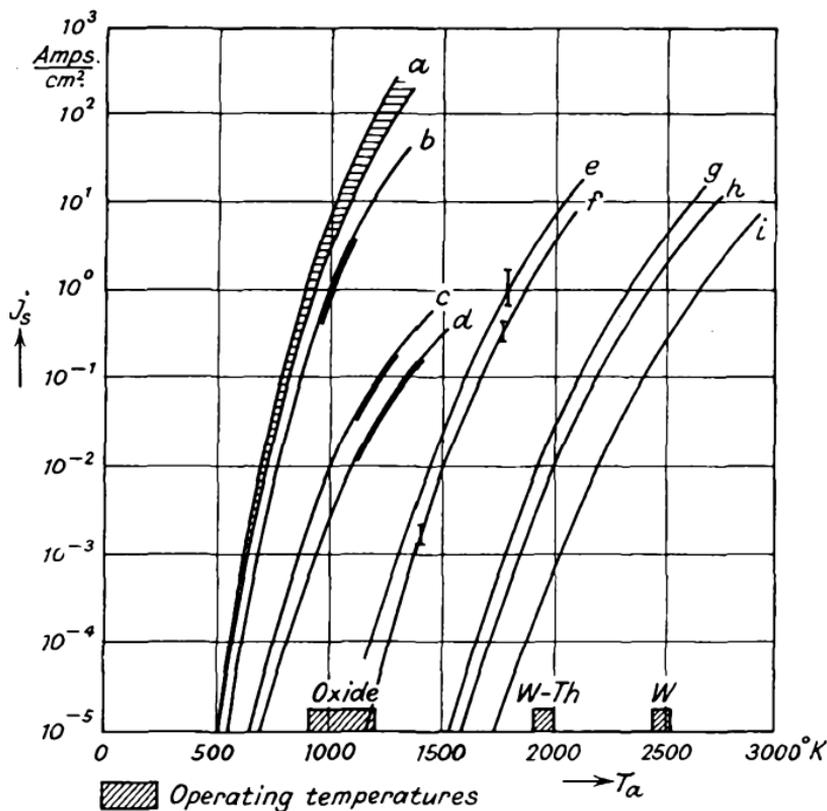


Fig. 50.—Densities  $j_s$  of the Saturated Currents from Different Types of Cathodes as a Function of Temperature: (a) Modern [BaSr]O Cathode according to Measurements of the Authors. (b) Condensation Cathode by Espe.<sup>2</sup> (c) Pure BaO Cathode by Espe.<sup>1</sup> (d) Early [BaSr]O Cathode by Koller.<sup>1</sup> (e) Thoria Cathode by Weinreich<sup>1</sup> and Hanley.<sup>1</sup> (f) W-Th Cathode, values according to Dushman and Ewald; Brattain and Becker, Reimann (cf. Vol. II, Table VII). (g) Niobium Cathode by Wahlin and Sordahl (cf. Vol. II, Table V). (h) Tantalum Cathode by Cardwell (cf. Vol. II, Table V). (i) Tungsten Cathode (mean values according to Vol. II, Table V).

curves in Fig. 50. The emission current is then equated to the saturated current, and it is assumed that the total heater power supplied is converted into radiation, losses by heat conduction being disregarded. The result of such a calculation undertaken for the pure tungsten cathode, for the atomic film cathode tungsten-thorium (covered fraction  $\theta = \theta_m$  and  $\theta = 0.9 \theta_m$ ,  $\theta_m = \text{maximum}$

coverage, cf. Vol. II, Sec. 5), and for the fully activated oxide cathode is shown by the full lines in Fig. 51. The heating of the oxide coating due to the emission current has been neglected in this calculation. Otherwise an infinite efficiency of the oxide cathode would be theoretically possible, as the emission current can be sustained without supplying heater power from outside if the cathode is suitably designed. The heater power is then entirely produced by the emission current which heats the coating when flowing through it; the heater power is in fact taken from the anode

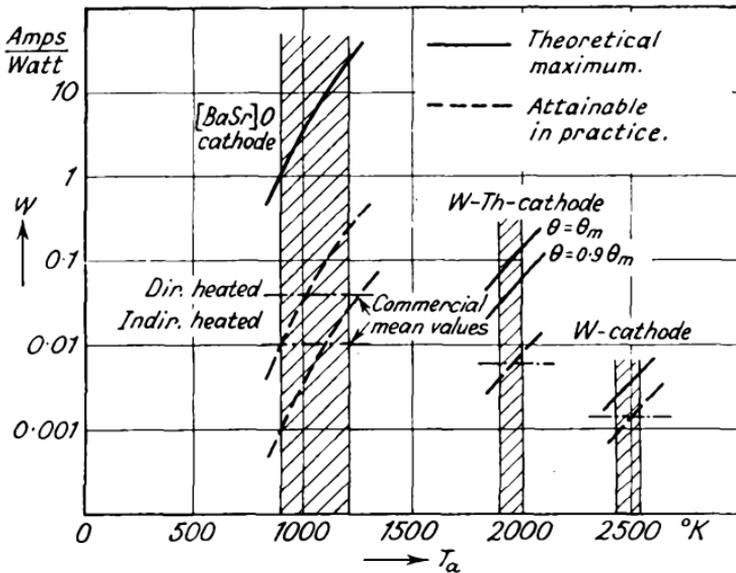


Fig. 51.—Efficiency of Different Types of Cathodes as a Function of Temperature.

battery. Such an emission state is very unstable and cannot be utilized commercially in valves whose electron current must be controlled (cf. Sec. 12).

The maximum efficiencies as shown by the full lines in Fig. 51 are only theoretically possible. The actual efficiencies which are obtained in practice can be calculated from the maximum efficiencies by multiplying these by the employment factor defined above. The employment factor of the pure tungsten cathode is about 0.3, that of the tungsten-thorium cathode between 0.03 and 0.15 depending on the value of  $\theta$ , while the employment factor of oxide cathodes is between 0.001 and 0.01, as discussed on page 94. The actual efficiencies are shown by the dashed lines in Fig. 51. This figure

demonstrates the superiority of the oxide cathode as given by its higher efficiency and its larger emission reserve. The calculated values in Fig. 51 correspond very well with the values obtained from the characteristics of commercial valves.

The progress made in the manufacture of oxide cathodes since their introduction into commercial use is best shown by the gradual improvement of their efficiency. This can be seen from Fig. 52, in which the average efficiency of European valves supplied with oxide cathodes has been plotted as a function of the year of their introduction. Only such valves have been taken into consideration which could be made satisfactorily and which were produced in

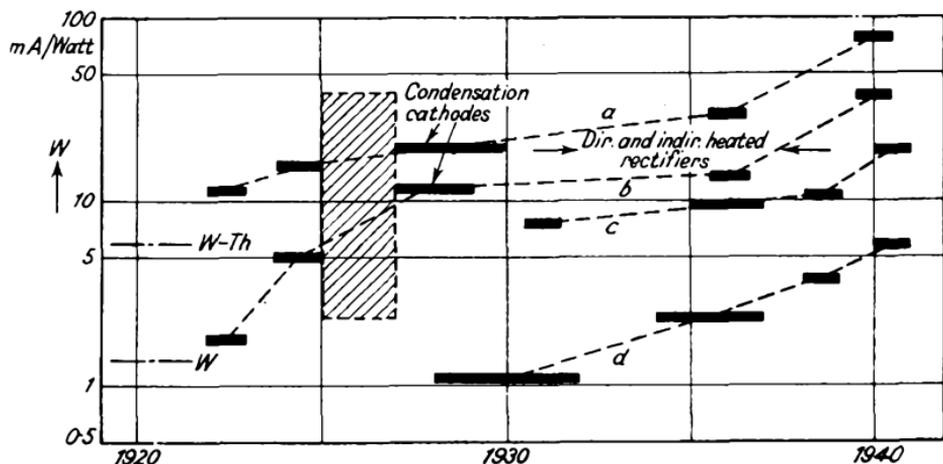


Fig. 52.—Improvement of the Efficiency  $W$  of Oxide Cathodes during their Development: (a) Directly Heated Output Valves, (b) Directly Heated Low-power Valves, (c) Indirectly Heated Output Valves, (d) Indirectly Heated Low-power Valves.\*

large numbers. The values for the years 1925 to 1927 have been indicated by the shaded rectangle in the figure, as these values show a very considerable spread due to the rapid development of broadcasting during these years. The relatively high values of efficiency during this time were obtained by employing higher cathode temperatures than is usual today (cf. Pohlmann and Gehrts<sup>1</sup>). The life of these cathodes was correspondingly short (Rukop<sup>1</sup>). The development in America was slightly different from that in Europe during the early years up to 1926. The Americans also used directly heated oxide cathodes, but there tungsten-thorium cathodes were more widely employed than in Europe. Afterwards the develop-

\* The plots shown in this fig. end with the year 1940. The efficiency of valve types developed since is, disregarding very few exceptions, not higher.

ments both in America and in Europe ran parallel. The efficiencies of the tungsten–thorium and the pure tungsten cathode have also been given in Fig. 52 for comparison.

The discussion of the emission values would be incomplete without considering the consistency of these values during commercial manufacture of the cathode. The consistency of the early cathodes can be seen from the distribution curves given by Arnold <sup>1</sup> for valves manufactured between 1915 and 1919 (Western Electric Company, U.S.A.). These curves may be compared with values obtained for a modern directly heated valve (KDD 1 Telefunken, Philips). The average emission density taken from the modern valve was the same as in Arnold's measurements. The distribution

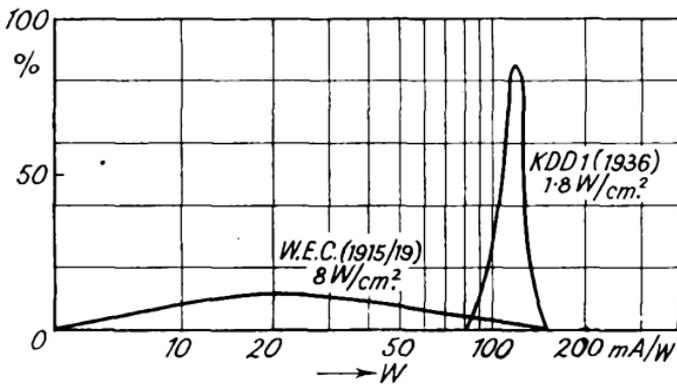


Fig. 53.—Distribution Curves of the Efficiency  $W$  of Early and Modern Oxide Cathodes.

of the efficiency of both types of valves has been plotted in Fig. 53. It may be pointed out that the measured values are not the operating currents of the valves but three to four times higher than these and that therefore the relatively high efficiencies shown by Fig. 53 are obtained. While the specific heater power of the early W.E.C. valves was 8 watts/cm.<sup>2</sup>, only 1.8 watts/cm.<sup>2</sup> heater power must be supplied for the modern valves. This difference is explained by the fact that the early cathodes were of the combined type with higher radiant emissivities and higher operating temperatures than those of modern cathodes. The improvement obtained with the modern oxide cathodes as shown by Fig. 53 would be still more impressive if the emission could be compared at the same specific heater power. It has been estimated that, when undertaking such a comparison, the shape of the distribution curve remains nearly the same, but the emission densities then differ by at least four powers of 10.

Before discussing the undesirable features of the oxide cathode the different characteristics of the cathode which were introduced and discussed in this section will be compiled in the following table.

TABLE XIV  
*Characteristics of the Oxide Cathode*

Total surface . . . . .	$S_t$
Coating surface . . . . .	$S_c$
Heater power . . . . .	$P_H$
Specific heater power . . . . .	$P_H/S_t$
Radiation from the cathode . . . . .	$P_{rad}$
Losses by heat conduction . . . . .	$P_{cond}$
Actual temperature . . . . .	$T_a$
Brightness temperature . . . . .	$T_b$
Total radiant emissivity . . . . .	$c_t$
Spectral radiant emissivity at the wavelength $\lambda$ . . . . .	$c_\lambda$
Emission current (in general) . . . . .	$I_e$
Saturated current . . . . .	$I_s$
Operating current (mean D.C.) . . . . .	$I_{op}$
Peak current . . . . .	$I^*$
Emission density . . . . .	$j_e = I_e/S_c$
Saturated current density . . . . .	$j_s = I_s/S_c$
Operating current density . . . . .	$j_{op} = I_{op}/S_c$
Peak current density . . . . .	$j^* = I^*/S_c$
Employment factor, referred to the operating current . . . . .	$\mu = I_{op}/I_s$
Employment factor, referred to the peak current . . . . .	$\mu^* = I^*/I_s$
Emission reserve, referred to the operating current . . . . .	$R = (I_s - I_{op})/I_{op}$
Emission reserve, referred to the peak current . . . . .	$R^* = (I_s - I^*)/I^*$
Efficiency . . . . .	$W = I_{op}/P_H$
Maximum efficiency . . . . .	$W_{max} = I_s/P_{rad}$

## 12. Undesirable Features of the Oxide Cathode

The values of the emission current quoted above can only be obtained with cathodes which are activated to the optimum. When manufacturing and operating the cathode, however, there are many factors which may impair or destroy the emission. The most important of these undesirable features which will be discussed here are: the evaporation of the oxide coating, the heating-up of the coating produced by the emission current, the heterogeneity of the coating, the inadequate bond between coating and core metal, the ion emission from the coating, and the tendency of the oxide to poisoning.

### 12.1 Evaporation of the oxide coating

For measuring the rate of evaporation the alkaline earth oxide is located on a metallic support and evaporated for a certain time at a known temperature on to a neighbouring surface. The quantity of

oxide evaporated is then determined by chemical analysis and the rate of evaporation is calculated from the value obtained. It is highly important with such a measurement that the temperature be measured accurately and be kept constant during the whole period of evaporation.

The results obtained by Claassen and Veenemans<sup>1</sup> and by Blewett, Liebhafsky, and Hennelly<sup>1</sup> for pure BaO correspond rather well, while the result by Herrmann<sup>1</sup> differs slightly, due probably to the method of measuring the temperature. The rates of evaporation

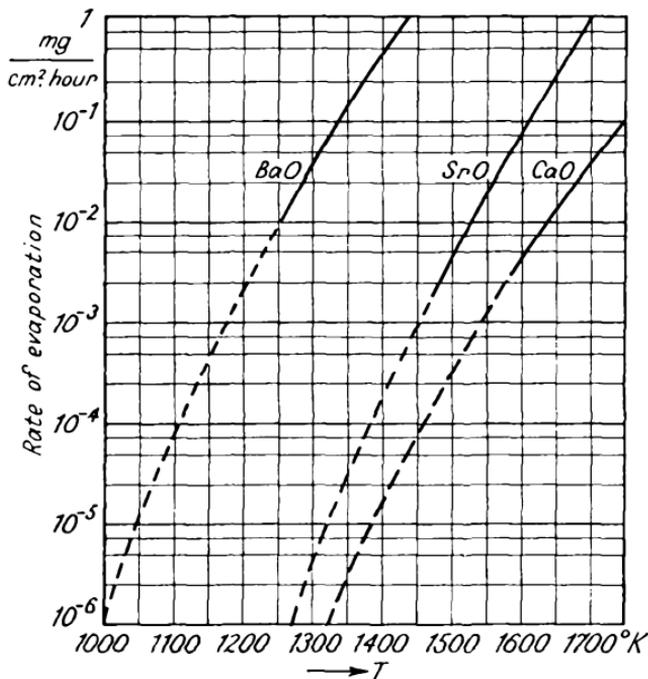


Fig. 54.—Rate of Evaporation of Alkaline Earth Oxides as a Function of Temperature (Claassen and Veenemans<sup>1</sup>).

of the three main oxides BaO, SrO, and CaO as measured by Claassen and Veenemans have been plotted as a function of temperature in Fig. 54. One sees from this that the rate of evaporation decreases considerably in the order BaO, SrO, CaO. If mixtures of BaO and other oxides are used, the BaO therefore evaporates almost exclusively out of these mixtures, as confirmed experimentally by the above two experimenters. The rate of evaporation of such mixtures decreases with time, because the BaO evaporates preferentially from the superficial parts of the coating and is not sufficiently replaced by diffusion from the interior (cf. Sec. 7 and Vol. II,

Sec. 26). Herrmann found that the rate of evaporation of barium oxide is independent of the type of core metal used. The evaporation of barium atoms from an activated cathode which takes place in addition to the evaporation of barium oxide will be discussed in Vol. II, Sec. 31.

It can be seen from the values of the rate of evaporation that this evaporation will mainly take place during the decomposition and the activation, while the evaporation occurring during operation of the cathode will be extremely low. The evaporation is detrimental because the barium oxide when evaporated condenses on the other electrodes of the valve and forms secondary oxide cathodes there which are activated by bombarding electrons or by evaporating barium in the manner described in Sec. 8.

## 12.2 Influence of the emission current on the temperature of the oxide coating

When drawing emission from an oxide cathode the coating is heated up by the emission current. This undesirable feature is observed with other types of cathodes only at much higher current densities. It is due to the fact that the electrical resistance of the oxide coating is considerably higher than that of a metal and in addition the specific heater power of oxide cathodes is small. The power producing the heating-up, given in watts, is:

$$P_{h-u} = I_e^2 R_c \quad . . . . . (11)$$

where  $R_c$  denotes the resistance of the oxide cathode normal to the axis of the cathode. If the cathode is operated with pulses the heating-up power must be derived from the mean square of the pulsed current. Using square pulses, this power is therefore obtained from equation (8) as:

$$P_{h-u} = I_e^{*2} w v_r R_c \quad . . . . . (12)$$

The heating-up of the coating is more or less counterbalanced by the cooling effect which is produced by the emission of the electrons. This cooling effect will be discussed in Vol. II, Sec. 9, and it will be shown there that different formulæ for the cooling power are obtained in the saturation and in the space-charge range. Under saturated conditions the cooling power given in watts is, obtained from equation (92), Vol. II:

$$P_{cool}^{(s)} = I_s \psi + 1.72 \times 10^{-4} I_s T \quad . . . . . (13)$$

where  $\psi$  denotes the work function of the cathode, and  $T$  its temperature. The corresponding formula for the space-charge range is, according to equation (95), Vol. II:

$$P_{cool}^{(sp)} = I_{sp} T \times 10^{-4} \left( 1.72 + 1.98 \log \frac{120 ST^2}{I_{sp}} \right) \quad . \quad . \quad (14)$$

$S$  denoting the surface of the cathode.

If the cathode is operated with square pulses, the equation for the cooling power is:

$$P_{cool} = I_e^* w v_r (\psi + 1.72 \times 10^{-4} T) \quad . \quad . \quad . \quad (15)$$

This formula can generally be employed for pulsed currents, as normally these currents are nearly saturated. The value of the work function to be used in the above formulæ for fully activated cathodes is  $\psi = 1.4$  eV.

Under operating conditions, both heating-up and cooling effects occur. The influence of these two factors is best seen from the energy balance of the cathode, which is given by the following equation:

$$P_H + P_{h-u} = P_{rad} + P_{cond} + P_{cool} \quad . \quad . \quad . \quad (16)$$

Either the heating-up power on the left-hand side or the cooling power on the right-hand side of this equation will prevail, depending on the values of the emission current, of the temperature, of the work function, and of the resistance of the coating. Correspondingly the cathode, when switching on the emission current, will either be heated up or cooled.

The coating resistance will depend on the specific resistance of the oxide and on the structure of the coating. The methods for measuring the specific resistance are discussed in detail in Vol. II, Sec. 22. The results of the measurements are very inconsistent, because the measurement of the resistance of a porous material, as formed by the oxide coating, is rather difficult. The most reliable measurements give values between 100 and 500  $\Omega$  cm. for activated barium oxide at the operating temperature of the cathode. From this value the resistance of a coating of 50 to 100  $\mu$  thickness and 1 cm.<sup>2</sup> area is calculated as between 1 and 10  $\Omega$ . The coating resistances, which have been measured directly by Graffunder,\* Coomes,<sup>1</sup> Fineman and Eisenstein,<sup>1</sup> and Wright,<sup>1</sup> correspond with the above values.

The temperature dependence of the resistance will be seen from

\* Unpublished measurements.

Table XV. Coomes,<sup>1</sup> when measuring pulse-operated cathodes, found that the coating resistance passes through a minimum during the life of the cathodes. Fineman and Eisenstein and Wright showed that the interface layer which is sometimes formed between the core metal and the oxide coating may have a resistance which is many times higher than the resistance of the oxide coating itself (cf. Vol. II, Sec. 32).

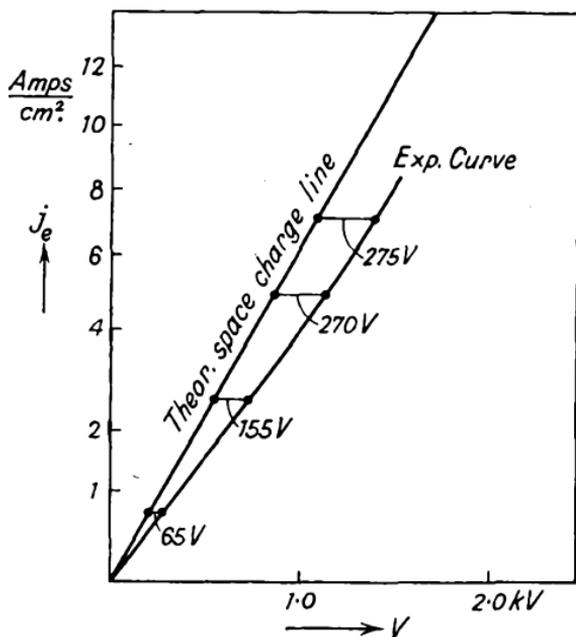


Fig. 55.—Theoretical and experimental space charge characteristics of an oxide cathode with interface layer (core metal Ni+5%Si, the numbers in the figure give the voltage drop across the coating) (Eisenstein<sup>2,3</sup>).

The total resistance of the coating may then be so high that, when drawing high pulsed currents from the cathode, a voltage drop of some hundred volts arises across the coating. Voltage drops of this magnitude which have for instance been detected by Eisenstein<sup>2,3</sup> will of course influence the characteristic of the valve containing the cathode. These voltage drops must therefore be accounted for when calculating such a characteristic (cf. Ferris<sup>1</sup>).

Fig. 55 shows the deviation between the theoretical space charge characteristic and the experimental characteristic as observed under such conditions.

TABLE XV

Resistance  $R_c$  of an Oxide Coating as a Function of Temperature  
(Thickness  $\approx 70 \mu$ ) (Wright<sup>1</sup>)

$T$ ( $^{\circ}$ K.)	$R_c$ ( $\Omega$ /cm. <sup>2</sup> )
750	27
830	11
900	6
950	4
1000	3
1050	2.2
1090	1.6

For estimating how the temperature of the cathode is influenced under certain conditions, the heating-up power,  $P_{h,u}$  and the cooling power  $P_{cool}$  have been plotted as a function of the emission current in Fig. 56. As the space-charge region is nearly always used for D.C. operation, the cooling power was calculated from equation (14), valid under space-charge conditions. The coating Resistance  $R_c$  was taken as a parameter, and several straight lines representing the heating-up power for the different resistances were obtained in this way. Heating-up and cooling power are equal at the intersection of one of these straight lines with the curve representing the cooling power. The intersection points therefore

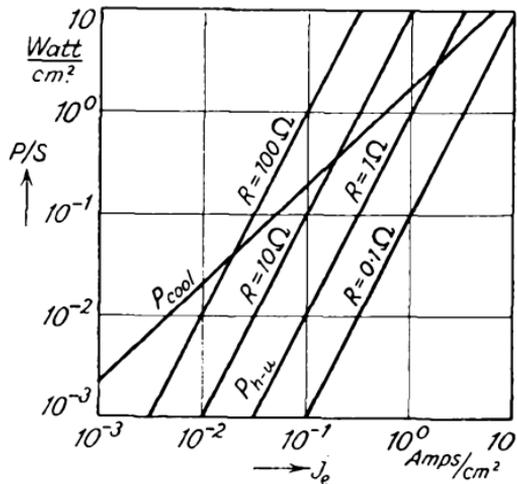


Fig. 56.—Heating-up Power  $P_{h,u}$  and Cooling Power  $P_{cool}$  as a Function of Emission Density.

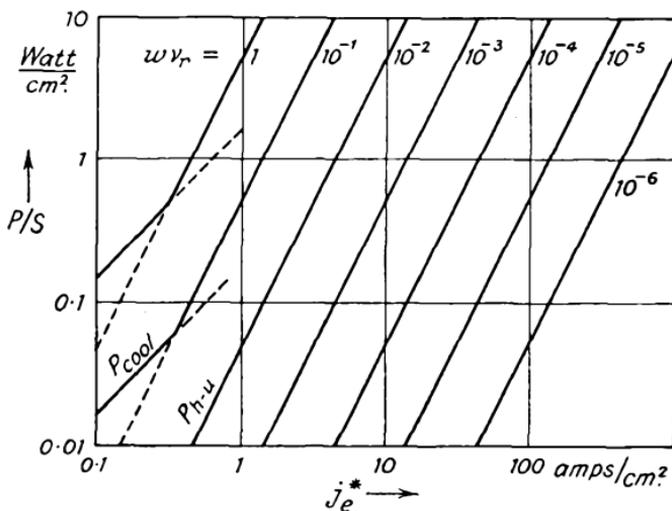


Fig. 57.—Heating-up Power  $P_{h,u}$  and Cooling Power  $P_{cool}$  as a Function of Peak-Current Density for Square Pulses (duty cycle  $wv_r$ , as parameter,  $R_c=5\Omega/cm^2$ ).

correspond to conditions at which the temperature of the cathode remains unchanged after switching on the emission current. The cooling of the coating predominates on the left-hand side of such

an intersection point, and the temperature will there decrease after switching on. On the right-hand side of the intersection point, however, the heating-up effect prevails and the temperature will increase correspondingly.

Fig. 56 is only valid for direct current operation. The conditions obtained if pulsed currents are drawn from the cathode will be seen from Fig. 57, in which square pulses and a coating resistance of  $5 \Omega/\text{cm}^2$  have been assumed. One sees from this figure that the cooling power can be neglected below a duty cycle of 0.1 and above 1 amp./ $\text{cm}^2$  peak current density. The magnitude of the rise in temperature produced by high pulsed currents is shown by Fig. 58.

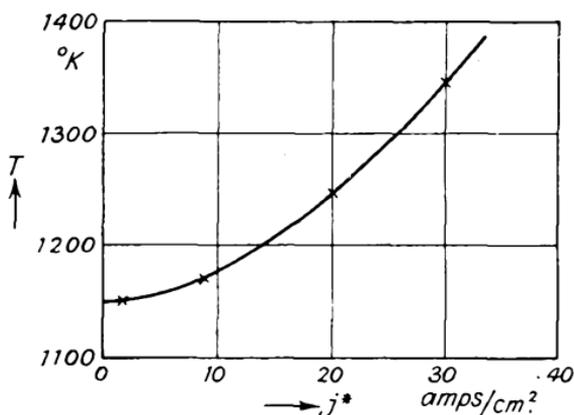


Fig. 58.—Rise in Cathode Temperature, Produced by Drawing Pulsed Currents, as a Function of Peak Current Density  $j^*$  (duty cycle 1/1000) (Coomes<sup>1</sup>).

If the resultant heating-up power ( $P_{h-u} - P_{cool}$ ) becomes of the same order as the heater power supplied externally, the temperature of the cathode becomes unstable. This may occur at direct current densities of about 1 amp./ $\text{cm}^2$  according to Fig. 56. If, then, the anode voltage is sufficiently high, the emission current will rise still more due to the increase in temperature, and by a cumulative process the cathode may be destroyed. As mentioned in Sec. 10, this process makes a static measurement of the saturated current at the operating temperature impossible.

### 12.3 Effects due to the heterogeneity of the coating and to the poor bond between coating and core (sparking)

As shown by Figs. 17 and 18 the oxide coating is not uniform, but consists of a loose conglomeration of particles of an irregular shape

with interspaces of different size. Furthermore, the surface of this coating is not smooth but very rough, consisting of protruding peaks and deep cavities. It is easy to understand that the mechanical strength of such a coating is much smaller than that of a homogeneous material. Consequently if a high electric field is applied to the cathode, the electrostatic force may tear from the cathode particles which are then attracted by the electrode producing the field and which will hit this electrode with a high velocity. Such a process which is, for instance, observed with rectifiers at high blocking voltages, produces a reverse current from the anode which causes great local heating of the oxide coating. A high emission current is thus obtained from the respective area of the coating, and this current, if high enough, may give rise to the formation of an arc and to the destruction of the cathode.

The occurrence of this disturbing phenomenon can be displaced to higher field strengths by using special methods for preparing the coating. If a colloidal emission paste is employed and deposited by electrophoresis the coating so produced has not only a much smoother surface but also a higher mechanical strength than the normal coating made by spraying. If such cathodes are used in rectifiers, field strengths up to several hundred kV/cm. may occur at the cathode surface in the blocking phase before oxide particles are torn from the cathode.

Another property of the oxide coating which is important in this connection is the bond between the coating and the core metal. This bond depends on the type of the core metal to a large extent. Core metals which give rise to the formation of an interface layer between core and coating, as, for instance, tungsten, have an unfavourable influence on the bond (Liebold,<sup>1</sup> Herrmann<sup>2</sup>). Furthermore, the bond between coating and core is influenced by the heat expansion of the core metal. If the coefficients of thermal expansion of core and coating are much different, mechanical forces between core and coating will occur which try to loosen the coating from the core. For this reason tungsten is again the least favourable core material, because the low coefficient of expansion of tungsten differs most from that of the alkaline earth oxide (cf. Table XVI). Another factor influencing the bond is the degree of sintering of the coating. A strong sintering may produce cracks and thus impair the cohesion of the coating. Oxide coatings which are very dense and which are operated at high temperatures will be especially prone to such cracks.

TABLE XVI

*Thermal Expansion of Core Materials and Oxide Coatings*

Material	Coefficient of thermal expansion ( $\times 10^{-6}$ )	Temperature range ( $^{\circ}$ K.)	Measured by
Ni	16.8	300-1300	According to Standard Tables.
Pt	10.2	"	
W	4.6	"	
[BaSr]O	14	300-1300	Authors. Eisenstein. <sup>1</sup>
[BaSr]O	26.6	300-1150	
BaO	17.8	"	
SrO	32.5	"	
ThO <sub>2</sub>	11.3	"	

The above considerations do not account for the emission current drawn from the cathode. Owing to the heterogeneity of the coating the electrons are not emitted uniformly from it; on the contrary there are differences between the emission from different parts of the coating. This is demonstrated by images of the coating surface taken with the electron microscope, as shown, for instance, by Fig. 92 (Vol. II). The difference between the saturated currents of different areas of the coating can be given as a function of the difference  $\Delta\psi$  in work function between the respective areas. By using equation (3) for the saturated current the following relation is derived for the relative difference in saturated current:

$$\frac{\Delta I_s}{I_s} = -\frac{1.16 \times 10^4}{T} \Delta\psi \quad . . . . . (17)$$

One sees from this that the variation of the saturated current along the surface increases with decreasing temperature provided the work function remains constant.

If the current drawn from the cathode is increased, the areas which emit the most and supply high current densities are heated up still more. The emission current from these areas will therefore rise and the differences in emission between the high-emitting and the low-emitting areas will become even more pronounced. If this process continues the temperature of the high-emitting areas will finally increase so much that considerable evaporation of the coating will take place from these areas with the evolution of appreciable quantities of gas. The ions produced during this process will then tend to annul the negative space charge in front of the cathode, and

the field strength there, which is negative under space-charge conditions, will become positive. Finally the particles of the coating will be removed by evaporation, by sputtering produced by the ions, and by electrostatic forces trying to tear the particles from the coating in the manner described above.

The final stage which is reached during such a process greatly depends on the conditions in the external circuit. If the maximum emission current drawn from the cathode is limited by the circuit, only a momentary bright spot at the respective area of the cathode, accompanied by a current impulse, is observed. This phenomenon is called sparking; it may occur again when the anode voltage is switched on for the next time. If, however, the conditions of the external circuit are unfavourable, a low voltage arc will arise between

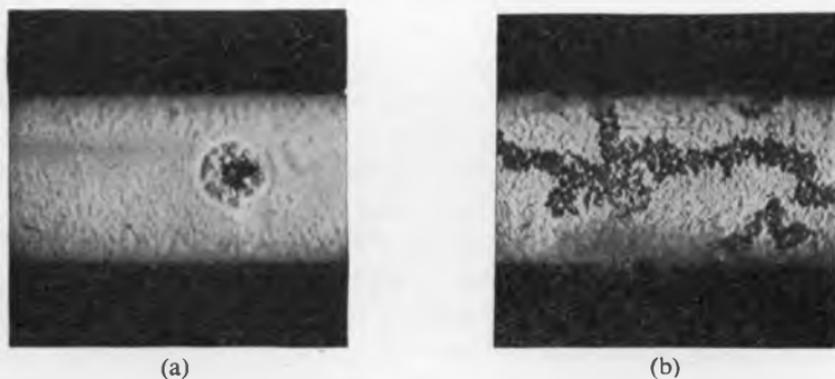


Fig. 59.—Oxide Cathode affected (a) by Sparking or (b) by Formation of an Arc (mag.  $\times 10$ ).

cathode and anode, and the cathode will be more or less destroyed by this arc. Fig. 59 shows the effects of sparking and of the formation of an arc on the oxide coating.

The sparking phenomenon as obtained with direct currents has been investigated by Knowles and McNall<sup>1</sup> for oxide cathodes operated in a mercury discharge. They used a circuit which prevented the cathodes from being destroyed and which made a frequent examination of the same cathode possible. They found that the critical current density at which the sparking starts is displaced to higher values, if the temperature of the cathode is raised or the activation improved. Furthermore, the type and pressure of the gas in the valve had a considerable influence on the occurrence of the sparking phenomenon. Investigations of the authors, however, showed that there is no relation between the current

density critical for sparking and the pressure in the valve, provided this pressure is lower than  $10^{-3}$  mm.

If the cathode is operated in a high vacuum, results similar to those of Knowles and McNall are obtained (cf. Schade <sup>1</sup>). The sparking phenomenon is always much stronger at low cathode temperatures, because the differences in emission between different areas of the cathode are larger at these temperatures, as shown by equation (17). The emission current will therefore concentrate more and more to a few small areas of the cathode with decreasing temperature. Furthermore, the cathode, when operated at sufficiently low temperatures, emits a current which is nearly saturated, and a high positive field strength in front of the cathode will be obtained more easily than with higher temperatures. It follows from this that the sparking phenomenon is most likely to be observed during the warming-up period, if the anode and heater voltages are switched on together. The longer the process of warming-up, the more likely it is that sparking will occur. For this reason indirectly heated cathodes in rectifiers are particularly endangered.

Since a cathode becomes more prone to sparking with increasing density of the emission current, one would expect that a strong sparking phenomenon is observed with the high current densities drawn from the cathode under pulsed operation. This was confirmed by Coomes.<sup>1</sup> When using cathodes activated to the optimum condition, he found that the sparking was obtained under space-charge conditions before the saturated current was reached. The critical current density at which the sparking started depended on the pulse width and on the composition of the cathode material. With a pulse width of 1  $\mu$ -sec. for instance, the critical current was three times as high as with a width of 10  $\mu$ -sec. To avoid sparking, the pulse width should therefore be chosen as small as possible. A further interesting result was that the critical current of cathodes made with a very pure core nickel was 130 amps./cm.<sup>2</sup> (for 1  $\mu$ -sec. pulse width at 1075° K.), while the corresponding value for cathodes made with the normal "Grade-A nickel" (cf. Table III) was only 50 amps./cm.<sup>2</sup>. This different behaviour can be explained by the fact that the alloyed additions and the impurities of Grade-A nickel form an interface layer between core metal and coating (cf. Vol. II, Sec. 32). Owing to the high resistance of this interface layer, the coating of these cathodes will be heated up more than without the interface layer, and the sparking will be obtained with a lower current density.

If the saturated current of the cathode is smaller than the critical value, the sparking phenomenon is displaced into the saturation range, and the voltage or the field strength in front of the cathode determines the onset of sparking. Fig. 60 demonstrates the two different causes of sparking, according to Coomes' results. Immediately after activation the sparking is produced by the critical emission current  $I_{cr}$  marked on the space-charge characteristic plotted in Fig. 60. During the life of the cathode the saturated current decreases, and the sparking is then produced by increasing the voltage above the value necessary for obtaining saturation, to a

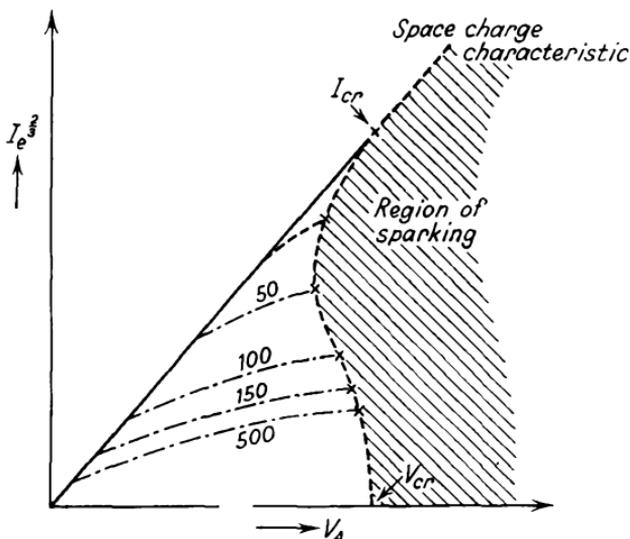


Fig. 60.—Sparking Diagram for an Oxide Cathode Operated with Pulses (numbers represent aging times in hours) (Coomes<sup>1</sup>).

critical value  $V_{cr}$ . This critical voltage depends on the type of oxide used for the coating. Its value is between 100 and 125 kV/cm. for barium oxide, but only 40 to 60 kV/cm. for strontium oxide. If the usual mixed barium–strontium oxide is employed, the same values as for strontium oxide are obtained.

The voltage drop existing in the coating at the onset of sparking was determined by Danforth and Goldwater<sup>1</sup> by means of probe measurements. They measured a critical voltage drop between 200 and 500 volts for [BaSr]O-coatings of 10 to 15 mg./cm.<sup>2</sup> weight.

Riethmüller,<sup>1</sup> when using pulsed operation, confirmed that the sparking phenomena are independent of the vacuum in the valve. Furthermore, he found that, when employing wide pulses, the sparking only starts during the second half of the pulse, after a

certain quantity of electricity has flown through the cathode. Biguenet <sup>1</sup> investigated the sparking as a function of the weight of the coating and obtained a maximum of the critical emission current  $I_{cr}$  for a weight of about 10 mg./cm.<sup>2</sup>.

Finally it may be mentioned that the oxide cathode is not always the primary cause of sparking. These phenomena are also influenced by the purity of the anode and by foreign bodies existing in the discharge space.

### 12.4 Emission of ions

Several investigations undertaken by mass-spectrographical methods have shown that an oxide cathode emits negative ions during normal operation. The details of these investigations will be discussed in Vol. II, Sec. 31. It may be pointed out here that most of the emitted ions are of chlorine, oxygen, and hydrogen, and that the ionic currents observed are of the order of  $10^{-10}$  amp. In spite of their small magnitude these ionic currents produce interference in cathode-ray and television tubes. As first described by v. Ardenne,<sup>1</sup> these ions affect the fluorescent screen of the tubes concerned by their impact. They cause the screen to become insensitive to the electrons impinging on it, and a permanent dark stain is so produced, normally in the centre of the screen, spoiling the image formed by the electrons.

Liebmann <sup>1</sup> showed that a permanent image of the cathode can be formed on the screen by the emitted ions under suitable electron optical conditions. This ion image on the screen is found to be a negative of the normal electron image formed by the emitted electrons. It thus follows that the areas of high light density in the electron image are those most impaired by the impinging ions, showing therefore that areas on the cathode with high electron emission are also areas with high ion emission.

A remedy against the detrimental effects of the ions on the screen can be found in two ways. It is possible to displace the ion stain by suitable electron optical means to an area outside the proper screen. Furthermore, the screen itself can be made resistant to the effect of ions by a suitable treatment. Details may be seen from the literature (cf. White <sup>1</sup>).

### 12.5 Sensitivity to poisoning

Phenomena during which active states are impaired or destroyed are generally called poisoning phenomena, as for instance in

catalysis. If the emissivity of an oxide cathode is decreased or destroyed by gases or other foreign materials, the term poisoning is used likewise.

The poisoning of an oxide cathode is most likely to occur at low temperatures and can therefore best be observed by underheating the cathode (cf. Fig. 49). For this reason cathodes operated at low temperatures are particularly prone to poisoning. The poisoning is produced by gases or solid materials which react with the oxide coating or with the excess barium in it. The poisoning materials originate either from the cathode itself or come from other electrodes during the manufacture and the operation of the valve.

The poisoning agents originating from the cathode may be gases or vapours given off by the core metal, by the heater, or by the insulating material. Solid materials which are either formed by reactions between the core metal and the coating or which exist as impurities in the coating can also cause poisoning. The other electrodes and components of the valve normally cause poisoning by giving off gases and vapours. When the valve is operated, the electron current bombarding the anode and the positive grids, heats these electrodes which, if not sufficiently degassed during manufacture, give off absorbed gases. Furthermore, it is possible that chemical compounds existing on the surface of the electrodes are decomposed by the bombarding electrons and that gases which produce poisoning are set free in this way. This undesirable phenomenon was recently examined in detail by Jacobs,<sup>1</sup> who studied the decomposition of different metal oxides and by Hamaker, Bruining, and Aten,<sup>1</sup> who investigated the halides.

The poisoning effect of different gases and vapours was examined in detail by Herrmann and Krieg.<sup>3</sup> They showed that all gases occurring during the manufacture of valves, except rare gases and hydrogen, produce poisoning to a greater or lesser extent. The poisoning effect is either due to a reaction between these gases and the alkaline earth oxide (with CO, CO<sub>2</sub>) or to a reaction with the excess barium necessary for the emission (with O<sub>2</sub>). The poisoning effect increases in the sequence carbon monoxide, carbon dioxide, oxygen. Halogens and water vapour, which bind the excess barium in the same way as oxygen, also produce heavy poisoning. The poisoning effect, of course, decreases with decreasing pressure of the gas; oxygen still impairs the emission at pressures of about 10<sup>-5</sup> mm. A favourable influence on the emission cannot be observed with any gas as long as fully activated cathodes are examined.

Cathodes in an inferior state of activation, however, can be improved under certain conditions by the effect of rare gases and hydrogen.

According to Herrmann<sup>2</sup> poisoning by solid materials existing in the oxide coating only occurs if chemical compounds between the foreign material and the alkaline earth oxide are formed. With oxides added to the coating the poisoning effect was found to increase with increasing acidity of the oxide concerned (cf. Vol. II, Sec. 26.2). As shown by Liebold,<sup>1</sup> the core metal may cause poisoning, if a chemical reaction between core metal and coating occurs during the manufacture and if the products of this reaction are detrimental to the cathode. This was observed, for instance, with chromium, iron, and molybdenum (cf. Vol. II, Sec. 32).

The detrimental influence of various hydrocarbons on the oxide cathode must also be considered as a poisoning produced by a solid material. The hydrocarbons dissociate at the surface of the oxide coating above a certain temperature depending on the thermodynamical stability of the hydrocarbon concerned. The carbon which is deposited reduces the emissivity of the cathode to such an extent that a decrease in emission by several powers of 10 may be obtained at the operating temperature without observing any blackening of the cathode.

All these poisoning phenomena, which are discussed in greater detail in Vol. II, Chap. 6, show that there are numerous ways in which the emission of an oxide cathode may be impaired. It is therefore necessary in every accurate investigation to check carefully whether all the possible causes of poisoning have been avoided. If such poisoning phenomena are not transient but permanent, or if they only occur after a certain time of operation, they will affect the life of the cathode.

### 13. The Life of the Oxide Cathode

If physical phenomena are to be used commercially, they must satisfy the demands for an adequate reproducibility and constancy. As the oxide cathode did not satisfy these demands in the early years after its discovery, it could not come into commercial use during that time. Only when it was possible to make consistent cathodes with an adequate life (cf. Arnold<sup>1</sup>) could these cathodes displace the earlier types. Some general aspects of the factors influencing and limiting the life of the oxide cathode will be given here, but quantitative statements will only be possible when further experimental evidence of the fundamental processes influencing the life has been obtained.

The variation of the emission current admissible during life depends very much on the application of the valve, since this variation can be equalized to a certain extent by special measures in the circuits associated with the valve (feed-back). The variations which are allowed in practice are between  $\pm 5\%$  and  $\pm 50\%$  (Dosse <sup>1</sup>). A positive variation of the emission current during life is relatively rare and occurs if the activation has not been brought to the optimum due to poisoning influences which gradually decrease during operation.

The decrease of the emission current which is normally observed during the life of the cathode depends on temperature and becomes more marked if the temperature is chosen too high or too low. The temperature limits within which the cathode can be operated safely, depend on the emission density drawn from the cathode; they become narrower if the emission density is increased. Exact values of the temperature limits cannot be given due to the involved nature of the phenomena influencing life. If indirectly heated cathodes with an average operating current of 20 mA/cm.<sup>2</sup> are used, the approximate limits are 900° and 1200° K.

The lower limit of temperature is determined, apart from the demand of an adequate emission reserve, by the tendency of the cathode to be poisoned, which increases with decreasing temperature. The upper limit, however, is determined by a variety of different phenomena, such as evaporation of the oxide coating or of its components, evaporation of the excess barium in the coating, evaporation of the core metal into the coating, and sintering phenomena in the coating. The evaporation of the oxide coating or of its components can be calculated from the rate of evaporation of barium oxide (cf. Fig. 54). If a coating weight of 5 to 10 mg./cm.<sup>2</sup> and a cathode temperature of 1200° K. are assumed, the time during which half of the coating would evaporate is found to be between 1000 and 2000 hours. At a temperature of 1000° K. this figure is 1,000,000 hours.

As the rate of evaporation of BaO is higher than that of SrO, the percentage of BaO in the coating will decrease during life and produce an appropriate fall in emission. This variation of the composition of the coating was detected and measured by Eisenstein <sup>1</sup> by means of X-ray patterns. It was found that the rate of the variation in composition is not altered if the cathode is operated with or without drawing emission current. Different results, however, were obtained by using cathodes with different core materials.

If a core nickel containing highly reducing additions was employed, the percentage of BaO decreased more quickly than with a pure nickel core.

An estimation of the evaporation of the core material has been given in Sec. 3. According to these values a life of some 1000 hours may be expected at the upper temperature limit. The sintering phenomena influence the life as shown by practical experience, but no quantitative results have yet been established. Probably these phenomena also increase greatly with the temperature.

Apart from these direct influences on life there are several indirect ones. For instance, the core wire or the heater of an indirectly heated cathode may break due to recrystallization and may thus end the life suddenly (catastrophic failure). These phenomena also increase with increasing temperature. As pointed out in Secs. 3 and 6, heaters and cathode sleeves of different design show very different behaviour during life (Michael<sup>1</sup>). Folded heaters, for instance, are more prone to breaking than spiral heaters, while sleeves extruded from tubes are superior to those folded from sheet. If directly heated cathodes with tungsten cores are used, the formation of an interface layer will influence the emission more and more with increasing temperature, and an upper temperature limit will thus be obtained. Finally, as observed by Raudorf,<sup>1</sup> the bond between oxide coating and core may loosen during life and the increased capacity at the interface may give rise to a variation of the characteristics of the valve with frequency.\*

A good vacuum in the valve is not only necessary for avoiding poisoning, but also for preventing ions from bombarding the coating and sputtering it away (Hull,<sup>1</sup> Rothe and Kleen,<sup>3</sup> Herrmann and Krieg<sup>5</sup>). This phenomenon is observed particularly with the cathodes of cathode-ray tubes because, due to the beam concentration, a heavy bombardment of ions on the cathode may occur. As shown by Reusse,<sup>1</sup> this process is mainly responsible for the life of cathodes in such tubes. The factors determining the life of cathodes in gas-filled tubes will be discussed in Sec. 16.

Summarizing, we may state that the life of an oxide cathode in a high vacuum becomes the shorter:

- (1) the poorer the vacuum,
- (2) the more the cathode temperature is outside the medium temperature range of about 1000° K.

\* *Note added during proof reading*:—As pointed out by Eisenstein<sup>4</sup> this effect can also be produced by formation of inter-face layers.

If the temperatures and emission densities are the same, cathodes with tungsten cores are inferior to those made with nickel cores. The optimum temperature range may possibly be shifted to lower values if the vacuum in the valve is improved further and the poisoning consequently reduced.

So far only cathodes which are operated with D.C. have been considered. Cathodes operated with pulsed anode voltages principally show the same behaviour, but the temperature range available for operation is still narrower with these cathodes than when

operating under steady current conditions. Details of the dependence of life on temperature for cathodes operated with pulses

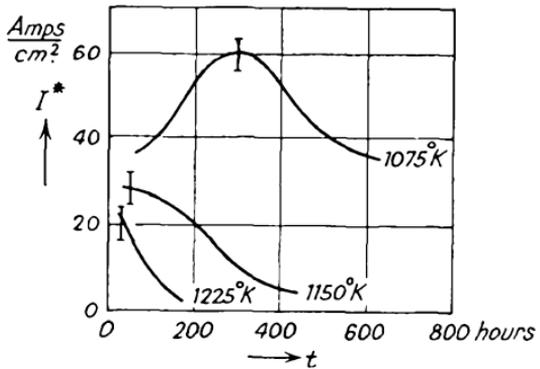


Fig. 61.—Peak Emission Current  $I^*$  Obtained by Pulsed Operation as a Function of Life for Different Operating Temperatures (pulse width  $1 \mu\text{-sec.}$ ) (Coomes<sup>1</sup>).

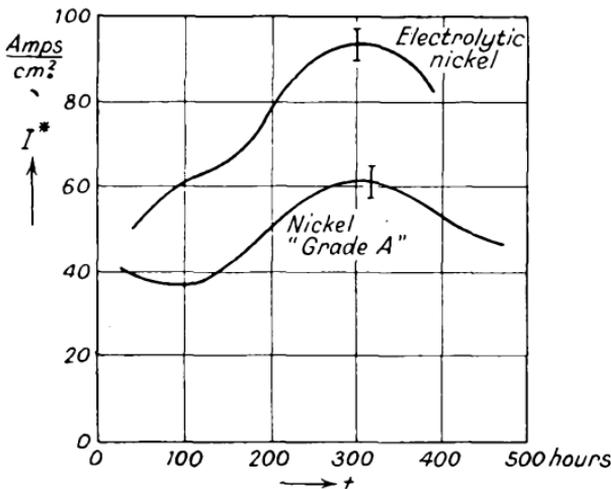


Fig. 62.—Peak Emission Current  $I^*$  Obtained by Pulsed Operation as a Function of Life for Cathodes Made with Different Core Materials (pulse width  $1 \mu\text{-sec.}$ ) (Coomes<sup>1</sup>).

were given by Coomes<sup>1</sup> (cf. Fig. 61) and Willshaw<sup>1</sup> and collaborators. The influence of the core metal is more noticeable with pulsed operation than with D.C. Cathodes made with a very

pure core metal give a longer life than those manufactured with the normal nickel containing reducing additions (cf. Fig. 62). This may be due to the fact that cathodes made with a core metal containing additions have interface layers which are detrimental to the emission.

The sparking described in the preceding section also influences the life considerably. Normal cathodes, when operated in magnetrons, may be destroyed after a few hours of operation due to sparking. The coating resistance of such cathodes must therefore be reduced

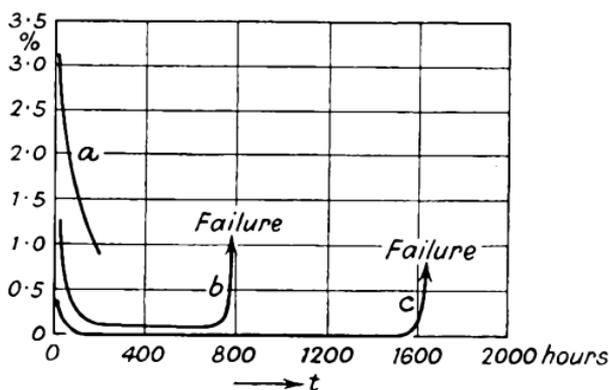


Fig. 63.—Fraction of Emission Pulses at which Sparking Occurs, Plotted as a Function of Life (pulse width  $5.7 \mu\text{-secs.}$ , pulse recurrence frequency 165/sec.):

- (a) Normal Oxide Coating on Nickel Core Covered with Nickel Gauze (cf. Fig. 7 (a));
- (b) Oxide Coating Intermixed with Metal Powder, Core as above;
- (c) Normal Coating on Nickel Core Covered with Sintered Nickel Powder (cf. Fig. 7 (b))

(Fisk, Hagstrum, and Hartmann <sup>1</sup>).

in order to remove the most important cause of sparking. This can be achieved in the manner demonstrated by Fig. 7. Fisk, Hagstrum, and Hartmann <sup>1</sup> examined the sparking obtained during pulsed operation by means of an automatic counting device which registered the number of sparks. They always observed a decrease of sparking during life, until at a certain time the sparking process occurred again very heavily, destroyed the cathode, and ended its life. Fig. 63 shows some of their measurements and demonstrates how the sparking was reduced and the life of the cathodes improved by introducing the specially designed cathodes discussed above.

When stating the factors influencing the life of an oxide cathode, the process of switching on the cathode must not be neglected. Purely mechanical influences, such as the expansion or the con-

traction of the cathode, or recrystallization phenomena due to the excessive temperature at the heater ends, may destroy the cathode during the switching process. This is more likely to occur with thin heater wires, while with thicker wires as used for 6-volt heaters no difference between a gradual and a sudden switching process was found (Michael<sup>1</sup>). Furthermore, the emissivity of the cathode can be reduced by repeated switching, if the anode voltage is applied during the switching. This is either due to sparking or to the fact that the cathode is more prone to poisoning at low temperatures. This latter effect is, of course, only observed with indirectly heated cathodes due to their long warming-up period.

The life which is normally demanded of an oxide cathode operated with D.C. is some thousand hours. If, however, cathodes with nickel or platinum cores are operated with low current densities (5 to 10 mA/cm.<sup>2</sup>), much longer lives, ranging from 10,000 to 20,000 hours, can be obtained with certainty.

In some cases a life of 100,000 hours and more has been measured without any considerable decrease in emission. Thus operating times of more than ten years may be attained.

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## SPECIAL CATHODES

## 14. Oxide Cathodes prepared by the Condensation Method

## 14.1 Manufacture

The condensation or distillation cathode, which has been in wide use on the continent of Europe, is made by evaporating barium metal on a tungsten wire which is previously oxidized. The barium combines with the oxygen of the tungsten oxide and forms a barium oxide cathode which is similar to a combined oxide cathode.\*

The tungsten wire is used either unplated or plated with copper.† The thickness of the oxide layer and the type of oxide obtained during the activation is of extreme importance for the consistency and life of the cathodes (cf. Hinsch <sup>1</sup>). Espe,<sup>1</sup> when examining core wires which were not plated with copper, found that the tungsten oxide should be in a low state of oxidation and that the thickness of the oxide layer should be a few microns. The oxidation is preferably obtained by passing the wire through a furnace, the oxidizing atmosphere being either dry air or a mixture of hydrogen, water vapour, and air.‡ The wire prepared in this manner may then be built into the valve system.

The barium source necessary for producing the barium metal is normally located on the anode. After sealing-in the assembly and pumping the valve, the cathode is formed by heating the oxidized core wire and evaporating the barium simultaneously. The temperature which is used for obtaining the reaction between tungsten oxide and barium is approximately 1000° K.; higher temperatures would cause the tungsten oxide to evaporate. Espe <sup>1</sup> pointed out that the formation of the cathode is improved by applying a positive voltage to the anode (or the grid). As the positive barium ions are then directed to the negative cathode, more barium will condense there than during a mere evaporation.

After sealing-off the valve, the condensation cathode is activated

\* German Patents 414517 and 443323.

† German Patent 499670.

‡ German Patent 588414.

by heating and drawing current in a similar way to cathodes made of emission paste. During this process the reaction between tungsten oxide and barium which was started during pumping is finished. The oxide coating finally consists of barium oxide containing excess barium and interspersed tungsten metal. Bruening<sup>1</sup> showed that on core wires plated with copper the barium produced forms an alloy with the copper and that a good emitter is obtained in this way. The quantity of excess barium in the coating is relatively small and is below 1% of the total weight of the coating according to unpublished measurements by Duesing. The coating is smooth and has a mat metallic colour. If damp air is admitted, the coating becomes grey and voluminous due to formation of hydroxide and carbonate.

## 14.2 Characteristics

The spectral radiant emissivity, determined at the operating temperature by Heinze and Hass,<sup>1</sup> was found to be  $e_\lambda = 0.73$  ( $\lambda = 0.65 \mu$ ). The total radiant emissivity has not been measured. However, a value of 0.9 can be estimated from the fact that approximately 5.5 watts/cm.<sup>2</sup> are necessary for operating a condensation cathode at 1000° K. One sees from this that the condensation cathode has a considerably higher specific heater power than the normal uncombined cathode made of carbonates.

The electron emissivity of the condensation cathode can be measured by one of the methods described in Sec. 10, but in most cases it is also possible to measure the saturated current flowing at the operating temperature. This can be explained by taking into account that firstly the density of the saturated current is smaller than with carbonate cathodes, secondly the thin coating which is intermixed with tungsten has a very low resistance, and thirdly the surface of the coating compared with the surface of a carbonate cathode is very smooth. The saturated currents measured at 1000° K. are between 0.5 and 1 amp./cm.<sup>2</sup> These values are higher than those which were obtained with carbonate cathodes during the years 1925 to 1930 (cf. Fig. 50). During these years, therefore, the condensation cathode, in spite of its higher specific heater power, had the same or even a better efficiency than the cathodes made of emission paste. As the condensation cathode also offered several advantages in manufacture, it was used for quite a number of years on the continent of Europe and was only gradually replaced by directly heated carbonate cathodes.

One of the disadvantages of the condensation cathode results from the occurrence of barium vapour during manufacture. This barium vapour condenses not only on the cathode but on all the other electrodes and insulating parts of the valve and thus gives rise to thermal grid emission and insulating faults. Furthermore, with increasing number of grids surrounding the cathode and with increasing number of turns on these grids, it becomes more and more difficult to obtain a uniform deposit of barium on the cathode. These disadvantages became even more acute with modern valves.

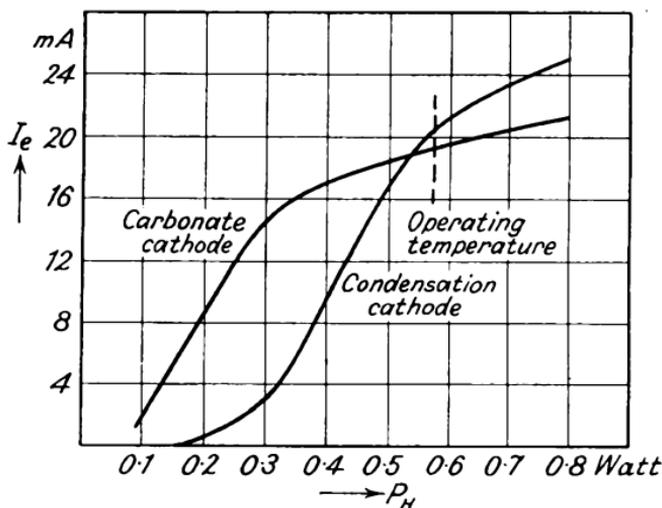


Fig. 64.—Underheating Characteristics of a Condensation Cathode and a Carbonate Cathode.

Another disadvantage results from the high specific heater power, which is two to three times higher than that of uncombined carbonate cathodes. If the same efficiency as with carbonate cathodes is required, the emission density to be drawn from the condensation cathode must therefore be chosen two to three times higher. Furthermore as the saturated current of the condensation cathode is smaller than that of a carbonate cathode, the employment factor of the former cathode will be considerably smaller. For this reason the condensation cathode is much more sensitive to under-heating. This is shown by Fig. 64, in which the underheating characteristic of a condensation cathode is compared with that of an uncombined carbonate cathode on a tungsten core. The dimensions of the valves and the voltages applied to the electrodes were the same in the two cases. The difference between the two types of cathodes is seen still better if the underheating characteristics are

referred to the specific values of current and heater power (cf. Fig. 65).

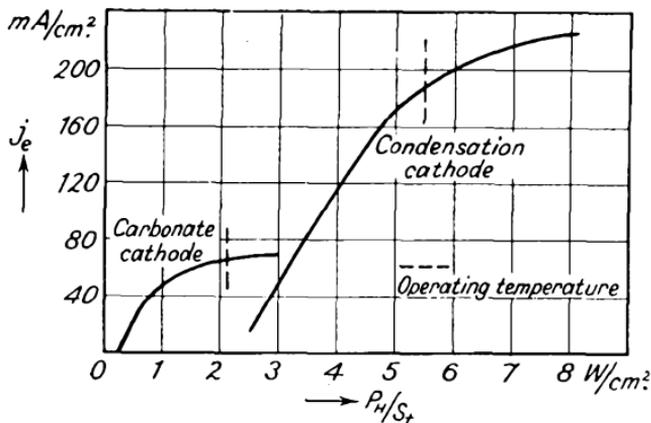


Fig. 65.—Underheating Characteristics of a Condensation Cathode and a Carbonate Cathode, referred to Specific Values of Emission Current and Heater Power.

TABLE XVII

*Characteristics of the Condensation Cathode*

	Spread	Average value	Unit
Specific heater power	4.5–6.1	5.5	watt/cm. <sup>2</sup>
Operating temperature	900°–1100°	1000°	° K.
Operating currents:			
Low-power valves	40–100	70	mA/cm. <sup>2</sup>
Output valves	80–200	110	
Efficiency:			
Low-power valves	7–17	12	mA/watt
Output valves	15–37	23	
Saturated current at operating temperature.	300–800	500	mA/cm. <sup>2</sup>
Employment factor	0.10–0.25	0.20	—

## 15. Thoria Cathodes and Core-Activated Cathodes

Before concluding the discussion of oxide cathodes operated in a high vacuum, two other types of cathode will be discussed which have not come into wide use up to the present. Various publications and patents referring to these cathodes, however, show that many attempts have been made to modify them for practical use.

### 15.1 The thoria cathode

In this type of cathode the alkaline earth oxide normally used is replaced by thoria (ThO<sub>2</sub>), which is deposited on a metal core in the

usual way. The cathode has been examined in detail by Weinreich,<sup>1</sup> Wright,<sup>1,2</sup> and Hanley.<sup>1</sup> The main difficulty in preparing this cathode is to obtain a sufficient bond between the thoria coating and the core. Weinreich and Hanley applied the electrophoretic method for depositing the coating, while Wright prepared his cathodes by spraying. The thickness of the thoria coatings varies between 10 and 100  $\mu$ . The core metals used are tungsten, molybdenum, and tantalum, either as wires and ribbons for directly heated cathodes or as folded sleeves for indirectly heated ones. For obtaining a better bond Wright covered the core with tungsten powder into which, after sintering, the emission paste was painted.

The activation of the thoria cathode can be produced by flashing at 2800° K. for a few seconds (Weinreich). According to Wright and Hanley, however, raising the temperature up to 2200° or only up to 2000° K. is also sufficient for activation. The operating temperature normally used is between 1900 and 2000° K. Lives of several thousand hours are reported.

The heater power necessary for obtaining the operating temperature is between 40 and 60 watts/cm.<sup>2</sup>, corresponding to a total radiant emissivity  $e_r \approx 0.55$ . This heater power, which is twice the value for the atomic film cathode tungsten-thorium, is a serious disadvantage of the thoria cathode. Weinreich, however, reduced the specific heater power by 60% by adding 2% zirconia to the thoria. A value lower than that of the thorium film cathode could so be reached. The spectral radiant emissivity  $e_\lambda$  is approximately 0.35 ( $\lambda = 0.65 \mu$ ). Weinreich found that  $e_\lambda$  depended on the treatment of the coating, and observed variations between 0.18 and 0.46.

The measurements of the emission current made by the different authors agree. The emission density measured at 2000° K. is between 3 and 12 amps./cm.<sup>2</sup> and independent of the core material (Fig. 50). Weinreich<sup>2</sup> found two different states for the activation of the thoria. Wright and Hanley, when drawing pulsed currents, obtained current densities which were two to four times higher than those measured with D.C.

The electrical resistance of the thoria coating at the operating temperature is so small that the cooling power is larger than the power of heating-up, even at the highest emission densities drawn continuously from the cathode. Wright gives the value 30  $\Omega$  cm. for the specific resistance, according to which the total resistance of a coating of 100  $\mu$  thickness is 0.3  $\Omega$ /cm.<sup>2</sup>. This value is about ten times smaller than the coating resistance of normal alkaline

earth oxide coatings. Due to the low resistance of the thoria coating sparking phenomena are not observed, even at the highest direct or pulsed emission currents. Contrary to the thorium film cathode (W-Th) the sensitivity of the thoria cathode to poisoning is low. As shown by Wright<sup>2</sup> an oxygen pressure of  $10^{-3}$  mm. Hg in the valve only produces 10% decrease in emission at temperatures higher than 1850° K., 40% between 1700 and 1800° and 75% below 1500° K. For these reasons the thoria cathode would be an improvement, provided the bond of the coating could be increased and the radiation be lowered.

Another type of thoria cathode is the so-called ceramic cathode, consisting of a sintered thoria rod or tube which can be heated either directly, or indirectly by an inserted tungsten wire. As the resistance of rods or tubes of pure thoria is rather high, this resistance must be reduced if direct heating is to be used. Such a reduction is obtained by adding either tungsten powder or the nitrides of titanium or zirconium to the thoria. The first variety was described and investigated by Fan,<sup>1</sup> while the second one was used by Bush, Vandegrift, and Hanley.<sup>1</sup> They added to the thoria 20% of one of the two nitrides and obtained at the operating temperature a resistance of 0.4  $\Omega$  for a rod of 2 mm. diameter and 15 mm. length.

## 15.2 Core-activated cathodes

The second type of cathode to be described here is called the "core-activated cathode." As this name shows, the core of this type of cathode contains the emissive material, whilst the surface obtains its emissivity by material diffusing from the interior of the core. The principle of this cathode seems to be simple and several advantages such as the absence of sparking phenomena and of the heating-up due to emission current might be expected from it. In spite of this the cathode concerned has had no practical applications in a high vacuum up to the present, and only a few applications in gas discharges are known. The discussion of this cathode will therefore be confined to a short review of existing patents. Four different sub-types of this cathode may be distinguished which were all suggested for application in both high-vacuum and gas discharges.

The first group comprises cathodes in which an active metal—normally an alkaline earth metal—is alloyed to the core metal in small percentages.\* As nickel and tungsten can be alloyed only

\* U.S.A. Patent 1921065, Austrian Patent 115413.

with very small quantities of barium, many suggestions have been made to increase the percentage of barium in these important core metals.\* Other refractory metals, such as molybdenum, have also been suggested.† Frequently the wires made of the alloys or mixtures with barium or other active metals are slightly oxidized for improving the magnitude and constancy of the emission.‡ Randolph, Duffendack, and Wolfe<sup>1</sup> checked the suitability of such cathodes for commercial application and made suggestions for decreasing the detrimental evaporation of barium.§

The difference between the first and the second group of these cathodes is that instead of the active metals, compounds of these metals are added to the core metal.|| These compounds can then be reduced, at least partially, by a suitable treatment.¶

The quantities of the compounds to be added can only be very small if the basic metal is to remain ductile. To overcome this difficulty the suggestion was made to utilize higher percentages of the active compounds by sintering a mixture of a refractory metal and the compound concerned into a body of a convenient shape.\*\* This type of cathode, the sintered barium cathode, which belongs to the third group to be discussed, is the only one which is used in practice for making gas-discharge tubes. In other cathodes of this group a non-metallic refractory material such as coal or silica gel is used, instead of the metal.†† An intermediate case between normal oxide cathodes and the core-activated cathodes of this group are those in which a high percentage of metal powder is mixed with the oxide of the coating so as to diminish tendency to sparking (cf. p. 118).

The cathodes of the fourth group have a core which is a hollow body—usually a tube—into which the active metal or metal compound is filled. This tube may subsequently be extruded to thin hollow wires.‡‡ When the cathode is heated, the active material diffuses to the surface and either an atomic film cathode or an oxide cathode with a very thin coating is formed.§§

If the core-activated cathodes are operated at temperatures suffi-

\* U.S.A. Patents 1925978, 2055467. † German Patents 523892, 568033.

‡ U.S.A. Patents 1874127, 1921065. § British Patent 396514, U.S.A.

|| German Patents 497475, 527151. Patent 1985855.

¶ German Patent 523892. \*\* German Patent 529392.

†† German Patents 403209, 567909. ‡‡ German Patent 521049.

§§ *Note added during proof reading* :—An improved modification of this type with a core consisting of porous tungsten has recently been described by Lemmens, Jansen, and Loosjes.<sup>1</sup> This cathode can be employed in high vacuum with reasonable life.

ciently high for an adequate emission density, they have a rather short life due to the thinness of the coatings which are formed on their surface. For this reason they have not yet come into commercial use. Finally it may be mentioned that the suggestion has been made to use core-activated cathodes as the core of normal oxide cathodes in order to improve the life of these cathodes.\*

### 16. Oxide Cathodes for Gas-filled Tubes

Oxide cathodes which are operated in a gas filling must be designed differently from those used in a high vacuum, because they are exposed to bombarding gas ions which, if their velocity is higher than a certain critical limit, will sputter the oxide coating. Furthermore, the bombarding ions heat up the coating considerably and give rise to an evaporation of the coating materials which is much higher than without ion bombardment. Both the sputtering and the evaporation tend to remove the coating and to destroy the emissivity of the cathode in this way. Moreover, the cathode material which is evaporated or sputtered away endangers the insulation of the tube, produces detrimental deposits on the glass bulb of discharge lamps; or gives rise to back-fire in rectifiers. For all these reasons the oxide coating must be made as resistant as possible against the effects of the ions.

The resistibility of the coating to sputtering and evaporation can be influenced by varying the composition of the emission paste. Numerous suggestions have been made for this, but in most cases the alkaline earth carbonates are used as basic material for the coating and only some suitable additions are made. If the current density drawn from the cathode is low and if the voltage critical for sputtering is not exceeded, it is sufficient to add a certain quantity of  $\text{CaCO}_3$  to the normal mixture of  $\text{BaCO}_3$  and  $\text{SrCO}_3$ . If a higher resistibility of the coating is required, alkali silicates or pure silica are added. In high-pressure discharge lamps, where a still higher resistibility of the coating is necessary, thoria is used as an addition. One of the advantages of thoria is its low rate of evaporation, which allows the cathode to be operated at much higher temperatures such as occur in high-pressure lamps. The percentage of thoria in the coating is therefore increased with increasing pressure of the gas discharge, and at the highest pressures used the coating is made exclusively of thoria. Finally a glass-like oxide coating may be

\* German Patents 497475, 713457.

mentioned which consists of a mixture of alkaline earth oxides, thoria, and silica and which also has a high resistibility against sputtering and application of high temperatures.\*

Another way of increasing the strength of the oxide coating is by varying the method of locating the emissive material on the core metal. Two different types of gas-discharge cathodes are therefore distinguished:

- (a) The normal surface-activated cathode, and
- (b) the storage cathode.

The first type is made in the same way as a high-vacuum cathode by depositing the emissive material on the core metal. Frequently a thin wire is wound round the core wire before depositing in order to improve the bond (multi-core cathodes, cf. page 20). The methods

used for depositing the coating on these cathodes are the same as with high-vacuum cathodes.

When making a storage cathode,† the emissive material is formed into a solid body S, which is located inside a metallic electrode, for instance in



Fig. 66.—Example of a Storage Cathode.

the interior of a tungsten helix W (cf. Fig. 66). The emissive material then traverses from the interior to the surface due to evaporation and surface diffusion, and the cathode is activated in this way. The storage cathode was described in detail by Pirani.<sup>2</sup> The emissive material used by him was barium chromate ( $\text{BaCrO}_4$ ) or barium aluminate ( $\text{BaAl}_2\text{O}_4$ ), which was reduced to barium oxide and barium by means of an intermixed metal powder (Si, Ta, Ti, Zr). The advantage of the storage cathode is that the emissive material which is evaporated or sputtered away can be replaced continuously. The store in the interior is bombarded by the ions to a much smaller extent and cannot be used up so easily due to its large volume.

Finally the resistibility of a gas-discharge cathode to sputtering and evaporation is influenced by a suitable selection of the operating temperature and of the dimensions of the cathode. If the temperature is too low, the electron emission will be too small, and the cathode fall arising in front of the cathode will give rise to sputtering. If, however, the temperature is too high, the evaporation of the

\* Austrian Patent 156720.

† German Patents 279028, 295023, 298431.

emissive material will become too large. This is particularly important for the "self-heated cathodes" (cf. page 135), where an optimum temperature must be reached by suitably selecting the heat capacity and heat conduction of the cathode and the resistance of the coating.\*

After having given some general lines, the two principal applications of the gas-discharge cathodes—rectifiers and discharge lamps—will now be discussed separately.†

### 16.1 Cathodes in rectifiers ‡

The application of the oxide cathode in rectifiers was first described in two publications by Wehnelt.<sup>1,2</sup> He pointed out that, when using such a cathode in a rectifier, a critical density of the operating current must not be exceeded, this density being approximately equal to the saturated current of the cathode. If this critical current is exceeded, the number of electrons emitted from the cathode can no longer increase. The additional electrons required are then produced by the cathode fall of the gas discharge, which will grow considerably. Consequently the ions formed in the cathode fall will obtain much higher velocities and will therefore affect the cathode coating to a much higher extent. The increased sputtering produced by the ions can be compensated by increasing the gas pressure in the tube, but this is only possible with low anode voltages. For this reason the conditions in rectifiers operated with low voltages are different from those working with high voltages, and the cathodes used in these two cases are therefore also different.

The "low-voltage rectifiers" are normally filled with rare gases of 0.5 to 2 mm. pressure. This rather high pressure reduces the danger of sputtering considerably, and the cathodes in these rectifiers can therefore be operated in the saturation range. A good efficiency is so obtained, and special measures for decreasing the heater power as described below are consequently not necessary. In smaller types of rectifiers (up to about 0.5 amp. operating current) the same cathodes as in high-vacuum rectifiers, consisting of V- or W-shaped coated nickel tape, are frequently used. If the currents drawn are higher, either directly heated tungsten spirals or indirectly heated nickel sleeves are used as cathode cores (cf.

\* German Patent 581872.

† The application of oxide cathodes in thyratrons has been discussed by Knight and Herbert.<sup>1,2</sup>

‡ Cf. Kluge.<sup>1</sup>

Fig. 67). The cathodes are normally surface-activated—either combined or uncombined ones—but the storage cathode has also been used as described by Germershausen.<sup>1</sup>

The specific heater powers of these cathodes in low-voltage rectifiers are between 5 and 10 watts/cm.<sup>2</sup>. The relatively high value is due to the considerable heat convection in the gas. The emission density is 2 amps./cm.<sup>2</sup> for the average operating current and 4 amps./cm.<sup>2</sup> peak value.



Fig. 67.—Directly Heated Spiral Cathode of a Low-voltage Rectifier. (Current density 3 amp./cm.<sup>2</sup>; AEG N 190/10;  $\frac{3}{4}$  natural size.)

These current densities, which are high compared with those of the high-vacuum cathodes, heat up the oxide coating considerably. The temperature of the cathodes, which is between 1150° and 1200° K. without drawing current, is raised by another 50 to 100 degrees due to this heating-up effect. Contrary to the cathodes operated in a high vacuum, however, this high temperature is not detrimental to the life of the cathodes because the gas filling reduces the evaporation of the coating considerably.

If the gas pressure is increased beyond the limit given above, the discharge starts to concentrate at small areas of the coating and to heat up these areas still more. Naturally the tendency of the cathode to sparking will be

greatly increased and the life considerably shortened by such an effect.

The “high-voltage rectifiers,” which owing to the high peak reverse voltages (1 to 20 kV) can only be operated at low gas pressures, are normally filled with mercury. As pointed out above, the operating current of these rectifiers must be small compared with the saturated current of the cathodes employed. The current densities used, in fact, are of the same order as the maximum densities drawn from high-vacuum cathodes (some 100 mA/cm.<sup>2</sup>). In small rectifiers of this type, supplying currents up to a few amps.,

spiral cathodes similar to those in low-voltage rectifiers can be used. Frequently these cathodes are shielded against excessive heat losses by a suitable screen (cf. Fig. 68).

If these normal cathodes are used for rectifying higher currents, a very large heater power would be required, making the rectifier uneconomical. A more favourable heat economy is achieved by Hull's multicellular cathode, which is shown in Fig. 69 (Hull,<sup>1</sup> Glaser,<sup>1</sup> Lowry<sup>1</sup>). This cathode utilizes the fact that a space charge cannot exist in the gas discharge, because the charge of the electrons is compensated by that of positive ions. In a gas discharge therefore the electrons can also be emitted from holes or cavities in the cathode. The multicellular cathode consists of a cylindrical structure which is heated indirectly by a tungsten spiral  $W$ . The heater current  $I_H$  flows through this spiral and returns over the internal tube surrounding the spiral. This internal tube, which also carries the emission current  $I_e$ , supports a large number of radial vanes  $V$  on which the emissive material is deposited. The whole system of vanes is surrounded by concentric metal cylinders  $C$  and a lid which act as heat shields. The electrons are emitted from this cathode through the holes  $H$  in the lid.

This design gives a cathode with a very good heat economy. Hull pointed out that with optimum dimensions, the heater power can be reduced to one-hundredth of the amount which would be required for a straight wire having the same emitting surface. The principle of this cathode is essentially based on the compensation of the space charge in the gas discharge. The magnitude of the electron current is thus determined by the total area coated with emissive material, while only a small fraction of this area emits in a high vacuum. A disadvantage of this cathode is its long warming-up time (up to 20 minutes), which results from the high ratio between



Fig. 68.—Directly Heated Double Spiral Cathode with Heat Shield Used in High-voltage Rectifiers (part of shielding cylinder cut away). (Current density 0.2 amp./cm.<sup>2</sup>; AEG G 10/4d;  $\frac{2}{3}$  natural size.)

heat capacity and heater power. Rectifiers for up to 200 amps. operating current are made with these multicellular cathodes. Experimental designs have been made up to 1000 amps.

The operating temperature of the cathodes in high-voltage rectifiers is between 1100 and 1150° K. The specific heater power, which depends on the losses by convection, is 0.5 to 2 watts/cm.<sup>2</sup> for

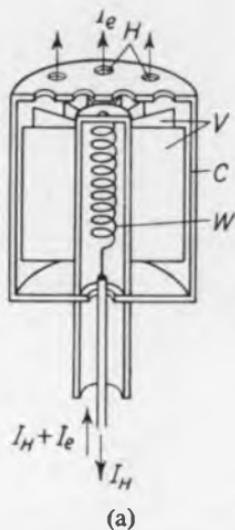


Fig. 69.—Hull's Multicellular Cathode: (a) Schematic Cross-section; (b) Commercial Cathode. (Current density 0.3 amp./cm.<sup>2</sup>; AEG S 15/40;  $\frac{2}{3}$  natural size.)

multicellular cathodes, but 2 to 5 watts/cm.<sup>2</sup> for directly heated spiral cathodes.

The life of the multicellular cathodes, which is limited by evaporation and sputtering, was improved by Hull.<sup>2</sup> He developed the dispenser cathode, in which the emissive material evaporating from the vanes is continuously replaced from a special source in the interior of the cathode. The heater of this type of cathode is not an ordinary spiral, but a "stocking" which is woven of thin molybdenum wires. This molybdenum stocking, which contains a eutect of BaO and Al<sub>2</sub>O<sub>3</sub> in its interior, is heated up to 1425° K. by passing current and thus acts as heater for the emitting radial vanes, which are arranged in the same way as with the original cathode. At the above-mentioned temperature, the barium oxide evaporates

from the eutect in the interior of the stocking and condenses on the emitting vanes. The barium oxide evaporated from the vanes during life can thus be replaced continuously. Such dispenser cathodes were examined by Hull for more than 30,000 hours without finding any fall in emission.

More recently Tarbés<sup>1</sup> and Barbault<sup>1</sup> investigated the suitability of folded and plaited nickel ribbons as cores of oxide cathodes in rectifiers. According to their results a commercial application of such cathodes seems to be possible.

## 16.2 Cathodes in discharge lamps

When considering discharge lamps in which the positive column of a gas discharge is utilized as a source of light, it is no longer possible to distinguish between cathode and anode. These lamps, which are normally operated with A.C., have two identical electrodes symmetrically located in the lamp. Each of these electrodes is alternately cathode and anode. The activation of these electrodes by means of metal oxides, especially alkaline earth oxides, was first suggested in 1906\* and has come into general use since.

The electrodes used for gas-discharge lamps have one more characteristic in which they are different from the high-vacuum cathodes, namely the manner of heating. This difference is due to the fact that the energy necessary for heating the electrodes of these lamps can be taken from the cathode or anode fall, or in other words from the energy of the ions and electrons bombarding the electrodes concerned. Furthermore, a fraction of the heater energy can be taken from the energy of heating-up produced in the coating by the emission current (cf. page 102). With quite a number of discharge lamps therefore no heater current is required. A "self-heated electrode" is so obtained. In some cases, if the gas pressure is low or the distance between the electrodes large, the available voltage is not sufficiently high for striking the discharge when switching on the lamp with cold electrodes. In these cases a heater current is required during the switching process. These electrodes are called "foreign-heated electrodes." After striking the discharge their heater current is switched off by a special switch, for example a bimetal switch.

Fig. 70 shows a specially designed electrode which is continuously heated but which has not been used in practice yet.\* The heater

\* U.S.A. Patent 1032914.

\* German Patent 417827.

spiral of this electrode is heated by the emission current and acts as a series resistance of the gas discharge. Owing to this the Joule heat produced in the series resistance is not lost, but is utilized for heating the electrode.

The core metal of the electrodes used for the discharge lamps is always a refractory metal, normally tungsten or more rarely nickel in some combination with tungsten. Manufacture and processing of this core metal are the same as with high-vacuum cathodes. Electrodes for very high currents are frequently made by a sintering process as described in Sec. 15.2 (Pirani <sup>1</sup>).

The decomposition and activation can be undertaken in the

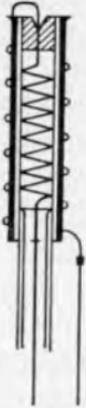


Fig. 70.—Gas-discharge Electrode according to German Patent 417827.



Fig. 71.—Electrode of a Superlux Lamp for 250 mA Operating Current (Osram, Berlin).

normal manner, by passing heater current only with the “foreign-heated electrodes.” The “self-heated electrodes” must be processed directly in the gas discharge. In some cases (for example, with low-pressure lamps) a special anode located directly in front of the electrode is used for the activation. This anode then acts as a shield against sputtering during operation.

The main types of electrodes in discharge lamps will be discussed by using the normal classification into low-pressure and high-pressure lamps. The “low-pressure lamps” are either filled with a rare gas (e.g. neon) of some mm. pressure, or they contain a metal vapour to which a rare gas of 1 to 10 mm. pressure is added in order to make the striking of the discharge possible. The metal vapours normally used are mercury or sodium, while the added gas consists either of argon or of a mixture of argon and neon. An important group among the mercury lamps are the fluorescent lamps, in which

the ultraviolet radiation originating from the mercury is transformed into visible light by fluorescent materials deposited on the glass wall.

The electrodes used for low-pressure lamps are surface-activated throughout. Fig. 71 shows the electrode of an earlier discharge lamp which was used for advertising (operating current about 250 mA). This electrode is normally protected against sputtering by a cylindrical shield, which has been removed in the photograph. The core consists of a tungsten spiral round which a tungsten wire

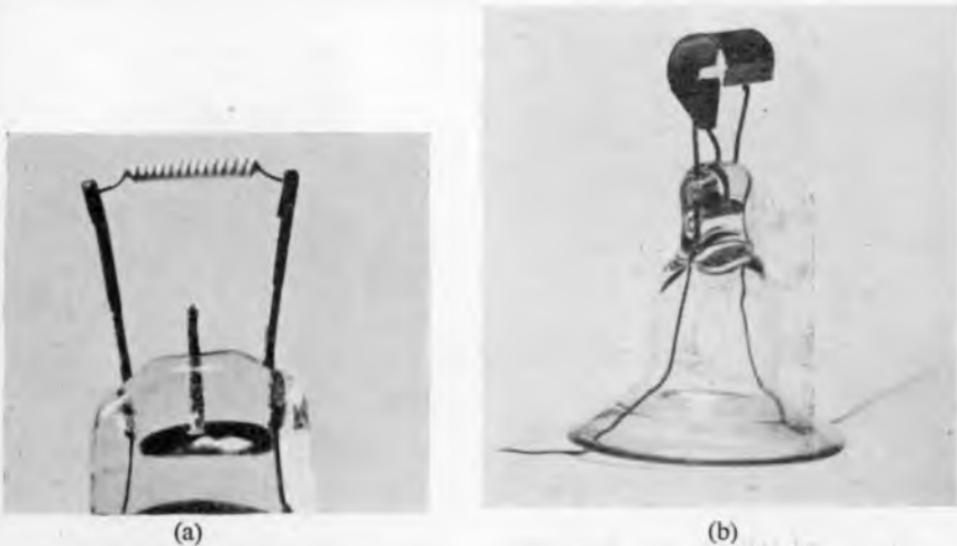


Fig. 72.—Improved Electrode for Fluorescent Lamps: (a) Without Shield (mag.  $\times 2$ ); (b) With Shielding Cylinder (natural size) (Osram HN 120).

is wound for improving the bond. The coating is made of a mixture of  $\text{BaCO}_3$  and  $\text{SrCO}_3$ , which is deposited by dipping and sintered to the core at  $2300^\circ \text{K}$ . in a protective atmosphere. The electrode is self-heated.

A much improved modern electrode which is used in fluorescent lamps is shown in Fig. 72. This electrode consists of a double tungsten spiral which is coated with an emission paste containing  $\text{CaO}$ , by an electrophoretic method (coating thickness  $\approx 100 \mu$ ). The electrode is foreign heated, or in other words it is heated during the striking process but not during operation. A small heater power and a short warming-up time which are especially important for the fluorescent lamps are combined in this electrode.

In the "high-pressure lamps," which are normally filled with

mercury, the dimensions of the tube and the current flowing through it are chosen in such a way that a high pressure is obtained. The discharge then contracts and a high current density is reached.\* The pressures employed range from 1 to 200 atm. For striking the discharge the lamps are filled with about 10 mm. argon in addition to the mercury. When switching on, the high pressure is only reached after a certain starting period.

The only surface-activated electrode which is known to be used in the high-pressure lamps is the above-mentioned electrode with glass-like coating (cf. Fig. 73), which is especially resistant against



Fig. 73.—Electrode with Glass-like Coating for High-pressure Lamps (Osram, Berlin).



Fig. 74.—Storage Electrode for High-pressure Lamps (Osram, Berlin).

sputtering. An example of a storage electrode used in these lamps is shown in Fig. 74. Another type of these storage electrodes is the "step electrode" as seen in Fig. 75. The emission material is only located in the wide lower part of this electrode, while the thin upper part consists of metal. This design divides the electrode into a striking or starting electrode which is needed for striking the discharge or for the starting period, and an operating electrode which is used during the operation of the tube. The starting electrode is formed by the lower part, which is covered with emissive material and which therefore possesses the low work function facilitating striking and starting. When the starting period is finished and the high operating pressure is reached, the mercury arc goes over to the

\* German Patent 656921.

upper part of the electrode. The sputtering during operation is so confined to the more resistant metal.

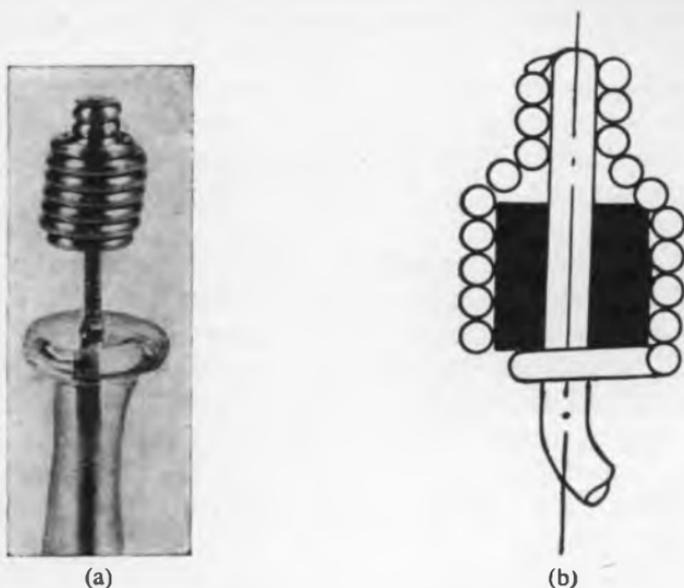


Fig. 75.—Step Electrode for High-pressure Lamps (Osram, Berlin).



Fig. 76.—Combination Electrode for High-pressure Lamps (Osram, Berlin).

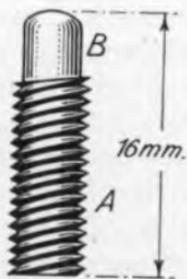


Fig. 77.—Combination Electrode for High-pressure Lamps (Francis and Wilson<sup>1</sup>).



Fig. 78.—Filled Electrode for Lamps Operated with Very High Pressures (Osram, Berlin).

The "combination electrode" shown by the schematic Fig. 76 is designed on similar lines. It consists of a vertical tungsten spiral

containing a core of emissive material, and a tungsten block W located above this spiral. The core-activated tungsten spiral acts as starting electrode, while the tungsten block forms the operating electrode. Another similar design, suitable for high current densities, was given by Francis and Wilson<sup>1</sup> (cf. Fig. 77). This electrode consists of a tungsten spiral with a protruding tungsten core. The tungsten spiral A, covered with emissive material, again forms the starting electrode, while the tungsten core B acts as operating electrode.

Finally, when working with the highest pressures, the emissive material must be protected against the discharge still further in order to make operation with the necessary current densities possible. A cathode designed for such very high pressures, the so-called "filled electrode," is shown in Fig. 78. It consists of a hollow body of sintered tungsten filled with thoria. The thoria can only be reached from the discharge space through small holes in the tungsten. Its only purpose is facilitating the striking of the discharge.

### 16.3. Cold oxide electrodes

Cold oxide electrodes are used as well as other electrodes (alkali electrodes) in the earlier discharge lamps which are operated with high voltages (neon lamps) and in the glow lamps. These electrodes are heated neither when striking the discharge nor during the operation; their operating temperature is only about 100° C. The cold electrodes are not a better emitter of electrons than the pure metal at their operating temperature; they are only used for decreasing the cathode fall of the discharge by their low work function. For obtaining this low work function the sheet or wire employed for the electrode is activated with a barium compound, usually barium azide,  $(\text{BaN}_3)_2$ . When baking the lamps, the barium azide decomposes into a mixture of barium nitride,  $\text{Ba}_3\text{N}_2$ , barium and barium oxide, possessing the required low work function. As this cathode is only used cold, it is a limiting case of the oxide cathode and it will therefore not be discussed in detail.

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