THE ROLE OF THE CORE METAL IN OXIDE COATED FILAMENTS

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Abstract

Temperature-power relations have been determined for numbers of oxide coated filaments. Part of these filaments had cores of platinum-10% iridium and others had cores of "Konel," an alloy of nickel, cobalt, iron and titanium. Oxide coated Konel is a much better radiator than oxide coated platinum-iridium which causes a considerable difference in their temperature -input power characteristics. N vertheless, emission measurements show that oxide coated Konel filaments yield higher electron emissions than oxide coated platinum-iridium under the same conditions of filament power. Experimental proof is also given that these filaments need no activation other than the decomposition of the alkaline earth carbonates to oxides in vacuo. The enormous difference shown between the emission characteristics of these two types of oxide filament necessitates the conclusion that the core metal has a definite function other than simply a mechanical support for the alkaline earth oxides.

Suggested mechanism of thermionic emission from oxide coated filaments. In order to account for this difference, a modification is suggested in existing ideas concerning the mechanism of emission from this type of cathode. This modification consists in assuming that the source of emission is the composite layer formed by occlusion of alkaline earth metal on the surface of the core and that the electrons emitted diffuse through the interstices in the oxide coating into the vacuous space. Argument is presented to show that this explanation will also account for other peculiarities in the behavior of oxide cathodes. (1) The decay of emission during life may be explained by a slow sintering of the coating and a consequent closing of these pores. (2) De-activation of the filament by over-heating may be attributed to the same cause. (3) Non-saturation may be due to a pseudo-space charge formed by occlusion of electrons on the surface of the coating particles.

Introduction

SINCE the discovery by Wehnelt[1] in 1904 of the exceedingly large electron emissions obtainable from glowing calcium oxide, this type of hot cathode has steadily become of greater and greater importance both for use in various thermionic devices and as a copious source of electrons in work of purely scientific interest. This popularity has followed closely upon necessary improvements in technique, resulting in a much greater degree of uniformity from filament to filament as well as in a constant improvement in their efficiency. An inspection of the values of the work function for the alkaline earth oxides obtained by various investigators in the chronological order in which their results were obtained is an excellent proof of this improvement. A table of this sort is appended for which we are indebted to Espe.[2]

[1] Wehnelt. Ann. d. Physik **14**, 425–468 (1904).

[2] Espe, Wissenschaftliche Veroffentlichungen aus dem Siemens Konzern, **5**, 29–46 (1927).

Observer	Material	$d\phi$ (volt)	$d\phi'$ (volt)
Wehnelt 1904	CaO	3.67	
	BaO	3.85	
Horton 1907	CaO	4.11	
Deininger 1908	CaO	3.76	
Jentzsch (1908)	CaO	3.48	
	SrO	3.87	
	BaO	3.58	
Schneider (1912)	CaO	3.45	
Cook and Richardson (1913)	CaO	2.4	
Germerhausen (1916)	CaO	2.54	
Wilson (1917)	CaO	3.28–3.94	
	BaO 50% / SrO 50%	2.02–2.16	
	BaO 50% / SrO 25% / CaO 25%	2.34–2.59	
Arnold (1920)	BaO+SrO	1.67–2.05	
Davisson and Germer (1923)	BaO+SrO	1.79	
Spanner (1924)	CaO	2.4	
	SrO	2.15	
	BaO	1.85	
Koller (1925)	BaO 60% / SrO 40%		1.04
Rothe (1926)	(Five Commercial Tubes)	0.64–1.24	
Espe (1926)	CaO	1.93	1.77
	SrO	1.43	1.27
	BaO	1.11	0.99

As a result of the composite nature of this type of cathode the phenomena attendant upon its use are quite complicated and of a somewhat different nature than those found upon examination of pure metallic cathodes. This complexity has given rise to several schools of thought in regard to the mechanics of electron emission from this class of material. It has been held:

1. That the emission is derived from the oxide *per se*,
2. That it is the result of a chemical reaction within the coating, and
3. That the emission comes from a layer of metallic barium on the surface of the oxide coat.

To the best of the author's knowledge the effect of the base or core metal has always been held to be negligible or has been entirely ignored. This is, perhaps, a natural consequence of the various ideas concerning the nature of the oxide emission which have been held up to the present and to the fact that nearly all students of this subject have used platinum as the core metal to the exclusion of everything else. Schottky and Rothe in Vol. 13, chapter IX page 227 of the Wein-Harms Handbuch der Experimental Physik (1928) have summed up the situation very nicely as follows: "Aus einer der ersten Untersuchungen der Oxydemission durch F. Deininger geht hervor, das diese (i.e., the work functions for various oxides) unabhängig von dem Material des Glühdrahtes und eine charakteristische Eigenschaft des betreffenden Oxyds ist, wie es auch allen unseren Anschauungen über die Wirkung von Oberflächenschichten entspricht."

Results which have been obtained in this laboratory indicate that the core metal does play a very important rôle in the behavior of this type of hot cathode and therefore that the explanations stated above are misleading as to the true nature of this emission, or at best, are inadequate. It is the purpose of this paper to set forth proofs that the core metal has a vital function in the phenomena of oxide emission. It is also our purpose to suggest an explanation of the mechanics of emission which will take into account this newly discovered factor as well as conform to the demands of their better known but equally important characteristics.

With the advent of the oxide coated filament into common use in radio receiving tubes, it became an economic necessity to find a satisfactory substitute for platinum-iridium as the core metal. Dr. Dayton Ulrey of this laboratory suggested that nickel was the logical metal to begin with. Experiment showed that quite as good emissions could be obtained from oxide coated nickel filaments as had ever been gotten from the oxide coated platinum filaments then in use. The subsequent almost universal adoption of this material for commercial use has entirely corroborated the results obtained by the author at that time.

The search for a satisfactory platinum substitute was not abandoned with the proof that nickel could be used with equally good results. A metal having a higher tensile strength at red heat and above was desirable to insure longer life before burn out as well as less danger of breakage.

An alloy of nickel, cobalt, iron and titanium was found to meet these requirements and also to give excellent thermionic results when coated with oxides of the alkaline earths in the usual way. This alloy has received some publicity of late under the name "Konel."

During the course of investigation of oxide coated Konel filaments in commercial tubes of the UX-112 type it was noted that the brightness temperature of these filaments appeared to be considerably lower than that of similar oxide coated platinum filaments operating at the same power per unit area. This observation seemed to call for a careful study of the relative operating temperatures of these two types of filaments, since neither theory nor experience could account for the effect noticed. This investigation was carried out in the manner described in the succeeding paragraphs.

Experimental Method and Results

The filaments used during the course of this investigation have all been of the type used in UX-281 Radiotrons. Both the platinum-10% iridium (referred to hereafter in this paper simply as platinum) and the Konel filaments were coated in the same fashion. Several applications of a water paste consisting of equal parts of $BaCO_3$ and $SrCO_3$ were baked on the ribbon in an atmosphere of CO_2. This carbonate coating was subsequently decomposed to oxide in vacuo during the outgassing process of the tube to be examined. Since all data given are averages obtained from a rather large number of filaments made from different spools of ribbon and coated at different times, their exact dimensions are irrelevant. Their approximate dimensions were

27 cm length by 0.06 cm width. Both the platinum and the Konel filaments had practically the same areas and resistance characteristics. This equality of area insures equal space charge limitations when mounted in tubes whose anodes are all of the same size. The filaments were mounted *M* fashion in standard UX-281 tubes save that for the temperature investigation no anodes were included. No corrections for cooling effects of the leads and hooks have been applied since a careful test showed that this effect was negligible when plotting the temperature of the center of the filament against the power input to the filament.

This test was carried out on a tube in which were mounted two filaments as shown in Fig. 1. These filaments were taken from the same spool of coated ribbon but were of different lengths. They were connected in series

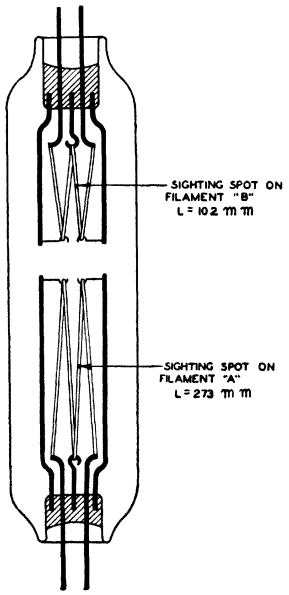

Fig. 1. Diagram of tube.

so that by subtracting the voltage drop through the shorter filament from that through the longer one the power loss in the uniformly heated central portion of the longer filament could be calculated. Further calculation showed that the end cooling on a filament of this length was responsible for an error in the curves of about 3 degrees in the lower range of temperature and about 1 degree in the upper range. The target for optical pyrometer observations on the base metal was formed by carefully scraping the coating from one side of the ribbon at the center of one of the middle legs of each filament for a space about equal to the width of the filament. Brightness temperature observations were made on this spot as well as on the surface of the coating at a point immediately adjacent to this bare area. Two Leeds & Northrup optical pyrometers calibrated against standard lamps furnished by Dr. Forsythe of Nela Park were used for this work, the results of

which are shown in Fig. 2. It may be well to call attention to the fact that each point plotted is an average of five separate observations and each point of a group was found for a different filament. A check test was run recently on two of the filaments previously studied using a different pyrometer. The results of this check are indicated by crosses. It seems entirely safe to conclude from the results shown that the brightness temperature curves given here are not in error by more than $\pm 5°C$.

Obviously, we are interested in the true temperature of the core metal and not particularly in that of the surface of the coating. In order to calculate the true temperature of the Konel filaments it became necessary to find the value of its spectral emissivity at $\lambda = 0.65\mu$ in the temperature region under investigation. This was accomplished by the spiral filament

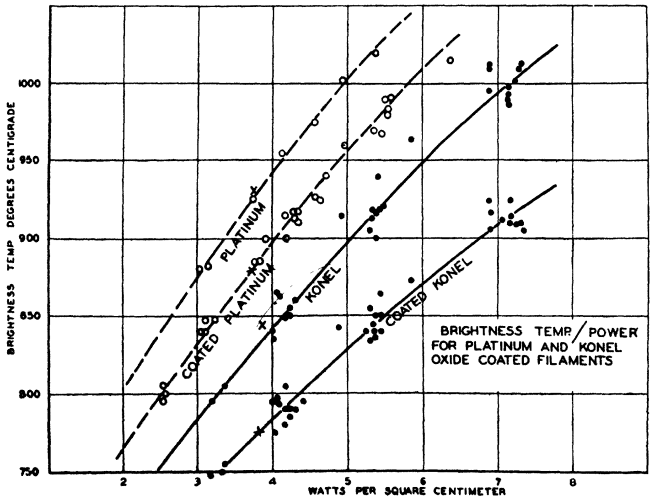

Fig. 2.

method described by Shackelford[3] with the result that a value of 83% was found for this factor. Foote and Fairchild[4] give this correction factor for platinum as 33% and for iridium as 30%. A rough calculation of the spectral emissivity of the coatings yields a value of the order of 25%. This value is of course only approximate since the difference in temperature between the surface of the coating and that of the base metal is not precisely known, although it can at the most be a matter of only 10 to 15 degrees C. Furthermore, these coatings, although appearing pure white by reflected light are quite porous as well as translucent, with the result that the above value is probably high.

By applying the proper correction factors to the curves of Fig. 2 we arrive at the values shown in Fig. 3 which refer of course to the true temperature

[3] Shackelford, Phys. Rev. **8**, 470–478 (1916).

[4] Foote & Fairchild, Symposium on Pyrometry, Am. Inst. Mining & Met. Eng. 338, (1920).

of the metal cores as a function of the power supplied to the filaments in watts per cm^2.

The difference in temperature between oxide coated platinum and Konel filaments operating under like conditions of power input is readily explained. Konel becomes considerably oxidized during the coating process described above and hence is a much better radiator than platinum. The oxide coating, although a poor radiator, allows an appreciable amount of the radiation from the core to escape owing to its porosity and translucence. As a result the energy radiated is dependent upon the nature of the core

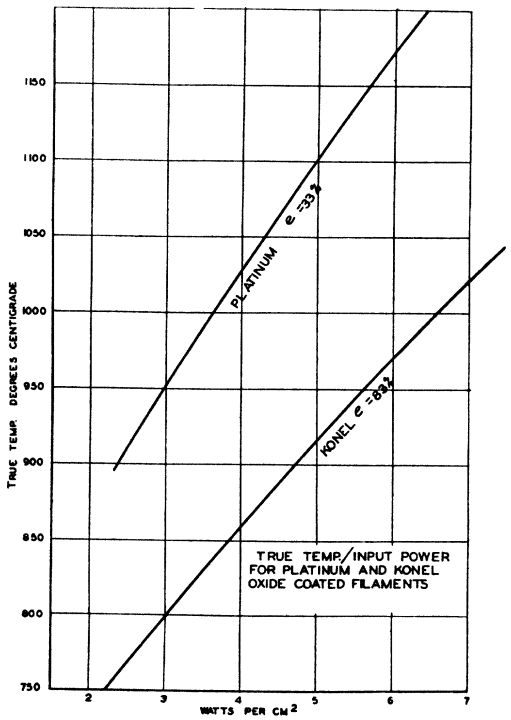

Fig. 3.

to a considerable extent and is not limited entirely by conduction through and radiation from the surface of the coating.

In Fig. 4 are shown some space current measurements made with UX-281 Radiotrons using similar filaments to those used in the tests described above save that these filaments have a length of approximately 17 cm. In fact, some of them were taken from the same spools of coated ribbon. These curves are also averages for numbers of tubes and show that when the currents are limited by emission rather than by space charge the values for oxide coated Konel are higher than for oxide coated platinum operating at the same power per unit area. It must be borne in mind that the results given here are to be considered as typical of this particular kind of coating. It is possible that different results might be obtained with, for example,

the barium azide method of coating. The whole process of making oxide filaments, coating them with oxides and their subsequent treatment on the pumps is of the nature of an art only to be acquired through long practice. The author would, therefore, hesitate to comment on the results to be obtained by some distinctly different process of coating. The filaments used

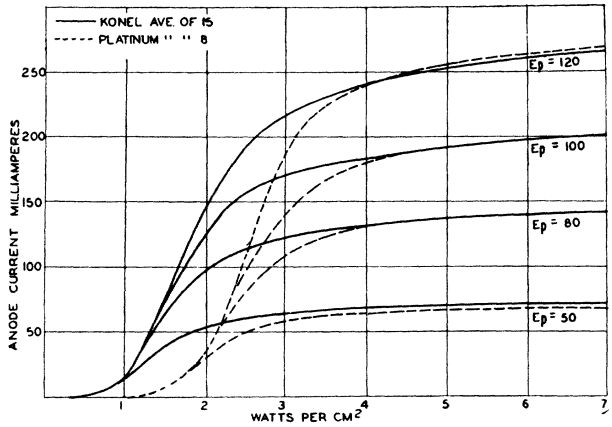

Fig. 4.

throughout this work were good representative samples of commercial oxide coated filament. The tubes used were also representative in every way, their only difference from commercial tubes being that the most extreme care was used in getting the highest obtainable vacuum in each one to obviate the possibility that any appreciable part of the space currents obtained was due

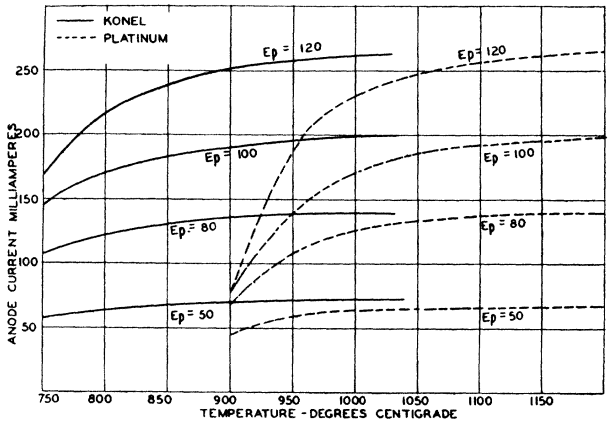

Fig. 5.

to the presence of gas. The normal value of emission for UX-281 Radiotrons is 0.170 amperes at $E_p = 100$ volts and a power input of approximately 4 watts per cm^2.

The results of the previous curves have been combined to obtain the results shown in Fig. 5. Here are shown the space current values obtained

at various anode voltages plotted against the temperature of the filaments in degrees C. It here becomes obvious that the core metal has an enormous effect on the thermionic activity of the coating. It is readily seen from these curves that the same anode current may be obtained from oxide coated Konel at 775°C. as can be obtained from platinum coated with the same oxides at 950°C. This is the phenomenon which we believe is new and for which we offer a possible explanation in the succeeding pages.

The Mechanics of Emission

As mentioned in the introductory matter of this paper, at least three distinctly different explanations of the mechanics of emission from oxide coated filaments have been set forth in the past. None of them take into account any function of the core metal other than as a mechanical support for the thermionically active oxides and as a means of furnishing the necessary thermal energy to them in a convenient manner. The experimental facts stated in the foregoing pages make it imperative that the role of the core metal be recognized and its effect explained. It is obvious that such an explanation must also be in accord with other phenomena peculiar to this type of cathode. Some of these phenomena are:

1. The formation process.
2. Destruction of activity by overheating.
3. Decay of activity with life.
4. Non-saturation.

The explanation most in favor during recent years has been that offered by Koller,[5] Espe,[6] Rothe[7] and others in which it is assumed that the source of activity is a layer of metallic barium on the surface of the oxide coating. Espe argues that this barium is formed by electrolytic decomposition of the oxide coating and that the barium diffuses to the surface of this coating where it serves as emission centers. The explanation submitted herein is a modification of this idea in that it is believed that the emission arises from a layer of metallic barium occluded on the surface of the core metal or alloyed with it. This modification seems necessary in that if the emission arises from the oxide itself or from barium "emission centers" on the surface of the coating, the thermionic activity of such filaments should be unaffected by the nature of the core. In such case both platinum and Konel oxide filaments should be equally active at like temperatures. This obviously is far from the fact.

In a way, it is immaterial to the argument at hand as to just the method by which the barium is produced. If it is formed by electrolytic decomposition according to Espe,[6] the barium ions would be positively charged and have a natural tendency to migrate toward the core. As a matter of fact this is probably the method by which a constant supply of barium on the core is maintained after the initial "activation."

[5] Koller, Phys. Rev. **25**, 671, (1925).
[6] Espe, reference 2.
[7] Rothe, Zeits. f. Physik **36**, 737–758 (1926).

It is also possible that metallic barium is formed by positive ion bombardment under certain conditions of activation. This explanation does not, however, account satisfactorily for a maintenance of a barium supply under high vacuum conditions.

With the type of coating used by the author in the course of this work it is, however, entirely probable that the barium is formed either by thermal decomposition of the carbonates in vacuo or by the reducing action of the metallic core. Figure 6 shows a curve of the behavior of a typical filament during the course of an experiment to prove this point. Tube #X2410 containing Konel filament #125–386 was baked at 400°C in the usual way, after which the metal parts of the tube were thoroughly outgassed in a high

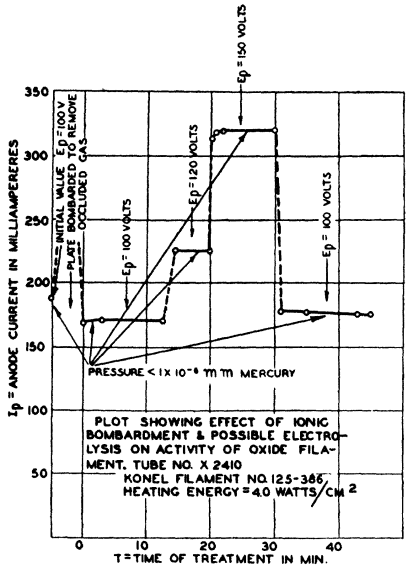

Fig. 6.

frequency furnace. The only heating received by the filament up to this time was that due to radiation from the hot anode. An instantaneous measurement of emission was then made and yielded a value of 5×10^{-6} amp. at a filament power input of 4 watts per cm^2 and an anode voltage of 100 volts. The filament was then heated at 8.5 watts per cm^2 for several minutes and then at 5–6 watts per cm^2 until the gas pressure in the tube had been reduced to less than 1×10^{-5} mm of mercury. During this treating out of the filament no anode voltage was applied and the plate was cold except for radiation absorbed from the filament. Another instantaneous determination of the emission now gave 0.186 amperes under the same test conditions as before. Subsequent treatment of various kinds gave no improvement as is indicated by the curve, which is self explanatory. This behavior is typical of this type of filament when properly handled. Similar results have been obtained with oxide coated platinum filaments, so the results described can-

not be ascribed to the kind of base metal used. Since a certain amount of vaporization of the barium from the core is to be expected at operating temperature especially in the case of platinum filaments, it is quite likely that the supply of barium is replenished by some such process as the electrolytic decomposition of the oxide coating. It certainly is not essential however to their initial activation. Again we must insist that this applies only to coatings of the type used in this work. If the carbonates are converted to oxide by long continued heating in the air and not converted in vacuo as in this case, an activation process of some length does have to be followed to bring the filaments up to normal activity.

Evidence of this and also of the fact that the emission is due to metallic barium was obtained in an experiment similar to the one just described in which the filament was burned in air at low pressure for a short time after it had been tested as above with identical results. The burning in air had the result of enormously reducing its activity (to about 5×10^{-6} amp.) and it was only by heating it for some hours in high vacuum with a constant application of 200 volts on the anode that its activity was restored to the same order of magnitude that it had originally.

A necessary consequence of our hypothesis is that the electrons leaving the emitting layer must diffuse through the interstices in the oxide coating. This consequence presents no serious difficulties. Indeed, it offers a solution to some of the perplexing problems connected with the behavior of this type of cathode. At best, the electrical resistivity of these oxide coatings is very high even at glowing temperatures. In fact, Dr. C. T. Ulrey of the Research Laboratory of the Westinghouse Lamp Company during the course of some yet unpublished work has not been able to obtain a discontinuity in the space current curve for such filaments when the anode was made to approach the filament until it actually touched the surface. Furthermore, these coatings are very porous. When viewed through a microscope they have the appearance of a light fluffy fall of snow. It seems reasonable to suppose therefore that the escaping electrons may diffuse through this oxide layer which, however, does offer some impedance to their progress. Suppose now that this coating should become more compact so that its pores are partially closed. The natural consequence would be that the apparent activity of the filament would be measurably impaired. This is precisely the type of phenomenon that does occur. It is well known that glowing the filament for a comparatively short interval of time at a considerable overvoltage will practically ruin its emission. It has been the author's experience at least that a filament which has been so mistreated cannot, in general, be reactivated to anything like its original characteristics. It is also true that such filaments will, after such reactivation as is possible, yield large emissions if very high anode voltages are applied. The net result of such an overheating of a filament is essentially to increase the impedance of the tube by an appreciable amount. This we believe to be caused by a partial closing of the pores of the coating. Preliminary microscopic examination of some such filaments actually showed a sintering or glazing of the coating until it had the appearance of a crackled enamel.

Exactly similar behavior is shown by filaments whose activity has gradually decreased during a long period of use. Such worn out filaments always retain an appreciable amount of coating. In fact, a fairly close inspection shows that they still possess nearly as thick a layer of oxide as they had initially. In this case also large emissions may be drawn if sufficiently high anode voltages are applied.

If the loss of activity in these cases were due solely to a loss of metallic barium due to vaporization it should be possible to cause these filaments to regain all their initial activity by electrolysis or by positive ion bombardment. As stated above it is rarely if ever that it is possible to do this.

The process of electron diffusion through a porous, poorly conductive coating may also explain the phenomenon of non-saturation which is commonly met with in this type of cathode. It follows logically that large numbers of electrons will become enmeshed in the pores of the coating or occluded on the surface of the particles of poorly conducting material composing it. It is quite possible also that the numbers of electrons so entrapped will vary somewhat with the anode voltage applied. This process will give rise to an effect similar to a negative space charge within the confines of the coating itself. The space currents obtainable then at any given anode voltage and filament temperature represent the number of electrons per second it is possible to drag out of or through this negative charge built up within the coating layer. The result will be that much higher anode voltages will be required to approach a saturation than if this pseudo space charge did not exist. At temperatures in the neighborhood of 1000°C the electron emission from these filaments is so enormous that it is next to impossible to obtain anything approaching saturation owing to the very considerable heating effects of the emission itself. At these temperatures also the conductivity of the coatings will be increased appreciably affording a better opportunity for the electron charge to leak off.

Conclusions

In view of the experimental results presented in the foregoing pages, we are forced to accept the fact that the base or core metal does affect appreciably the electron emission from the alkaline earth oxides. This situation in turn demands a modification of existing ideas concerning the mechanism of emission from oxide cathodes.

An hypothesis is offered concerning this mechanism in which:

1. The source of emission is assumed to be a layer of metallic barium (or other alkaline earth metal) occluded on the surface of the base metal or alloyed with it. In this case the constants of the well-known Richardson equation must be characteristic of the composite surface.
2. The electrons emitted from this composite surface must diffuse through the pores of the coating.
3. The coating in turn, as a function of its porosity, offers considerable impedance to the progress of the electrons.

4. The occlusion of electrons on the particles of the coating sets up a pseudo space charge effect which serves to explain the phenomena of non-saturation as well as the fading of emission during short periods of operation.

5. The gradual decay in activity of coated filaments during life is due to a slow sintering of the coating resulting in a closing of its pores and a consequent increase in the impedance offered to the passage of electrons. A similar process occurs if the filament is strongly glowed for a comparatively short interval of time with or without anode voltage.

It is admitted that no crucial tests of this explanation have been offered with the exception of that showing the pronounced influence of the core metal; which, of course, is the effect which makes the above modification in existing ideas necessary. Numerous experimental investigations are now under way in this laboratory which have been designed as tests of the various assumptions made herein. It is hoped that these tests will be far enough along to permit of their publication in this magazine in the near future.

In conclusion, the author wishes to express his gratitude to Dr. C. T. Ulrey of the Westinghouse Lamp Company Research Dept. and to Drs. D. L. Ulrey and N. Rashevsky of this laboratory for their interest and for the helpful suggestions received from them during the progress of this work.