A Standard Diode for Electron-Tube Oxide-Coated Cathode-Core-Material Approval Tests*

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Summary—**A diode has been designed and used for testing various samples of cathode material in several plants and laboratories during recent years. Several criteria have been used for evaluating the emissive power of the various materials tested. To simulate the usual space-charge-limited emission test commonly used on receiving tubes, a cathode-temperature versus emission characteristic has been taken on each test lot. Temperature-limited emission has been examined under both low-field, low-temperature conditions and normal-temperature, high-field conditions. Results indicate that this method has several important advantages over the present approved method.**

I. Introduction

THE ROLE played by the core material in the emission of electrons from oxide-coated nickel base cathodes has been the subject of considerable conjecture and controversy almost since the discovery of the oxide-coated cathode. Various hypotheses have been proposed from time to time to account for the apparent superiority of one core material over another. These hypotheses were not always in complete agreement, and attempts to resolve their differences frequently led to inconclusive results. The main difficulty seems to be in the complexity of the emission phenomena. Emission from oxide-coated cathodes is subject to time changes and fatigue effects, and to a very pronounced degree is dependent upon the composition, method of application, and processing of the materials used in the tube assembly. So far, it has been very difficult to isolate the single variable of core material for comprehensive studies.

Despite the fact that the mechanism of emission is not clearly understood, tube manufacturers have been producing, for many years, good oxide-coated-cathode tubes at relatively low cost. However, the possibility that a low-emission epidemic may suddenly shut down his production lines has caused every tube manufacturer to spend considerable time and money trying to immunize his product from all known carriers of this disease. Since the source of emission is the cathode, the material from which it is made obviously is one of the first places to look for trouble. For this reason, it has been standard practice for many years in radio-tube plants to check the performance of each new melt of nickel cathode material on one or more production tube types before accepting it for production use.

In the past, the type of tube chosen for such tests, the conditions under which the test was made, the acceptance criteria, and the interpretation of test results has varied widely from company to company, and even from division to division of the same company. Since it was obviously impossible for a company to test each new melt of nickel on all production tube types under all conceivable operating conditions, most manufacturers tested two or three tube types as representative of various classes of tube service, such as rectifiers, oscillators, and power-output types. Sample quantities of each new cathode-nickel melt in a tubing size to fit these types would be ordered with the fervent hope that the type chosen would be in production when the samples arrived. In the happy but infrequent event that all test results, both initial and life-test performance on the various types run for approval, indicated that the new melt was inferior to, equal to, or superior to the comparison melt, the course of action presented no problem. In the more usual case, when test results disagreed, it was sometimes necessary to resort to occult practices to effect a decision. It is not particularly surprising, therefore, that new melts of core material accepted by one company or division would be rejected by another.

Nickel for seamless-cathode electron-tube use is produced in melts of about 10,000 pounds. Prior to World War II, usage of cathode nickel in the electron-tube industry was such that it was possible for a cathode supplier to hold a melt of this size for the period of approximately three months required to obtain melt approval from the various tube manufacturers. However, this situation was at best only tolerable, as it involved some financial risk on the part of the cathode supplier. If all companies should reject the melt, its value depreciated to that of Commercial Grade A material, this loss being sustained by the cathode supplier, who would then channel this material into less critical usage. If some companies accepted and some rejected the melt (the normal situation), the cathode supplier would purchase another melt to submit to the companies rejecting the first melt, and so on until all companies were satisfied. This method required considerable juggling of melts on the part of the vendor, who assumed the risk of supplying the proper-size cathode cylinder of the approved melt to each customer.

By 1944, the usage of seamless cathode material had reached a new high, and, in addition, new applications for tubing, particularly in the aircraft industries, placed an added drain on the cathode vendor and the raw material supplier. It became increasingly difficult to supply

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each radio tube manufacturer with the particular nickel melt which met his melt approval requirements.

In January, 1945, a meeting was called by one of the cathode base material vendors to discuss this problem. Representatives of all cathode-tubing vendors and users were invited. It was the consensus of this group that the problem could best be studied through the medium of four committees, whose membership would be drawn from the various companies represented at this meeting. One committee was to propose referee methods for the chemical analysis and sampling of nickel melts. A second committee was to outline metallurgical test methods and a program for metallurgical development. A third committee was to prepare a specification for a standardized diode test to serve as a starting point for a laboratory test method. The fourth and last committee was to propose methods for presenting data on the multitube production test method of melt approval. These four committees were organized and later incorporated as Section A, Committee B4, Subcommittee VIII of the American Society for Testing Materials. This paper is a report on the work of the Diode Committee.

II. The Standard-Diode Approval-Test Method

The primary purpose of the diode structure, as conceived by the committee members, was to provide a standard tool for the investigation of the various cathode-material melts supplied for production use. It was felt that by providing a single structure which could be run conveniently in every tube plant, many of the variables introduced by the previously mentioned multitube tests could be eliminated. A secondary purpose of the diode was to investigate the effect of variations in the additives in the nickel melt and variations in processing and testing methods. In deference to the primary purpose of the diode, that of melt approval, it was agreed that the structure should consist of standard receiving-tube parts, so that standard receiving-tube equipment and techniques could be employed in processing them, thus insuring that a melt accepted for production use on the basis of diode tests would have been tested under conditions prevalent in the factory in which the melt would be used. It was realized that a structure utilizing receiving-tube parts and techniques might limit the effectiveness of the diode as a sensitive instrument for the investigation of melt additives and process variations.

The structure designed by the Diode Committee is shown in Fig. 1. Table I lists the important tube dimensions. The heater is designed for 6.3-volt, 300-ma operation. Under these conditions, the cathode operating temperature is approximately 1050°K. The anode was designed with an oval barrel to permit the use of a grid, should the occasion arise.

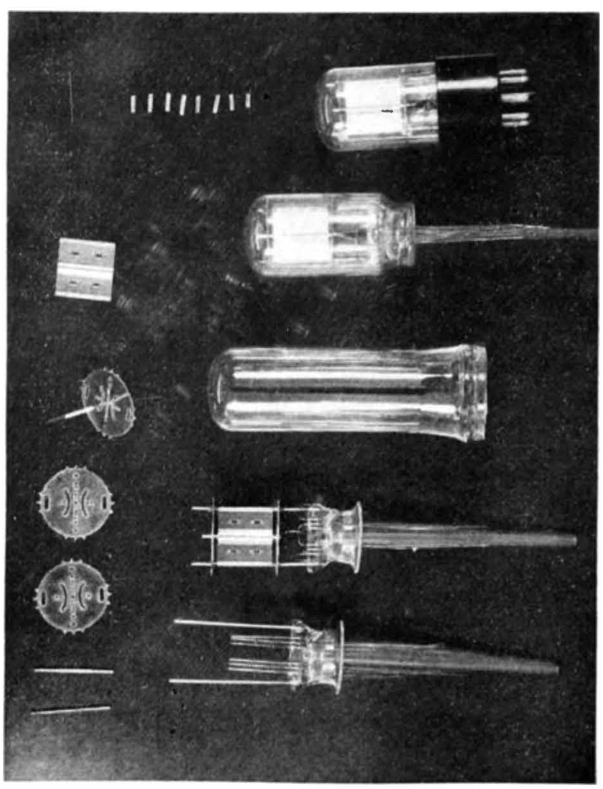

Fig. 1—Structure of the standard diode designed by the Diode Committee.

TABLE I

Standard Diode—Construction Details

Anode	
Material	0.005 inch Grade A Nickel
Dimensions	Inside diameter oval cross section: 0.132 ×0.185 inches
	Barrel length: 0.75 inches
Cathode Cylinder	
Material	Electronic Grade A seamless nickel tubing
Dimensions	Outside diameter: 0.045 inch
	Length: 1.06 inches
Cathode Coating	
Material	ASTM barium-strontium double-coprecipitated carbonates
Dimensions	Coated length: 0.475 inch (centrally located on cylinder)
	Coating weight: 3.40 ±0.4 milligrams
Stem	
Material	Lead glass (G12)
	Nickel-dumet-copper welds
Getter	
Material	Barium-cored iron wire
Heater	
Material	Cleaned and straightened tungsten wire
Dimensions	Wire weight: 12.0 milligrams ±1½ per cent per 200 mm
	Wire cut length: 7.05 ±0.04 inch
Form	Six-leg folded
Insulation Coating	Alundum
Bulb	Lime glass; T9
Base	Standard octal
Spacers	Mica 0.011 ±0.001 inch thick

The diode melt-testing method has several advantages over the multitube test method. It is a simple structure, easily produced on equipment available in all tube plants. Standard parts have been made available to all companies interested in diode testing, so that, regardless of where the tube is produced, uniformity of parts is assured. It is necessary for the cathode-material vendor to produce only one size of cathode cylinder for melt-approval use if all testing is done on the diode. A comparison melt has been set aside for diodes which provides a uniform standard of comparison. Standardization of design, processing techniques, test methods and controls are possible, and changes found to improve the accuracy or reliability of the test method by one laboratory can be applied readily in other laboratories.

The general procedure used in conducting melt-approval tests on the diode is as follows: Test lots, as a rule, are run in groups consisting of at least ten "control" diodes employing the standard control-melt cathodes (Melt 66), and at least ten each of diodes employing cathodes of the melt or melts under test. All parts other than cathodes are obtained from a common inventory. Identical parts-processing and tube-processing schedules are used on all lots within the group. In general, these processes are standardized for a particular plant; i.e., all diode-test lots in one plant are processed under the same schedules. Some of these processes have been proposed as industry-wide diode standards by the Chemical Committee; e.g., parts cleaning, cathode-coating preparation, and certain testing schedules. Each plant has been allowed to set its own exhaust and aging schedules, because the approval of melts on the basis of diode tests implies the acceptance of the melt for production use, and the tube manufacturer is most interested in knowing how the melt will perform under his particular plant conditions.

III. Testing of the Standard Diode

To evaluate the emissive power of a cathode, it was assumed by the Diode Committee that some method of observing its total emission current (not limited by space charge) was necessary. If one attempts to test the diode structure, or any receiving-tube structure, for total or temperature-limited emission current, at its normal cathode temperature under static conditions, the rated wattage dissipation of the anode is usually exceeded long before temperature-limited current is drawn. Anode overheating usually results in gas evolution and subsequent cathode poisoning.

To avoid this difficulty, tubes may be tested for total emission by reducing the cathode temperature so that the temperature-limited current drawn does not exceed the rated anode dissipation. With this in mind, the Diode Committee fixed the anode potential for emission test at 40 volts, which, at normal cathode temperature, would give a space-charge-limited emission current in the neighborhood of 50 ma in the diode structure. This corresponds to a current density of about 120 ma per square centimeter, which is somewhat higher than is required by conventional emission tests on receiving-tube types. The full cathode-temperature versus emission-current curve at this fixed 40-volt anode potential was then taken on each tube under test and the position of the "knee" of the curve (that is, the transition point between temperature-limited emission and space-charge-limited emission) was taken as a measure of the relative emission capabilities of the cathode. Fig. 2 shows this curve on a normal tube and on a tube deficient in emissive power. It will be noted that, at rated cathode temperature, both tubes have the same space-charge-limited emission, but that on tube B the temperature-limited emission is somewhat lower than on tube A.

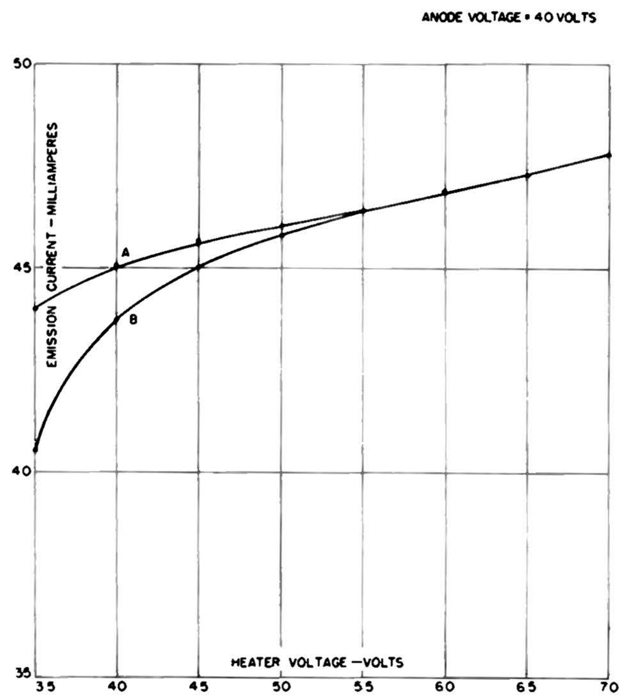

Fig. 2—Emission-current versus heater-voltage characteristic, American Society for Tetsing materials standard diode.

It was this sort of data that the Diode Committee set out to obtain on each new melt of cathode nickel submitted for test. Practically all conclusions reached to date in this program are based on cathode performance under this type of test. However, it was found that this cathode-temperature versus emission test has at least one serious limitation; the emission currents observed under these conditions at very low cathode temperatures were apt to be unstable. This may be due to the relatively high anode potential used on the test. It is well known that certain oxides and chlorides, which are on the surface of the anode as a result of the cleaning and processing of the tube parts and structure, tend to break down when the anode voltage exceeds about 4.5 volts. Oxygen or chlorine are released, and may poison the cathode surface. This effect should be particularly noticeable at low cathode temperatures, where the rate of barium production within the cathode is low. If the rate of poisoning exceeds the rate of barium production, slumping emission will result.

To avoid this difficulty, data have recently been taken under low field conditions, with an anode potential of 4.0 volts, which should be safely below the breakdown voltage of the oxides and chlorides likely to be found on the anode surface. To obtain temperature-limited emission at this low anode voltage on the diode, it was necessary to lower the heater input voltage to 1.75 volts, which corresponds to a cathode temperature of about 640°K. Emission currents obtained under these conditions are relatively stable.

During the late war, there was considerable interest in the pulse-emission properties of cathodes, and, since many receiving tube types were being used in pulsed applications, the Diode Committee thought it desirable to examine new cathode melts for their pulsed-emission properties. Peak emissions as of high as 100 amperes per square centimeter were reported on nickel-base cathodes by observers at the MIT Radiation Laboratory,[1] the Bartol Foundation,[2] and elsewhere. The pulsed-emission testing techniques developed by these laboratories were borrowed and utilized for diode pulse testing by one of the companies involved in the diode program. The pulse technique has one significant advantage over the two static emission tests mentioned previously, in that it permits examination of temperature-limited emission at rated cathode temperatures without exceeding the rated anode dissipation of the diode.

Life Tests

The electron-tube manufacturer is interested not only in the initial performance of a cathode melt, but also in the performance against time under operating conditions. The Diode Committee has incorporated a life test as part of the melt approval procedure. The conditions of this test have been modified as data were accumulated under various drain conditions. The present life test schedule consists of a minimum of 500 hours operation at rated heater voltage ($Ef = 6.3$ volts) and a drain of approximately 100 ma per square centimeter.

IV. Diode-Test Results

From the time of its inception, the Diode Committee has been conducting diode tests of three general classes:

1. Tests directed toward improving the structure and standardizing processing and testing procedures
2. Melt-approval tests on commercial cathode nickel
3. Tests directed toward examining the effects of variations in chemical composition of the cathode nickel.

Tests in the first class have been and are being conducted in considerable volume. Results from this class of tests are the basis for the formulation of diode structure and process specifications.

Melt-approval tests are represented in the summary in Table II, by the compilation of test results on commercial melts 70 through 76.

Melt-composition tests have been conducted on about fifty different nickel-base materials. Test results on only a few of these lots are shown in Table II, for comparison with the 220-alloy commercial melts. The test results reported here represent only a very small portion of the total diode tests run during the three-year period of diode investigation, but serve to illustrate the effectiveness of this structure in differentiating between the emission capabilities of cathodes as a function of core material. The data reported are based solely on the information obtained from the 40-volt static characteristic curves (see Section III). Low-field-emission test, pulsed-emission test, and life-test results are not included in this report, because these data are still incomplete. Since it is difficult to characterize the 40-volt static characteristic test data by a complete heater-voltage versus emission-current curve, a "figure of merit" rating based on the difference in slope of these curves in the region between heater 4.5 and 6.5 volts has been substituted. This "figure of merit" was determined in the following manner:

$$\text{F.M.} = \left[\frac{Is_{6.5} - Is_{4.5}}{2}\right]_{\text{control}} - \left[\frac{Is_{6.5} - Is_{4.5}}{2}\right]_{\text{test}}$$

where

$Is_{6.5}$ = emission current with 6.5 volts applied to heater

$Is_{4.5}$ = emission current with 4.5 volts applied to heater.

Thus, for example, a "figure of merit" of −0.5 for melt 70 (Company "2") indicates that the slope of the Ef versus I_s curve for the average of the ten tubes made with melt 70 cathode material was 0.5 ma/volt steeper in the region between 4.5 and 6.5 volts heater voltage than its control lot (melt 66).

V. Discussion of Diode Test Results

The seven melts, 70 through 76, whose "figure of merit" ratings are given in Table II, are 220-alloy seamless tubing material submitted to the radio tube indus-

TABLE II

Summary of Initial Test Results on Diode Tests of Commercial Cathode Material Melts Seamless Tubing

"Normal" 220 Alloy Material Figure-of-Merit Rating

Melt Number	Company "1"	Company "2"	Company "3"	Company "4"	Company "5"	Company "6"	Test Description
70		*−0.5	−2.1	−0.3	+0.7		
71		−1.8	−1.0 −1.9	−1.9	+0.1		Initial sample
71C		+0.1	−0.2				Initial sample cleaned
71R	+0.5	−0.1	+0.1	−0.3	+0.5		Second sample, melt 71
72	−0.4	−0.4	−0.2		−0.1	−0.4	
73	−0.8	−0.1	−0.2		−0.1	−0.2	
74	−0.5	−0.3	−0.4		−0.1	+0.5	
75	−0.5	−0.2	−0.5		0	−0.1	
76	−0.2	0	+0.4		+0.1	−0.3	
Lockseam Tubing							
W	−9.6	−7.5	−15.9				"Passive" material, 499 alloy
K	−10.0	−11.4	−15.4				"Passive" material, 707 alloy
X	−0.2	+0.1	−1.3				"Active" material, 599 alloy
M	−0.4	0	−1.3				"Active" material, 766 alloy

[1] E. A. Coomes, "Pulsed properties of oxide cathodes," *Jour. Appl. Phys.*, vol. 17, pp. 647–654; August, 1946.

[2] M. A. Pomerantz, "Magnetron cathodes," Proc. I.R.E., vol. 34, pp. 903–910; November, 1946.

try for approval testing. Most of the data obtained by the Diode Committee so far has been on this alloy, although approval tests have also been conducted on other alloys in lockseam tubing. For comparative purposes, "figures of merit" are shown in Table II for the three grades of cathode tubing commonly employed by the receiving-tube industry. These three grades are termed "normal," "active," and "passive" alloy base materials by the ASTM.[3] This classification refers to the relative barium-producing potential of the alloy, as determined by the percentage of reducing agent present in the melt. "Active" alloys contain a relatively high percentage of reducing agents, such as silicon and magnesium; "passive" alloys contain relatively low percentages of reducing agents; and "normal" alloys contain a moderate amount of reducing agents. Typical chemical analyses of these three grades of material are listed in Table III.

TABLE III

TYPICAL CHEMICAL COMPOSITIONS OF "NORMAL," "ACTIVE" AND "PASSIVE" CATHODE BASE MATERIALS†

	"Normal"	"Active"	"Passive"
Carbon	0.15%*	0.12%*	0.10%*
Copper	0.20	0.04	0.04
Iron	0.20	0.05–0.01	0.05
Magnesium	0.01–0.1	0.0 –0.15	0
Manganese	0.20	0.10	0.02
Sulphur	0.008	0.005	0.005
Silicon	0.01–0.05	0.15–0.25	0.01
Nickel and Cobalt	99.0 min.	Balance	Balance

† All figures are percentages by weights. Compositions are maxima unless a range is indicated.
* Carbon content is generally lower as wall thickness is reduced through successive annealings. At 0.0022 inch wall, carbon is 0.02 per cent nominal, while at 0.005 inch wall, carbon may exceed 0.05 per cent nominal.

Certain minor constituents may be found in varying amounts according to melting practice for the alloys. Such elements may be aluminum, titanium, boron, etc.

The differences observed in "figure-of-merit" ratings for melts 70 through 76 as reported by the six companies reporting diode-test results were considered by the diode committee to be random variations within the sensitivity of the test method, with one exception, the initial sample of melt 71. It was felt that some significance could be attached to the fact that three of the four companies reporting diode results on this melt found it somewhat inferior to the control melt 66. Company "3" repeated the test on their initial sample, and again found it poor. Investigation showed that the three companies reporting poor results on the initial sample had obtained their melt-approval samples from one run of cathode tubing, while the company reporting good results, Company "5," on the initial sample had obtained its melt-approval sample from a later drawing of the material. Surface contamination of the initial sample was immediately suspected. Companies "2" and "3" therefore tried surface cleaning of their initial sample. The results of these tests, indicated as melt 71C on Table II, indicated that this suspicion might be well founded. Company "3" found a definite improvement in emission performance from the suspected melt after etching the bare sleeves. Company "2," employing a different cleaning procedure, found the performance of this suspected lot of tubing could be brought above that of the control melt by this means. The original sample processed along with this test uncleaned, was still very poor.

As a result of these findings, the cathode-tubing supplier prepared a new sample of melt 71, with special care being taken to avoid all possible contaminants in the drawing operations. These samples were submitted to the same companies who had reported on this melt previously. Results on this second sample are shown in Table II as melt 71R. All companies testing this sample found it better in emission performance than its control melt 66. To substantiate the conclusion that the initial sample of melt 71 was bad, two comparative tests were run later by Company "2" on a production tube type under normal factory conditions. In both cases, a high initial shrinkage due to poor emission was obtained on the initial sample, whereas normal results were obtained on the comparison melt run at the same time.

Results on a few melts of "active" and "passive" alloys are also tabulated on Table II. Melts W and K show the effect on emission of reduction in silicon and magnesium content of the base material. The "active" alloy tests X and M show performance characteristics very similar to the "normal" alloy tests. It should be borne in mind however, that these lots represent results on only single samples of these alloys, and should not be not be taken as necessarily representative of the average emission performance characteristics of these materials.

VI. CONCLUSIONS

An inventory of the results achieved in the three years of diode testing shows a very favorable balance. Correlation between test results reported by the various plants testing cathode-core-material melts has shown marked improvement with diode testing. The study of testing methods has brought about a better understanding of the effects of tube design and processing upon emission. This has resulted in improved tube-to-tube and test-to-test uniformity. Work on processing, testing, and materials standards has been started, and in most cases completed. The effects on emission of various additives in core materials, and the significance of modifications in core material melting, drawing, and cleaning methods has been evaluated. In some cases, the cause of poor activity in a particular test sample has been isolated.

Full understanding of the emission problem still seems remote. However, because active interest in the problem has been aroused and crystallized into a joint effort, the immediate goal, that of a satisfactory melt-approval test method, now seems attainable.

[3] A specification covering Radio Tube Core Material classifications is now being prepared by Section A, Committee B4, Subcommittee 8, ASTM.