Microanalysis of Gas in Cathode Coating Assemblies*

HAROLD JACOBS† AND BERNARD WOLK†

Summary—A study of gases evolved from oxide-coated cathode assemblies was made during degassing and activation conditions. It was found, first, that the volume and nature of gases evolved from uncoated nickel cathode sleeves were practically independent of the three different cleaning methods used; and, second, that hydrogen-fired cathodes liberated slightly larger quantities of hydrogen when heated in vacuum. The release of hydrogen from nickel cathodes was not instantaneous, but was observed to continue even after two and one-half hours of continued heating at 900° C. Br.

When a similar analysis was made of gases liberated from nickel sleeves coated with alkaline earth carbonates, the evolution of hydrogen was reduced considerably, but with a corresponding increase of CO.

The chemistry of the gas condition in the tubes during cathode degassing is shown to be related to the speed of exhaust.

I. Introduction

THE PROBLEM of finding the relative values of those factors that affect electron tube life, whether detrimental or beneficial, is one with which tube engineers have been concerned for many years. Two related variables that generally have been considered as having a direct effect on tube life[1] are: initial activation conditions, and the evolution of gases.

Therefore, a program was set up in which tube performance was studied in relation to the gases that evolved when the various parts were heated. Along with this work, an attempt was made to find any correlation that might exist between these gases, thermionic emission, and life.

The purpose of this program was outlined as follows:

1. To determine the nature of the gases evolved, in order to provide suitable getter materials for particular gases.

2. To determine the time at which these gases appear, so that activating and bombarding schedules might be varied to produce optimum conditions.

3. To observe whether some gases when introduced during activation period enhance thermionic emission, and, if any were found, to investigate a means for simulating such conditions on rotary exhaust so that the desired effects could be produced.

The investigation which is reported here began with a study of gases coming from the following parts: (a) the unprocessed nickel cathode sleeve itself, (b) the cathode sleeve processed in various ways, and (c) the coating plus the cathode sleeve and heater.

II. Uncoated Nickel Cathodes

The initial phase of the work concerned only the cathode and heater parts, in which the cathode sleeve was uncoated. Four different lots of uncoated sleeves were studied. One lot was unprocessed. The other lots were prepared in three different ways as follows: (1) degreased, (2) hydrogen fired, and (3) electropolished.

The cathode sleeve employed in all of the foregoing work is of the lock-seam variety, having a major diameter of 0.084-inch, minor diameter of 0.034 inch, and length of 28.5 mm. The wall thickness is 0.0025 inch. A spectrographic analysis of the nickel material showed the presence of Fe, Co and Mg in quantities anywhere from 0.1–1 per cent; Al, B, Ca, Mn in still smaller concentrations (0.01–0.1 per cent); and Pb and Si present as a faint trace (0.001–0.01 per cent).

After various treatments on exhaust, the gases evolved from the parts were collected and quantitatively analyzed.[2]

Tubes were mounted and sealed in pilot-line production, using the lock-in stem.

Discussion

The gases evolved from 6.3-volt tungsten heaters coated with Al_2O_3 are recorded in Table I. It is interesting to note in observing Tables II and III that the materials from which the most gas evolved during the first half-hour of heating were the hydrogen-fired nickel sleeves.

TABLE I

Analysis of Gases in Filaments
(Heated to from 1000°C. Br.–1100°C. Br.)
(Al_2O_3 coated tungsten wire)

Average	*½-Hour Heating* 3 tubes	*Additional 2-Hour Heating* 2 tubes
Total amount of gas in liter microns	3.08±0.31	1.44
% CO_2	21.4±1.9	0
% H_2	45	95.0
% O_2	0	0
% CO	0	0
% N_2	31.6	5.0

The percentage of hydrogen yield seems quite high, even for the unprocessed and degreased specimens. It is interesting to note, too, that the only nickel sleeves which did not show carbon dioxide and oxygen, i.e., an oxidizing influence, were the degreased sleeves.

The unprocessed sleeves showed some CO_2 and O_2, as did the hydrogen-fired parts, though to a lesser extent. It is possible that this result is due to grease contamination, since degreasing seems to have eliminated the CO_2 and O_2 yield of the material.

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† Sylvania Electric Products Inc., Kew Gardens, L. I., N. Y.

[1] Effect of operating time on electrical characteristics.

[2] Saul Dushman, "Vacuum Practice," chap. 9, John Wiley and Sons, Inc., New York, N. Y., 1949.

TABLE II

UNCOATED NICKEL CATHODES ½-HOUR HEATING AT 900°C. (Plus 3 minutes at 1000°C.)

Average	*Unprocessed* 5 tubes	*Degreased* 5 tubes	*Hydrogen-fired* 6 tubes	*Electro-Polished* 5 tubes
Total amount of gas in liter microns	9.59 ±0.87	8.22 ±0.67	11.2 ±0.51	10.1 ±0.33
% H_2O	trace	trace	trace	trace
% CO^2	5.4 ±1.3	0	6.0 ±2.1	7 ±2.5
% H_2	41.2 ±2.2	47.7 ±2.4	52.0 ±1.8	39.9 ±5.6
% O_2	7.2 ±0.44	0	2.8 ±0.04	1.5*
% CO	35.1 ±0.7	42.5 ±2.1	28.2 ±1.6	42.2 ±2.4
% N_2	11.1 ±0.5	9.8 ±0.85	8.9 ±1.1	11.1 ±1.9

* Found in only two out of 5 samples.

TABLE III

UNCOATED NICKEL CATHODES (Additional 2-hour heating at 900°C.)

Average	*Unprocessed* 2 tubes	*Degreased* 3 tubes	*Hudrogen-fired* 2 tubes	*Electro-Polished* 2 tubes
Total gas in liter microns	7.76 ±0.05	5.60 ±0.31	8.61 ±0.0	5.91 ±0.21
% CO_2	5.2 ±0.0	0	4.91 ±0.0	0
% H_2	91.0 ±0.8	97.65 ±0.05	92.5 ±1.1	98.0 ±0.15
% O_2	0	0	0	0
% CO	0	0	0	0
% N_2	3.7 ±0.7	2.35 ±0.05	2.6 ±1.1	2.0 ±0.15

In the second group of materials (shown in Table III) in which gases were collected for two hours at 900°C. after the previous half-hour period, the larger quantity of gas can be attributed to hydrogen. The fact that it takes a much longer time to drive the hydrogen out of the nickel than it does for any of the other gases is new information, as far as the authors have observed.

The reasons for this slow evolution of hydrogen is not known, but it is possible that hydrogen can form a compound with some of the impurities, such as iron, in the nickel cathode sleeve, and that much more thermal energy would be required for exhausting the compound than for diffusing hydrogen out of the nickel.

III. OXIDE-COATED NICKEL CATHODES

Following the study of gases in cathode nickel, another series of tests was initiated to determine the nature and quantity of the gases evolved during breakdown and subsequent prolonged heating of oxide-coated cathodes. The intention here was to approach more closely the problems involving tube life, initial emission, and the appearance of gases in tubes.

Method

The cathodes used in this phase of the work were of the same lot previously analyzed and reported. These cathodes were unprocessed prior to coating, and the coating used was a standard mixture of triple carbonate suspended in nitrocellulose lacquer.

Tubes were prepared, using a cathode coated to a diameter of 0.044 ± 0.001 inch, and containing 8.5 to 9.5 mg of material. Results are shown in Table IV.

Results

The heating schedules used in this phase of the work follow a definite set of purposes. The elevated temperature (1000°C. Br.) was required in order to break down the alkaline earth carbonates as in (1)

$$\begin{pmatrix} Ba \\ Sr \\ Ca \end{pmatrix} CO_3 \rightarrow \begin{pmatrix} Ba \\ Sr \\ Ca \end{pmatrix} O + CO_2 \uparrow . \qquad (1)$$

The 900°C. Br. treatment which was then given to the cathode represents an attempt to approximate the aging and operating conditions.

From Table IV, column A, it can be seen that of all the gases liberated during the breakdown process, CO_2 is the largest single component. This was expected, but the total quantity of gas was so great that the McLeod gauge was too small to determine this quantity exactly. However, the approximate figure of slightly greater than 400 liter microns was obtained. The individual components of the gas mixture were obtained by an analysis of a portion of the total sample.

Columns B and C record the composition of the gases evolved during a heating period of one-half hour after cathode breakdown had taken place. For data in column B, the system was previously closed to the pumps during the three-minute breakdown schedule, whereas the data in column C were obtained for the same half-hour period but with the initial breakdown gases immediately pumped off. Thus, a convenient method was available for noting the effects of retarded evacuation on the nature and quantity of CO_2 and H_2O, and an equally abnormal total lack of H_2 and O_2 gases. From previous work on uncoated nickel sleeves (Table II) it was found that the bulk of the gas evolved in the same half-hour period was H_2 and CO, along with a small quantity of O_2 and CO_2. It is, therefore, evident that in the presence of a large excess of CO_2 a series of reactions takes place, as in (2):

$$CO_2 + H_2 \rightleftarrows H_2O + CO. \qquad (2)$$

In column C, with less residual CO_2 during the half-hour aging at 900°C. Br., there is found a normal trace of H_2O, a smaller quantity of CO_2, and a large quantity of H_2.

Data in columns D and E show that initial slow removal of gases has only a slight effect on the gases evolved during the subsequent two hours of continued heating.

Only in the earlier stages of activation and aging does the speed of removal of gases change the nature of the gases surrounding the cathode.

With an early and rapid removal of gases, column C can be expected to show more H_2 and more CO on a per-

centage basis, and with a slow exhaust (column B), the atmosphere can be expected to tend more to H_2O and CO_2.

In addition, another point is of interest. Comparing Table III with columns D and E, it is found that in the two-hour period, i.e., longer life period, more total gas (7.76 ± 0.05 liter microns) escapes from the uncoated cathode than from the coated cathode (5.45 and 5.78, respectively). This difference may be due to the suppression of gas evolution by the formation of oxide interfaces at the cathode.

For instance, in the case of N_2, which is relatively inert, a smaller quantity was released in the two-hour period from the coated than from the uncoated cathodes. This theory seems to be consistent with the fact that oxidation increases the hot tensile strength of nickel, and it may be expected, then, that as hot tensile strength is increased, diffusion is decreased.

Discussion

When the study of gases evolved from oxide-coated cathode assemblies was completed up to the point of degassing and activation conditions, it was found, first, that the gases evolved from uncoated nickel cathode sleeves were qualitatively practically independent of the three different cleaning methods of factory processing commonly, used, and, second, that hydrogen-fired cathodes liberated slightly larger quantities of hydrogen when heated in vacuum. In addition, the release of hydrogen from nickel cathodes was not instantaneous, but was observed to continue even after $2\frac{1}{2}$ hours of continued heating at 900°C. Br.

When a similar analysis was made of gases liberated from nickel sleeves coated with alkaline earth carbonates, the evolution of hydrogen was reduced considerably, but with a corresponding increase of CO, indicating the reaction (see (2)):

$$CO_2(g)\ (\text{excess}) + H_2(g) \rightleftarrows H_2O(g) + CO(g).$$

The gas condition in the tubes during cathode degassing was shown to be related to the speed of exhaust. The lower speed of exhaust produces a condition leading to the right side of (2), and a high exhaust speed produces conditions tending to retard the reaction to the right.

IV. Effects of Gases on Thermionic Emission

As the third step in this investigation, a procedure was set up to determine the effects of some of these gases on thermionic emission.

TABLE IV*

	Gases evolved from coated cathodes heated to 1000°C. Br. for 3 minutes	*Gas evolved in first ½ hour of heat treatment at 900°C. Br.*	*Gas evolved in first ½ hour of heat treatment at 900°C. Br.*	*Gases evolved during a 2-hour period of heat treatment at 900°C. Br.*	*Gases evolved during a 2-hour period following a treatment similar to that described in Col. D*
	A	*B*[3]	*C*[4]	*D*[3]	*E*[4]
Total gas yield in liter microns	>400 LM	34.2±3.1	5.43 LM ±0.31	5.45 LM ±0.2	5.78 LM ±0.0
H_2O	trace	12.2%±0.9	trace	trace	trace
CO_2	95.4%±0.3%	71.4%±2.6	12.0%±5.6	4.8%±0.8	0
H_2	trace	0	37.3%±3.2	91.1%±1.5	94.6%±0.6
O_2	0	0	0	0	0
CO	2.7%±0.8%	15.5%±1.5	44.0%±5.0	0	0
N_2	1.6%±0.1%	1.2%±0.15	6.7%±0.8	5.2%±1.5	5.4%±0.6

* All values shown represent averages.
[3] System closed from the pumps during initial breakdown.
[4] System open to pumps during initial breakdown.

TABLE V

Emission from Gas-Contaminated Oxide-Coated Cathodes

Sample Number	1	2	3	4	5	6	7	8
Contaminating Gas	*Emission Current* (Temperature Limited)							
Control	2.1 ma	2.0 ma	1.9 ma	2.5 ma	2.2 ma	1.7 ma	2.5 ma	2.5 ma
Oxygen	8 μa	4 μa	<1 μa	<1 μa	—	—	—	—
Hydrogen	2.2 ma	2.1 ma	3.0 ma	1.6 ma	—	—	—	—
CO_2	14 μa	30 μa	12 μa	—	—	—	—	—
H_2O	1 μa	2.5 μa	2.5 μa	—	—	—	—	—
CO	2.0 ma	15.0 ma*	15.0 ma*	22.0 ma*	5.0 ma*	5.4 ma*	2.0 ma	2.0 ma

* Some tubes did not appear to saturate, indicating a gassy condition. Further activation in some cases resulted in tubes which saturated between 2 and 5 mils. This was characteristic only of CO contamination.

In order to test thermionic emission, standard diodes were made up using partially opened cylindrical nickel anodes, and were tested on the gas analysis system. For details of the exhaust schedule used, see Appendix I. The method of preparation of the gases is described in Appendix II.

Results

The saturation plate currents recorded in Table V show the effects of the contamination of oxide-coated cathodes by the different gases. (The testing procedure is given in Appendix III.) Molecular hydrogen does not appear to exert any enhancing influence on the emission level, and the oxidizing gases, such as O_2, CO_2 and H_2O, markedly destroy the cathode activity. Furthmore, CO not only results in no enhancement, but also appears to be the cause of a gassy condition. Only after additional activation and degassing do these latter tubes respond with a saturation level of two to three mils.

Discussion

In general, it was found that the oxidizing gases have a detrimental effect on the emission. Both oxygen and water vapor appear to have a somewhat more harmful effect than CO_2. An interesting feature, also, is the failure of a reducing gas, such as hydrogen, to enhance cathode emission when it is introduced during the period of cathode activation. As indicated in previous work, the cathode sleeve itself supplies about 4 to 5 liter microns of hydrogen during the first half hour of activation. In the present work, however, 20 to 50 liter microns of hydrogen was used. In effect, this means that even with an increase by a factor of 5 of the hydrogen employed during activation, no difference in the emission level could be detected.

It is well known in actual practice that the use of hydrogen or carbon monoxide flushing results in a considerable oxide cleaning up of anode and grid surfaces, thereby providing higher emission. But such a method is an indirect one, and as far as the direct or primary effects on emission are concerned, no initial enhancement due to heating the cathode in low pressures of either H_2 or CO_2 was observed.

In connection with the use of CO, a further observation should be made. There was in some instances a gassy condition that developed in tubes previously treated with CO. It is difficult to account for this condition in a definite manner, but it was noted that after heating the cathode in carbon monoxide, a considerably longer length of time was required for degassing than when the cathode was processed by heating in other gases. This would indicate that some secondary chemical process had taken place. One of the possibilities which could be pointed out is the formation of barium carbide in the following manner:

$$3Ba + 2CO \rightarrow BaC_2 + 2BaO \qquad (3)$$

on further heating

$$BaC_2 + 2BaO \rightarrow 3Ba + 2CO. \qquad (4)$$

There is relatively little information on barium carbide in the literature, but there is some information on calcium carbide which can be applied.[5] It is pointed out that calcium carbide melts above platinum at approximately 2300°C., indicating an exceedingly stable compound. If reactions occur, such as in (3) and (4), and if barium carbide is as stable as calcium carbide, then a considerable length of time for the reactions to go to completion could be expected. This theory is to some extent verified by the type of gases that were found to be coming off during the measurements of emission. By raising the liquid air to the condensation trap, it could be demonstrated that this gas was uncondensable, thereby precluding the existence of water vapor or carbon dioxide. Since the gas persisted even upon heating the palladium tube, it was demonstrated that the gas was not hydrogen. After so much processing, the gas could not have been nitrogen, since previous work on gas analysis indicated only a negligible amount of N_2. Only two gases remained—oxygen and carbon monoxide. Since the poisoning was not permanent and a good level of emission resulted after the gas was removed, it can be concluded that the gas was not oxygen. Thus, the remaining possibility is that the gas was actually CO. If it were simply adsorption, one would expect the gas to be very quickly released, but since the gas persisted despite high temperatures, certain chemical reactions must have taken place. One of the possibilities is therefore indicated in (3) and (4).

V. Conclusion

The speed of exhaust appears to be a very important factor from the point of view of activation of the cathode coating. This is due to the fact that the gases which are liberated from the cathode during breakdown, if given sufficient time, react with each other to form new compounds. Specifically, it was found that there exists an equilibrium equation as follows:

$$CO_2 \text{ (excess)} + H_2 \rightleftarrows CO + H_2O,$$

and that the formation of the products on the right will be favored by slow exhaust speeds, while rapid pumping suppresses the reaction to a great extent.

The gases most detrimental to emission are the oxidizing gases, CO_2 being the least harmful. Reducing gases, such as H_2, introduced during the activation period in pressures from 5 to 20 microns appear to have no enhancing effect on emission. When oxidizing gases were introduced into the system during the activation of one tube, other tubes which were sealed on the manifold exhibited the effect of poisoning when processed

[5] W. Segerblom, "Properties of Inorganic Substances," Chemical Catalog Company, Inc., New York, N. Y., p. 38; 1927.

later, although the gases had been removed previously. Although no quantitative data are presented here, this poisoning by gases, perhaps occluded on the glass, was observed for long periods of time. (It can, therefore, be expected that an equivalent condition could occur when sudden leaks develop during Sealex operations.)

Although hydrogen is useful in removing oxide from the various tube elements around the cathode, it can be quite troublesome when applied to hydrogen firing of cathodes. Such cathodes have been found to evolve quantities of hydrogen, even after two hours of heating at 50 per cent above rated filament voltage. Since cathodes without a tube-processing history of hydrogen firing also seem to yield hydrogen after prolonged heating, a hydrogen gettering material would have considerable usefulness.[6]

Appendix I—Exhaust Schedule

1. The tubes were baked out at 350° to 400°C. for 30 minutes.
2. The plate was degassed with rf at 900°C. for 5 minutes.
3. E_f of 14 volts was applied for 3 minutes. (The tube contained a 6.3-volt indirectly heated cathode.)
4. The filament voltage was turned off and the tube exhausted for 3 mintues.
5. E_f of 9.5 volts was applied and the plate was simultaneously rf heated to 900°C. Br. for 3 minutes.
6. Liquid air was applied to the mercury pump trap.
7. E_f of 9.5 volts was maintained for an additional 5 minutes.
8. The system was closed off from the pumps and 20 microns of contaminating gas was admitted. The filament was heated while the gas was being introduced.
9. Heating of the cathode was continued at 9.5 volts E_f for an additional 5 minutes in the presence of the gas.
10. The system was opened to the pumps, thus exhausting the vacuum system, and the cathode was kept heated for a period of 20 minutes.
11. The plate was again heated by rf during the last 5 minutes of the 20-minute schedule in step 10.
12. The filament voltage was turned off.

[6] The nickel material used in making cathode sleeves is melted under an atmosphere of hydrogen by the manufacturer.

Appendix II—Preparation of the Gases

1. *Oxygen*: This gas was introduced by the heating of silver oxide.
2. *Hydrogen*: Hydrogen was introduced by applying a gas flame to an electrically heated palladium tube until the McLeod gauge indicated the proper pressure.
3. *Water Vapor*: By heating the platinum wire located in the Toepler pump section of the apparatus, the combustion of oxygen and excess hydrogen could be initiated to form water. This water vapor was condensed in the cold trap prior to its use by means of dry ice and methanol. When it was released for contamination of an oxide cathode, its pressure was observed on a Pirani gauge which was previously calibrated for water vapor.
4. CO_2: Carbon dioxide was stored for future use by means of the liquid air trap condensation of the cathode breakdown product.
5. CO: The preparation of carbon monoxide was somewhat more complex in that an additional cathode assembly was required. A tube containing a flag getter and a coated cathode was sealed to the gas analysis system so that it was external to the regular manifold section. After thorough degassing, its getter was flashed and immediately thereafter the cathode was broken down. The combination of the CO_2 thus released with the free barium yields CO according to the following reaction:

$$Ba + Co_2 \text{ (excess)} \rightarrow BaO + CO. \qquad (5)$$

The CO was then collected in the Toepler pump prior to its release for contamination of the cathode as described in Appendix II, Step 8. The excess CO_2 in (5) was condensed by the liquid air trap.

The total time for cathode activation was thus in the order of 30 minutes. The control tubes were given the same treatment and activating time, except that in Step 8 no contaminating gas was introduced.

Appendix III—Testing Procedure

1. After exhaust processing mentioned above, two minutes were allowed to elapse before bringing E_f up to 4 volts, and an additional 2 minutes for temperature equilibrium to be established.
2. Plate voltage was slowly increased to 150 volts (maximum) and behavior of the filament current recorded.