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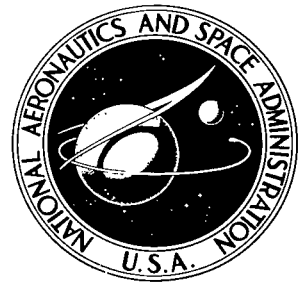

THE EFFECT OF VARIOUS GASES ON THE THERMIONIC EMISSION OF TANTALUM WIRE FILAMENTS

by Thomas M. Heslin, John J. Park, and Edward L. Sanford

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16. Abstract

Oxygen and nitrous oxide decrease the thermionic emission of yttrium-doped tantalum wire used as neutralizer filaments in cesium-ion microthrusters. This finding resulted from experiments prompted by the emission-limited behavior of neutralizers at unexpectedly low voltages during microthruster testing on one of the Applications Technology Satellites.

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SUMMARY

The effect of various gases, at low pressures, on the thermionic emission of an yttrium-doped tantalum wire used in cesium-ion microthrusters was investigated. It was found that both oxygen and nitrous oxide decrease this emission, with oxygen having the greater effect. When operated in either O_2 or N_2O gas, neutralizer filaments of tantalum wire become emission-limited at significantly lower voltages than in the absence of these gases. Ultraviolet light does not observably affect emission either in the presence or in the absence of the gases investigated. None of the gases used affect a cold filament.

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INTRODUCTION

The thermionic emission of yttrium-doped tantalum wire, used as neutralizer filaments in cesium-ion microthrusters, was studied as a function of environment. The emission-limited behavior of neutralizers at unexpectedly low voltages during microthruster testing on one of NASA's Applications Technology Satellites (ATS IV) led to this series of tests.

ATS IV was planned as a gravity-gradient-stabilized satellite in a geosynchronous orbit. However, because of failure of the Centaur stage of the launch vehicle to achieve a second burn, the spacecraft remained attached to the Centaur in a parking orbit (218 km perigee, 760 km apogee).

At its perigee, where thruster testing was performed, ATS IV brought hot neutralizer filaments into contact with portions of the heterosphere containing the gaseous atoms and molecules of oxygen, nitrogen, hydrogen, and helium.

Total gas pressure of the heterosphere ranges from 1.4×10^{-6} torr at 200 km to 6.8×10^{-10} torr at 700 km, during a maximum in the sunspot cycle (Reference 1). The neutral atmosphere composition is shown as a function of altitude in Table 1. As shown in the table, near the base of the heterosphere the main components are molecular nitrogen, atomic oxygen, and molecular oxygen (Reference 2). As a result of diffusive separation, the percentage of atomic oxygen, the lightest of the three species, increases with altitude. Above about 200 km there are relatively little molecular oxygen and increasingly smaller proportions of nitrogen molecules.

Operationally, a microthruster neutralizer is a simple vacuum diode, but with the Cs plasma beam replacing the collector plate. The characteristic curve of an operating neutralizer has a linear space-charge limited region which becomes almost horizontal as it enters an emission-limited region. For a given filament, the electron emission characteristics are dependent, among other things, upon its temperature, the work function of the elements, and the alloy composition. A 7-mil diameter tantalum-50 ppm yttrium alloy had been selected by the contractor, Electro-Optical Systems, Inc., Pasadena, California, as the filament material in the Ion Microthruster Experiment (Reference 3). It is noteworthy that a 3-mil diameter wire of the same alloy had been heated to approximately 2000°C for 3012 hours without failure in Vac-Ion system tests conducted by Materials Research and Development Branch personnel.

Table 1

Composition of the Heterosphere from 100 km to 700 km During Sunspot Maximum.*

Altitude (km)	Total Pressure (mm Hg)	Percentage of Constituent Based on Number Density (%)					
		N_2	O_2	N	O	He	H
100	4.4×10^{-4}	77.664	16.989	0.007	5.339	0.00033	trace
120	3.6×10^{-5}	73.536	11.170	0.025	15.173	0.0029	trace
140	8.9×10^{-6}	65.967	8.090	0.047	25.887	0.0094	0.00003
160	4.3×10^{-6}	59.748	6.471	0.065	33.698	0.017	0.00006
180	2.4×10^{-6}	53.822	5.297	0.083	40.769	0.029	0.00011
200	1.4×10^{-6}	48.139	4.341	0.101	47.376	0.050	0.00018
250	4.9×10^{-7}	34.774	2.572	0.146	62.403	0.103	0.0005
300	1.9×10^{-7}	23.696	1.451	0.193	74.439	0.218	0.0012
350	8.3×10^{-8}	15.265	0.773	0.235	83.302	0.422	0.0027
400	3.8×10^{-8}	9.513	0.405	0.275	89.026	0.775	0.0056
500	8.9×10^{-9}	3.493	0.105	0.345	93.707	2.328	0.0220
600	2.3×10^{-9}	1.239	0.026	0.402	91.900	6.354	0.0777
700	6.8×10^{-10}	0.415	0.006	0.430	83.445	15.459	0.244

*Part of Table 4-2, p. 26, Reference 2.

EXPERIMENTATION

The electrical measuring circuit, Figure 1, used in this test program was a basic thermal electron emission measuring circuit. A dc power supply was used to heat the filament, and a second dc power supply provided a bias voltage to the collector. Absolute values of emission were not required, though reproducibility was emphasized. One of the most important considerations for the electrical circuit was supplying stable electrical power to the filament and the collector. Another consideration was the ability to measure the various electrical potentials to a high degree of accuracy.

In order to measure the electron emission from the filament, a 1000-ohm resistor shunt

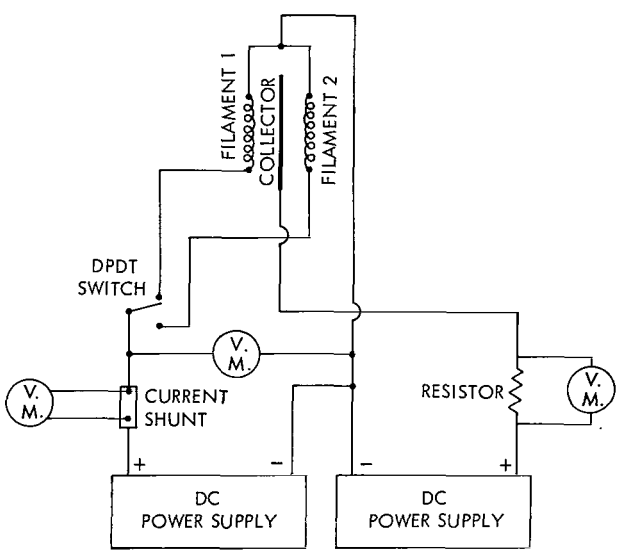

Figure 1—Thermal electron emission measuring circuit.

was placed in the positive lead to the collector. The voltage to heat the filament, the bias voltage to the collector, and the electron emission from the filament were measured by digital voltmeters. These were calibrated periodically with a 1-volt standard cell to assure repeatability from test to test. The current to the filament was measured by inserting a current shunt in the power line and recording the reading from a millivolt potentiometer. The overall error in the measuring circuit was estimated at ±0.75 percent; the repeatability of the readings was ±0.5 percent.

The filaments were 7-mil diameter tantalum-yttrium wires. Two wires were located on opposite sides of the collector plate, ensuring redundancy and permitting more frequent tests. The filaments were approximately 1/2-inch long, spot-welded to the electrical posts, and were about 1/8 inch away from the collector plate. The test arrangement is shown in Figure 2. Variables included the gas pressure, the filament temperature, and bias voltage between filament and collector plate. With a steady current to the filament, the emission curves were reproducible to better than 1 percent.

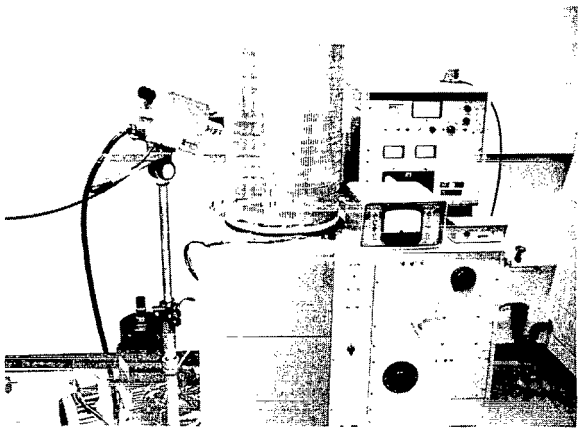

Figure 2(a)—Vacuum system used.

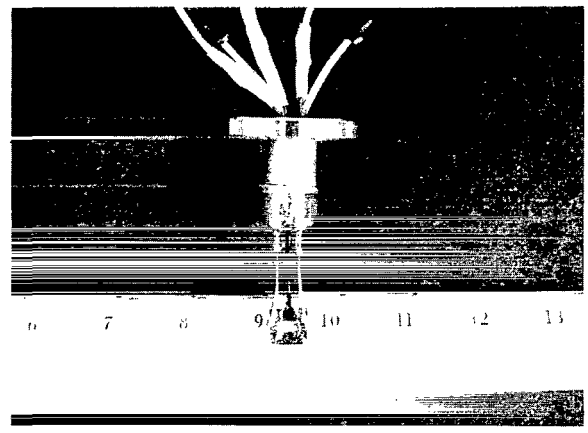

Figure 2(b)—Filament holder used.

Attempts to operate at a specific temperature were unsuccessful. The problem was related to the human variability with an optical pyrometer, to the small target area offered by a 7-mil diameter filament, and to idiosyncrasies of an automatic pyrometer. The final arrangement was to provide a constant amperage through the filament and to operate with a bias voltage near the "knee" of the emission curve, where the emission begins to change from the space-charge-limited region to the emission-limited region.

In an attempt to ensure reaction between gas and filament, the gas pressure for the first trial runs was in the micron range. However, one filament burned out with an N_2O pressure of 89 microns. Also, arcing occurred in the system with a pressure of 8.5 microns N_2O gas. Consequently, modifications were made to the gas inlet system to meter and control the gas flow at a reduced rate.

One additional anomaly was noted and corrected. An ultraviolet lamp, emitting at 1849A, had been selected for attempts to disassociate N_2O gas into its components. This wavelength had been

calculated as the suitable energy to break the bonds of the N_2O molecule, providing the N atoms. The lamp originally had a black bakelite base cemented to the glass shell. Turning on the lamp caused an increase in chamber pressure. In fact, the outgassing products from the lamp caused a decrease in emission from the filament. Consequently, all extraneous material was removed from the lamp, leaving only the glass shell.

Thus oxygen, nitrogen, and nitrous oxide were the only gases introduced into the chamber. These gases were relatively pure; their analyses are given in Table 2.

The potential reactions of a hot tantalum wire with oxygen or with nitrogen included dissolution of the atoms into the interstices of the tantalum crystal structure, followed by compound formation at the surface.

Most of the data heretofore reported in the literature was not specifically relevant, having been obtained at relatively high gas pressures. For example, kinetic studies of the reactions of tantalum with air, nitrogen, and oxygen were carried out by Albrecht et al. (Reference 4) in the temperature range of 400° to 1500°C at 1 atmosphere pressure. They also determined the variation of the rate constant of the tantalum-oxygen reaction at 1000°C as a function of pressure for

Table 2

Analysis of Gases Used.

Oxygen	
Impurities in O_2 listed by producer:	
Argon	12 ppm
Nitrogen	7 ppm
Krypton	14 ppm
Methane	13 ppm
Xenon	1 ppm
Water	7 ppm
Threshold less than 1 ppm	
Nitrogen	
Impurities in N_2 listed by producer:	
Argon	4 ppm
Threshold less than 1 ppm	
Nitrous Oxide*	
Impurities in N_2O determined using gas chromatography (Code 735):	
Hydrocarbons	0 ppm
Air (N_2, O_2)	$<<1$ ppm
CO_2, C, CO	<10 ppm
H_2O	Unknown

*Gas quoted by producer as 98% pure N_2O.

pressures of 0.2, 0.4, 0.6, and 1 atmosphere. The Ta-O reaction follows a linear rate law in which the weight gain (as milligrams of gas reacted/unit surface area) is a direct function of time. At 1300°C and above, catastrophic oxidation occurred as soon as oxygen at 1 atmosphere pressure was added to the system. Nitrogen reacts much more slowly with tantalum than does oxygen. In the 400 to 700°C range, the nitriding reaction follows cubic behavior, where (weight reacted)^3 is equal to the rate constant × time. For the 800 to 1475°C range, the rate was parabolic; there was no variation in the parabolic rate constant with nitrogen pressure in the range of 1/8 to 1 atmosphere. Above 1100°C, adherent dark-brown films were formed, composed of tantalum nitrides.

The solid-solubility limits for carbon, oxygen, and nitrogen in tantalum were determined at 1500°, 1000°, and 500°C by Vaughan et al. (Reference 5). Tantalum can dissolve 3.70 atomic percent nitrogen and 3.65 atomic percent oxygen. The low-temperature modifications of Ta_2O_5 and the Ta_xN compounds are the initial precipitates in these systems.

RESULTS

The effect of oxygen is to decrease emission significantly. The general form of this emission decrease is shown in Figure 3. When a hot filament is exposed to oxygen, emission starts to decrease, slowly at first; it then decreases more rapidly, and finally levels off at what appears to be an "equilibrium" value. This value depends on the pressure of the gas, as shown in Figures 4 and 5. Furthermore, as indicated in Figure 3, the entire emission decrease is reversible, and recovery to the starting emission is achieved by shutting off the gas flow and heating the filament in vacuum.

A number of variables were observed to characterize the effect of oxygen on emission. For example, the rate of decrease in emission is a function of pressure, as shown in Figure 5, the rate increasing with gas pressure. It is also observed to be a function of previous history, as shown in Table 3. The three tests shown in Table 3 were run consecutively; a reduction of the emission by 10 percent occurred in a little more than 5 minutes for run I, in less than 5 minutes for run II,

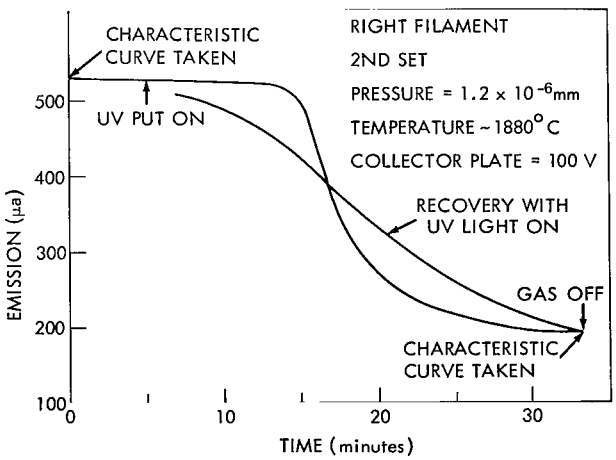

Figure 3—Effect of oxygen on emission.

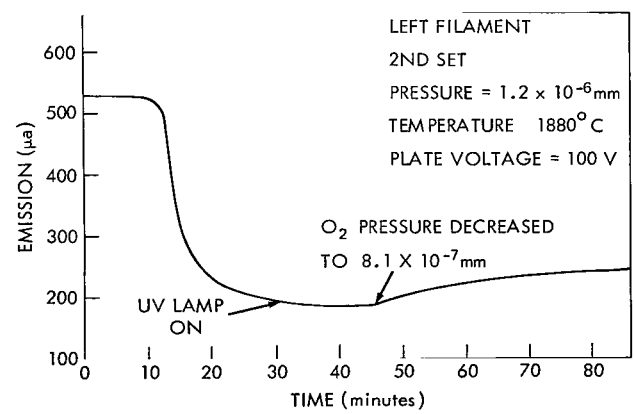

Figure 4—Effect of oxygen on emission.

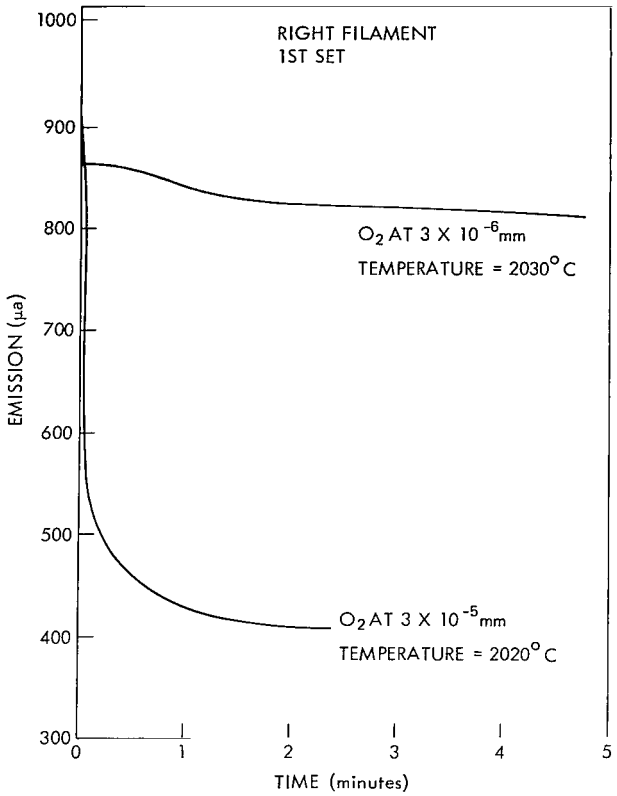

Figure 5—Effect of oxygen on emission.

Table 3

Effect of Repeated Exposures
to Oxygen Pressure 1×10^{-6} mm Hg.

Time (min)	I*	II†	III‡
0	867 μa	863 μa	856 μa
1	864	856	790
2	862	848	705
3	859	827	632
4	852	795	585
5	826	754	558
6	711	683	—
10	534	542	509
15	489	513	494
20	474	500	—
25	465	—	—
30	460	—	—

*UV lamp was turned on at 5 minutes, plate voltage was on continuously.
†Plate voltage was turned on 5 seconds before each reading.
‡Plate voltage was on continuously.

and in less than 2 minutes for run III. The amount of emission decrease, i.e., its "equilibrium" value, appears to be primarily a function of gas pressure, as shown in Figure 4. As gas pressure increases, the equilibrium value of emission decreases. In addition, as indicated in Figure 6, after exposure to oxygen but before recovery, the neutralizer filaments become emission-limited at significantly lower voltages.

Emission-vs-time experiments were run in the presence and absence of oxygen with and without exposure to ultraviolet light. The light energy in no case affected emission, as indicated in Figures 3 and 4. An analysis of the oxygen used is given in Table 2.

The effect of nitrous oxide is essentially the same as that of oxygen at low pressure. A graph (Figure 7) of emission vs time shows that initially there is a plateau lasting from 15 to 30 minutes during which time the reaction is proceeding at a very slow rate. Emission then decreases relatively fast to a steady equilibrium value. As with pure oxygen, gas pressure affects rate and extent of emission degradation, and the original emission is recoverable by heating in a vacuum. Exposure to ultraviolet light did not affect emission either in the presence or in the absence of N_2O.

The similarity in the effect of N_2O and pure oxygen indicates that perhaps an oxidation reaction is causing emission degradation with N_2O. However, the analysis in Table 2 indicates that less than 1 ppm of oxygen is present in the gas, although water was not detectable with the gas

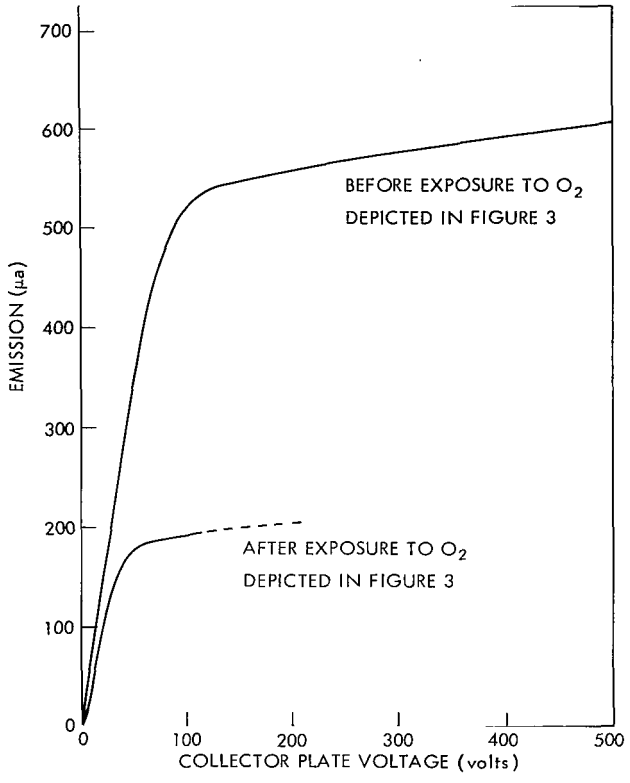

Figure 6—Effect of oxygen: emission-limited behavior at lower voltages after exposure to oxygen.

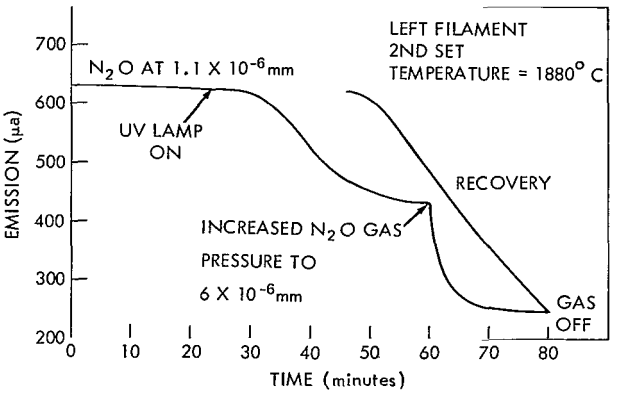

Figure 7—Effect of N_2O and ultraviolet light on emission.

chromatography technique that was used. Other than by direct reaction with N_2O, water is considered the most probable source of oxygen. With gas pressure on the order of 3×10^{-5} torr to 1×10^{-6} torr, the residual oxygen partial pressure in the gas would be on the order of 10^{-12} torr or less; and, using a figure of at least 98 percent gas purity, H_2O pressure is, at most, on the order of 10^{-7} torr.

In regard to the reactions with nitrogen, previous history and length of exposure to gas appeared to be important factors. However, the effect of N_2 on emission was quite small and was not found to be wholly consistent.

In one of the early tests, N_2 at a pressure of 6×10^{-6} torr reduced the electron emission by 2 percent in 13 minutes, and by 31 percent in 37 minutes at which time the gas valve was closed. The other filament was then tested at a lower temperature, its electron emission being 96 μa (microamperes) at the start, rather than 605 μa as in the previous test. At the lower temperature, the emission decreased by 27 percent to 70 μa in 25 minutes. These tests would indicate that the tantalum-nitrogen reaction has an effect upon electron emission. However, in longer tests at a later date the results were not so obvious, as the following would indicate.

When exposed to N_2 gas, a previously unburned filament increased in emission in what appeared to be a "cleaning up" process (curve 1, Figure 8). The same filament, when burned in N_2 gas after a series of exposures to O_2 and N_2O, experienced first the above-mentioned increase in emission, followed by a decrease of about 7 percent to a minimum, after which a rise in emission occurred as shown in curve II, Figure 8. This rise in emission occurred even though there had been no change in gas pressure or in test conditions. This effect was not reproducible with the same filament even after the identical exposures to O_2 and to N_2O (curve III, Figure 8). In fact, an exposure

of over 6 hours in nitrogen at 1×10^{-6} torr pressure resulted in an emission increase of approximately 2 percent. Because the reactions with N_2 were not wholly consistent, some experimental anomaly must have occurred in conducting the various tests prior to the taking of curve II in Figure 8. In any event, changes in emission in the presence of N_2 were very small relative to changes observed with O_2 and N_2O under the same conditions. As with O_2 and N_2O, exposure of the filaments to ultraviolet light while in the presence of the gas had no effect.

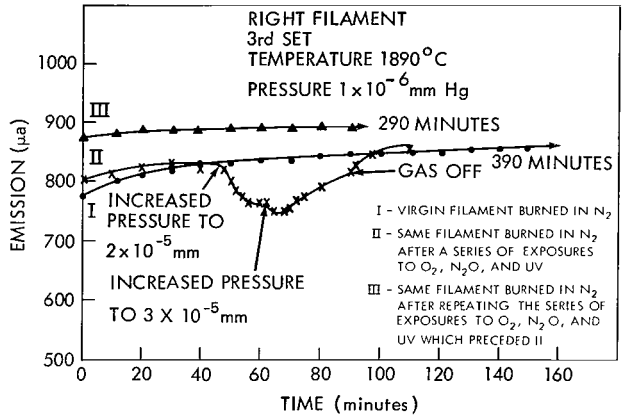

Figure 8—Effect of N_2 on emission.

It was observed that none of the gases used affected a cold filament. A characteristic curve was taken before and after testing one filament, and is shown in Figure 9. As the figure indicates, exposure of the cold filament to ultraviolet, to N_2O, to N_2, or to O_2 had no effect on emission.

It was observed that conditioning a filament by heating it in a vacuum increases emission slightly. This effect is shown in Figure 10. A

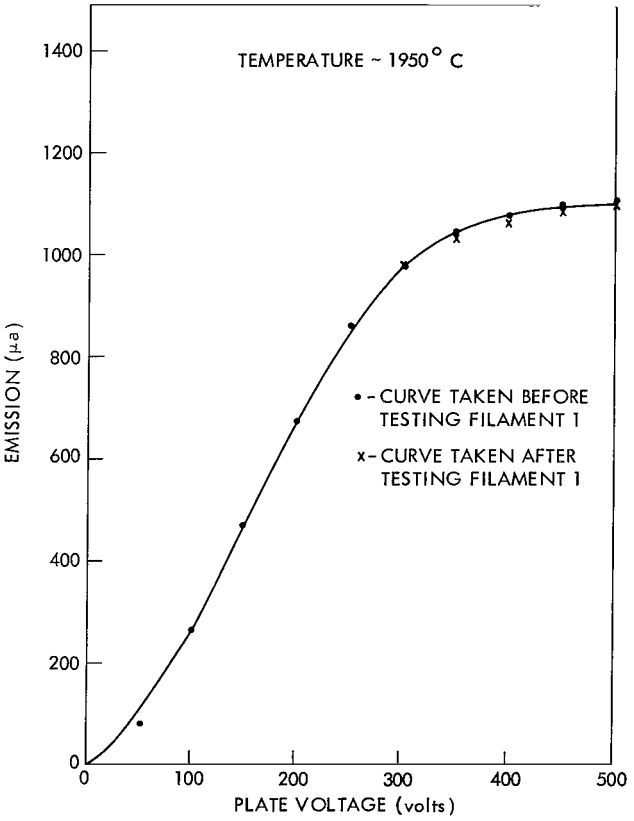

Figure 9—Effect of O_2, N_2O, N_2, and ultraviolet light on a cold filament.

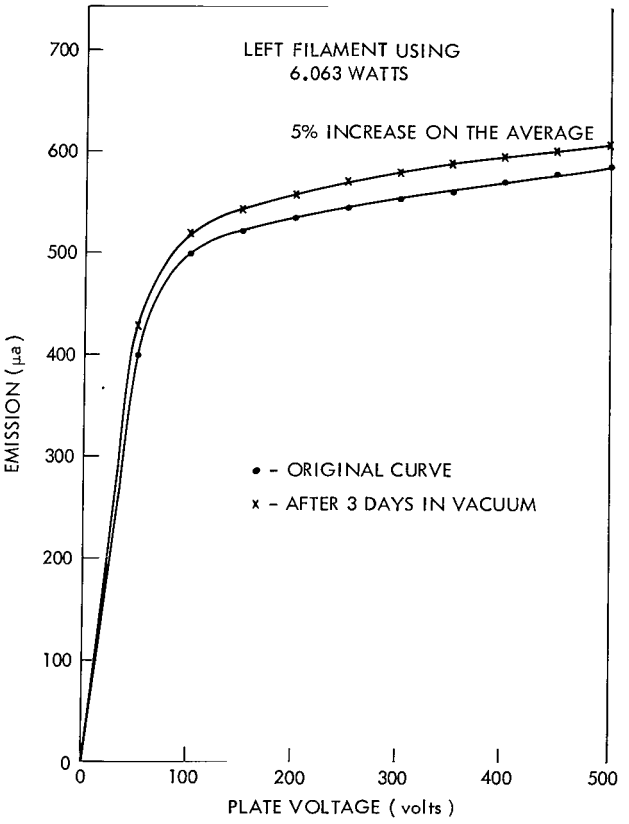

Figure 10—Effect of conditioning on emission.

characteristic curve was taken for two filaments and the power input noted. During that day, the filaments were characterized as to power input vs emission using a constant plate voltage and a vacuum of 6×10^{-7} torr. The sample remained under vacuum for two days. On the third day, using the same power settings, the emission-limited portion of the characteristic curve averaged 3 percent higher for one filament and 5 percent higher for the other.

Two samples were examined using a scanning electron microscope, and the results are shown in Figure 11. Filament 6 showed a decrease in emission during one exposure to N_2 which was not

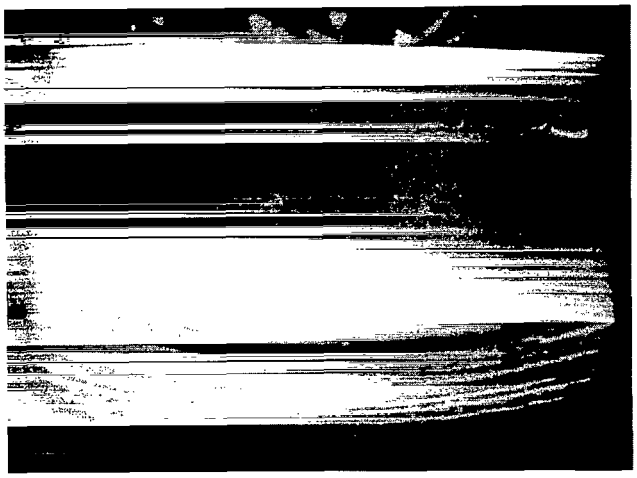

Figure 11(a)—Filament number 5.

Figure 11(b)—Filament number 6.

reproducible, and filament 5 never showed a decrease in emission on exposure to N_2. Figure 11 shows little observable difference between the samples. Other than the marks from wire-drawing, no detectable "fissures" or reaction products were noted.

CONCLUSIONS

Using the sunspot maximum data shown in Table 1 and using 1×10^{-6} torr as a working figure for total gas pressure at the perigee of its orbit, it can be inferred that ATS IV may have experienced static partial pressures of N_2 and O on the order of 5×10^{-7} torr and pressures of O_2 on the order of 4×10^{-8} torr. This does not take into account the ram pressure that the satellite motion creates. Experimentally, it was observed that molecular oxygen at pressures of 1×10^{-6} torr markedly lowers emission and causes filaments to become emission-limited at significantly lower voltages. It was also observed that photodissociation of O_2 [illegible] atomic species had no effect on emission, indicating that it makes little difference whether oxygen is present in the molecular or in the atomic form; the effect on emission remained the same. Judging from these results, it appears likely that atomic oxygen pressures on the order of 1×10^{-6} torr would also significantly

lower emission. It can be concluded also that nitrogen at 5×10^{-7} torr would have little if any effect on the emission of these filaments.

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National Aeronautics and Space Administration
Greenbelt, Maryland, December 2, 1969
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