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GLASS ENVELOPE UV-SENSITIVE FLAME DETECTORS

by

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Report No. 72CRD201

July 1972

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<small>AUTHOR</small> Glascock, HH Jr	<small>SUBJECT</small> flame detector	<small>NO.</small> 72CRD201 <small>DATE</small> July 1972
<small>TITLE</small> Glass Envelope UV-Sensitive Flame Detectors		<small>GE CLASS</small> 2 <small>NO. PAGES</small> 7
<small>ORIGINATING COMPONENT</small> Physics and Electrical Engineering Laboratory		<small>CORPORATE RESEARCH AND DEVELOPMENT</small> SCHENECTADY N. Y.
<small>SUMMARY</small> The need for fast-response, low-voltage flame sensors, able to operate for long periods in ambients presenting a wide range of temperatures, prompted the construction and testing of a number of gas amplification UV-photosensitive detectors utilizing 9741 glass envelopes and a variety of gas fills and electrode and getter materials. Addition of 1 mole percent H ₂ to a He gas fill reduced the required minimum time between counts for a given sensor operating voltage without significantly changing the threshold voltage. All sensors with H ₂ additive ultimately became solar sensitive. Sensors performed well at temperatures as high as 350°C		
<small>KEY WORDS</small> flame detector, gas multiplication, photoemission, ultraviolet, gettering, helium, hydrogen		

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GLASS ENVELOPE UV-SENSITIVE FLAME DETECTORS

H. H. Glascock, Jr.

I. INTRODUCTION

Photosensitive Geiger-Muller type tubes responding to ultraviolet photons have been used as flame detectors for a number of years. CRD work on a low operating voltage wide ambient temperature range form of this device is discussed in GE TIS reports 69-C-358 and 70-C-158. This device requires external quenching of the discharge and is limited to counting rates less than 2 kHz.

One commercially available detector has an ultraviolet transparent glass envelope and a fill of hydrogen gas. This detector has a number of shortcomings:

1. It operates at high voltage (of the order of 800 to 1000 volts).
2. It frequently loses its solar blindness after operating for a while.
3. It is limited in the maximum ambient temperature at which it can be used (probably because of gas release from the tube walls).

The primary merit of the hydrogen fill is the fact that it rapidly recovers after a count. This allows high counting rates so that sufficient information for a yes-or-no flame decision can be accumulated in a short time for a sufficiently intense nearby flame. The rapid recovery depends upon the presence of a diatomic or polyatomic gas. ⁽¹⁾ Choice of the gas is restricted by the fact that it must not adversely affect the cathode which in most applications should have a work function near 4.5 eV. The gas should not decompose at the highest temperatures experienced by the sensor and the gas should not have metastable states. These restrictions remove nearly all gases as candidates except hydrogen and possibly methane. While these two gases have rather high breakdown potentials, satisfactory operation might be achieved if they are used as additives to noble gases. It should be noted here that use of SF₆, BF₃, Br₂, and certain other electronegative gases as additives to noble gases might produce a sensor which would be solar blind at relatively high altitudes because the work function of its cathode would be high. While some such gas combinations, sufficiently dilute to avoid electron attachment problems, ⁽²⁾ might recover rapidly after a count the sensitivity of the sensor to the ultraviolet output from a burning hydrocarbon would be low. We did not test any of these gases.

II. SENSOR STRUCTURE AND MATERIALS

The sensor structure shown in Fig. 1 was generally used. The envelope was formed from 9741 UV transmitting glass and a conventional vidicon stem

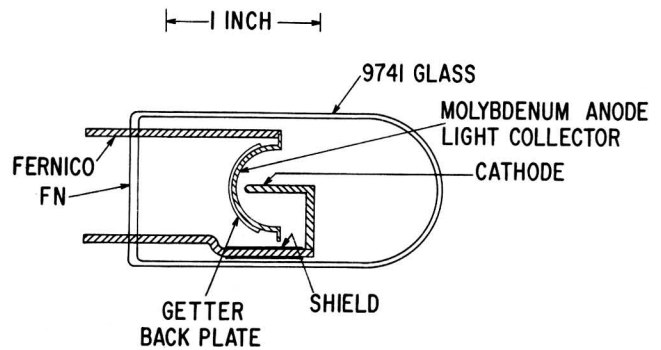


Fig. 1 Glass envelope flame sensor (schematic).

made from FN glass. In all tubes the cathode was pointed into the anode hemisphere so that light reflected from the anode impinged upon the cathode. Generally the cathode was in the form of a rod with its hemispherical end positioned about 0.050 inch from the anode. Several cathodes were formed from wire wound in the form of a cylindrical coil. No significant difference in sensor performance could be attributed to the difference in cathode geometry; however the coil could be flashed clean by heating, rather than sputter cleaned, and could be held at a temperature above ambient during detector operation by running current through the coil. Cathodes were formed from tungsten, molybdenum, tantalum, aluminum, and thorium. The first three materials performed well and, after cleaning, exhibited spectral responses in good agreement with the literature values of their work functions. Sensors with cathodes of aluminum and thorium generally were unstable with high breakdown, narrow operating ranges, and time dependent thresholds. This behavior may be due to heavy oxygen contamination of these relatively active metals during cathode fabrication which involved the arc melting of the cathode rod end in an argon box. Since those sensors using aluminum and thorium cathodes were considered to be unsatisfactory in performance, they will not be discussed further in this report.

Molybdenum anodes were used. Molybdenum is easy to fabricate into hemispheres, is relatively inert, and has a high reflectivity in the ultraviolet.

Noble gas filled sensors were generally gettered with titanium. Aluminum and copper were used as getters in detectors containing some hydrogen since titanium would remove the hydrogen. Sensor performance indicated that aluminum and copper removed little if any hydrogen. As shown in Fig. 1, the getter material was mounted on the back side of the anode where it could be radio-frequency heated and partially

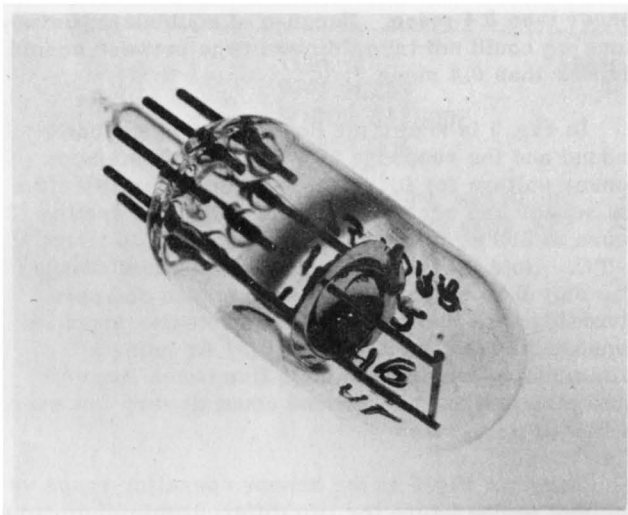


Fig. 2 Glass envelope flame sensor (photograph).

evaporated onto the tube wall. A photograph of the sensor is shown in Fig. 2.

III. GAS COMPOSITIONS EXAMINED

Minimum breakdown voltages were measured under ultraviolet excitation with several sensor tubes using some or all of the following gases or gas mixtures--He, Ar, (99.5% He + 0.5% Ar), H₂, (99% He + 1% H₂), (99% He + 1% H₂), and (90% He + 10% CH₄). The mixtures are given in mole percent. The best choice of fill pressures for an operating sensor seemed to be at the Paschen minimum (to minimize voltage) or somewhat to the right of the minimum (so that sufficient current could be drawn through the tube to trigger the counting circuit used). In Fig. 3 are shown representative plots of minimum breakdown voltage vs pressure at room temperature for most of the gas compositions listed above as measured in one diode structure. The (90% He + 10% CH₄) curve is not shown here, but should lie above the H₂ curve. The data for (99.5% He + 0.5% Ar), (99% He + 1% H₂) and (99% Ne + 1% H₂) agreed within experimental error. All of these dilute noble gas-hydrogen mixtures and helium are considered satisfactory in terms of low breakdown voltage over a wide range of pressure.

IV. SENSOR PERFORMANCE

A. (99.5% He + 0.5% Ar) Fill

Titanium-Forsterite-sapphire sensors using this fill have been built and tested; this work is described in TIS Reports 69-C-358 and 70-C-158. The same electronics were used in this study. Glass envelope sensors with titanium getters employing this fill performed satisfactorily, but required larger minimum times between count than did the metal-ceramic variety probably because of contaminating gas release from the glass envelope. These glass sensors could

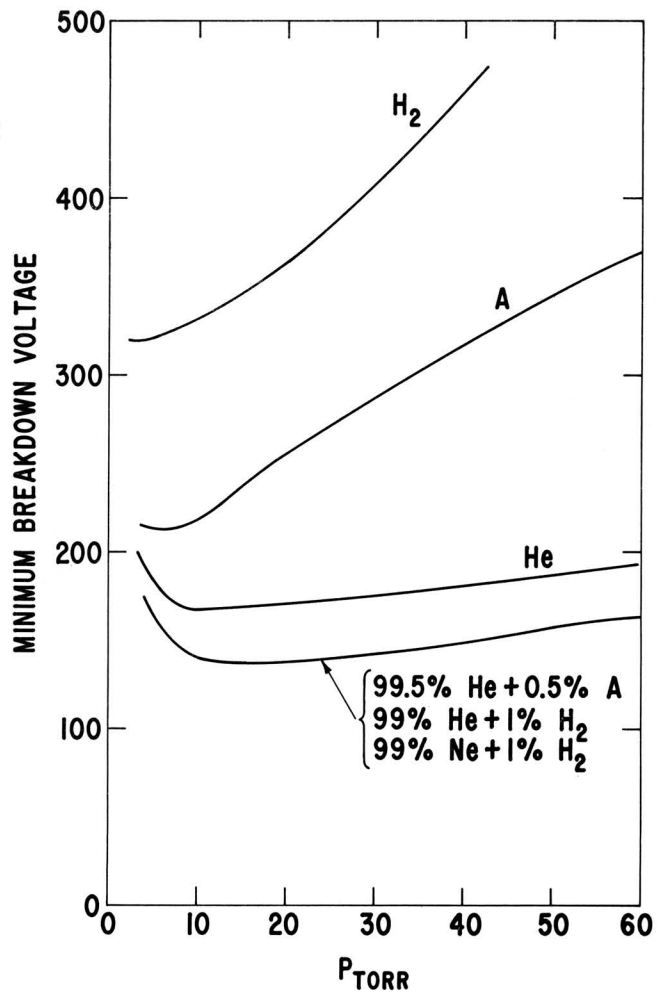


Fig. 3 Minimum breakdown voltages for gases in a diode.

be operated for at least a few hours at 300°C with no ill effects. No long life tests were run. Operation at 400°C caused significant reduction in the operating voltage range. In general, the threshold wavelength of sensors filled with this noble gas mixture were representative of the work function of the clean W Mo, or Ta cathode. One tube with a tungsten rod cathode, a fill pressure of 101 torr, and a threshold voltage of 166 volts, was operated at 10 volts above threshold in direct sunlight with no counts in 10 seconds. Under these conditions the sensor responded strongly to ultraviolet light with energy above 4.6 eV. The room-temperature counting rate rose rapidly due to memory effects if the minimum time between count was decreased below 9 msec.

Both molybdenum and tungsten coil cathodes were tested and found to perform in a manner similar to rod cathodes. Cleaning by flashing, rather than sputtering, offered no apparent advantage. Use of a coil did make it possible to keep the cathode warm in a cool ambient. It was demonstrated that warming

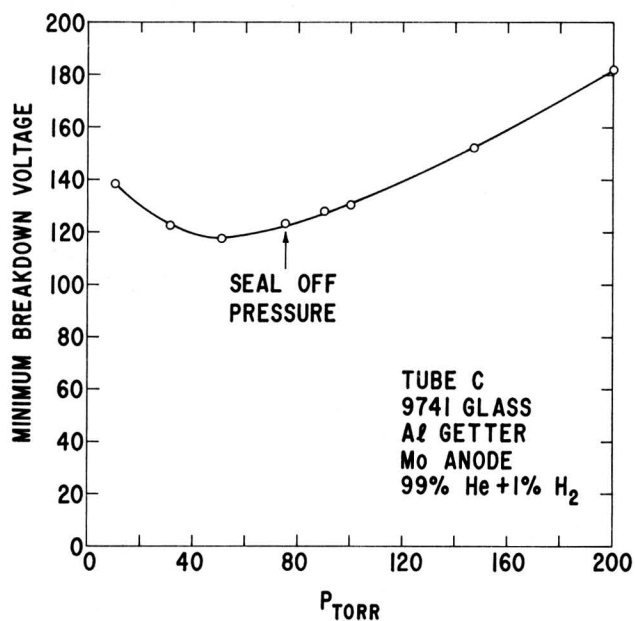


Fig. 4 Minimum breakdown voltage for (99% He + 1% H₂) in diode #C.

the cathode can increase the operating voltage range by 50% or more without introducing significant thermionic background. The mechanism giving rise to this effect is not understood.

B. (99% He + 1% H₂) Fill

Several sensors were filled with this gas mixture and tested. The aluminum getter tubes proved to be superior to the copper getter tubes. This may be due to greater success at evaporating aluminum. After some initial operation the sensors, independent of the choice of cathode material, lost solar blindness and indeed responded to fluorescent, but not to incandescent, overhead lights. Except for this deficiency, which can be lived with in some applications, these sensors proved to be the best built. One of them, #C, will be described at length.

Tube #C contained a tungsten rod cathode, a molybdenum anode, and aluminum getter, and a fill of (99% He + 1% H₂). A plot of breakdown voltage vs pressure at room temperature was obtained prior to sealing off this sensor and is shown in Fig. 4. While the minimum breakdown voltage occurred at 50 torr (117 volts) the sensor was sealed off at 75 torr where breakdown occurred at 123 volts.

Tube #C was placed in an air oven and measurements were made upon it. In Fig. 5 is shown a set of curves of 10 second response to a standard flame vs minimum time between counts while the sensor was aged at various temperatures up to 350°C. No significant memory effects were observable at reasonable operating voltages for minimum time between counts

longer than 0.4 msec. Because of equipment limitations we could not try minimum time between counts shorter than 0.4 msec.

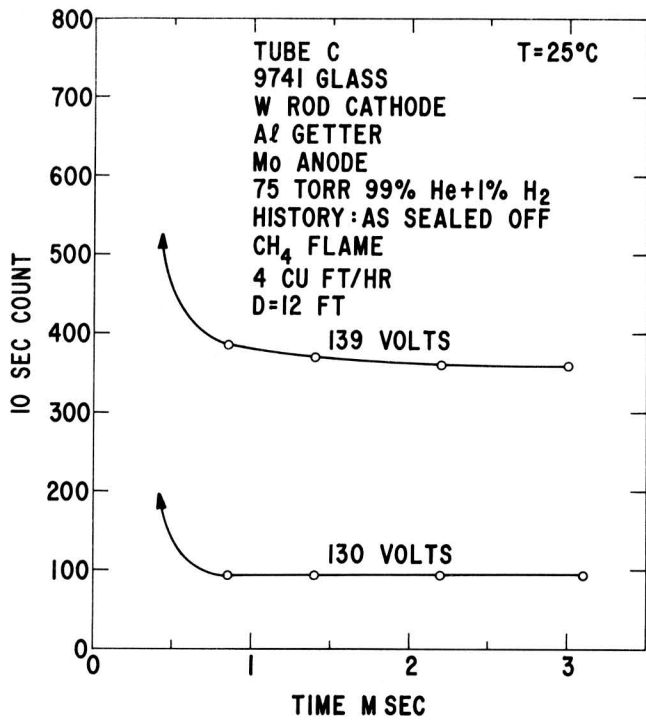
In Fig. 6 is shown the dependence of the background and the response to a standard flame upon sensor voltage for four different temperatures after the sensor had accumulated a history of operating 72 hours at 350°C, 100 hours at 250°C, and 570 hours at 150°C. Note that the minimum time between counts was only 0.85 msec. This performance compares favorably with that of titanium-Forsterite-sapphire sensors filled with 99.5% He + 0.5% Ar using a minimum time between counts five times longer. Note also that the background count is very low even at 350°C.

Shown in Fig. 7 is the sensor operating range vs ambient temperature for two different minimum time between counts. The lowest line represents the threshold operating voltage for both minimum times between counts. The center and upper lines, respectively indicate the maximum practical operating voltages for minimum times between counts of 0.85 and 3.9 msec. For comparable width of operating range, a glass He-Ar filled sensor would need minimum times between counts much longer than those used here. As in the case of He-Ar filled tubes the operating range narrows as the temperature is reduced below 150°C. The cause of this behavior is not known.

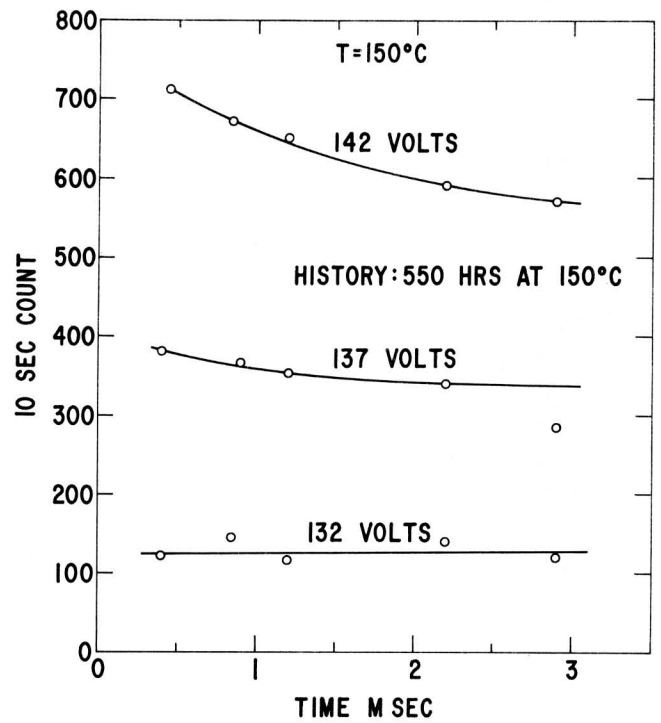
After operation at elevated temperatures, the spectral response of tube #C to the output of a monochromator with a deuterium lamp became nearly temperature independent between room temperature and 350°C. It has a long wavelength tail out beyond 3000Å as shown in Fig. 8, which also shows the typical response of a tungsten cathode in a He-Ar filled titanium-Forsterite-sapphire sensor. It has been suggested by others working with metal photoemitters in H₂ filled glass tubes that this tail is due to alkali metals adsorbed on the cathode presumably coming from the glass walls. We observed this tail in all glass sensors containing H₂. It represents a serious defect only for sensors exposed to sunlight or to fluorescent lamps.

C. (99% Ne + 1% H₂) Fill

The performance of sensors filled with this gas mixture was very similar to those filled with 99% He + 1% H₂ in terms of required minimum time between counts, operating voltage range, and spectral response. Because of the relatively high light output in the visible region produced by discharges of the gas, it was frequently possible to see individual counts occurring in the sensor. This fill offered no apparent advantage over 99% He + 1% H₂. It may be useful if loss of He by diffusion through a sensor envelope proves to be important.

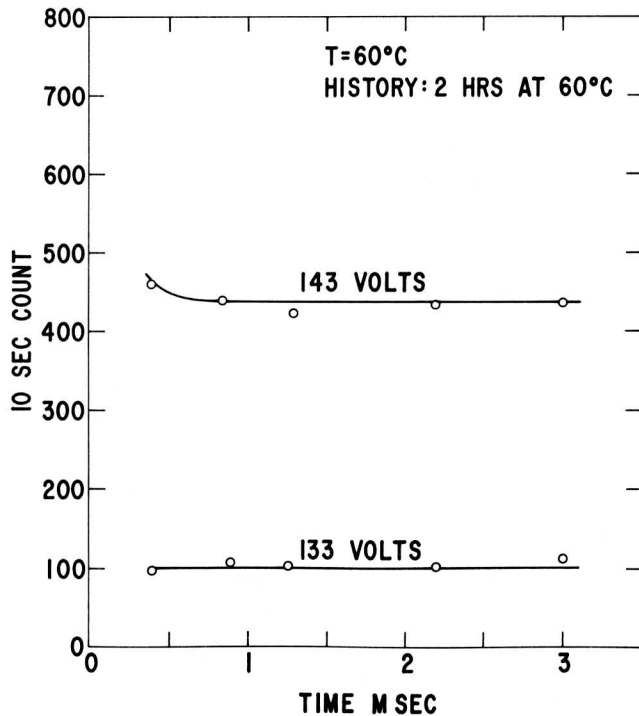


(a)

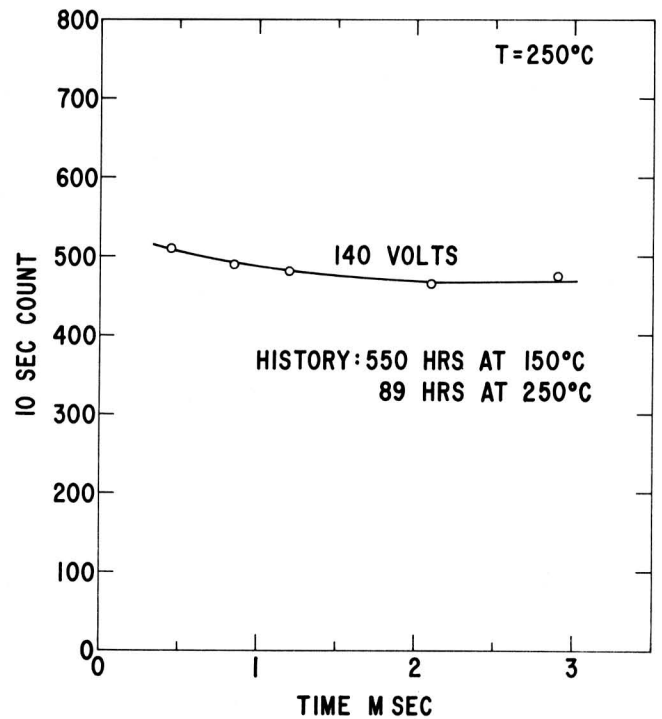


(c)

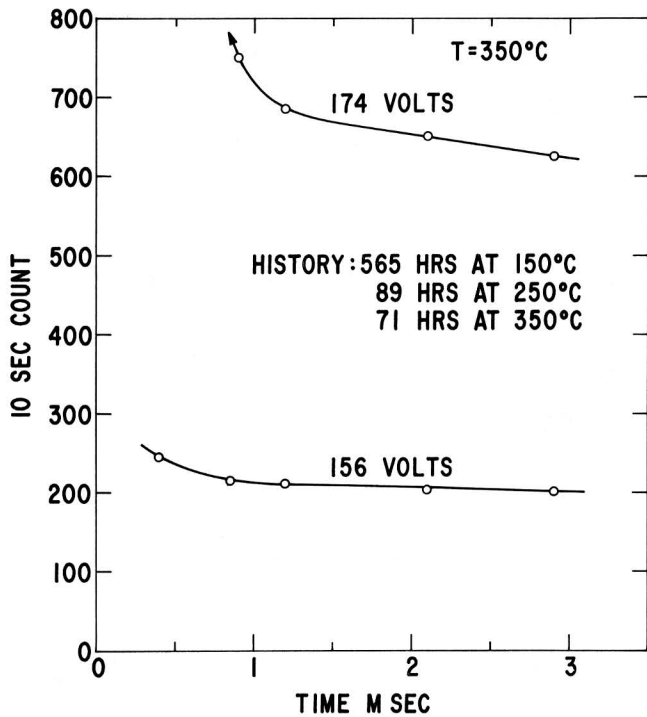
Fig. 5 Ten-second response to standard flame vs minimum time between counts as tube #C is aged at various temperatures.



(b)



(d)



(e)

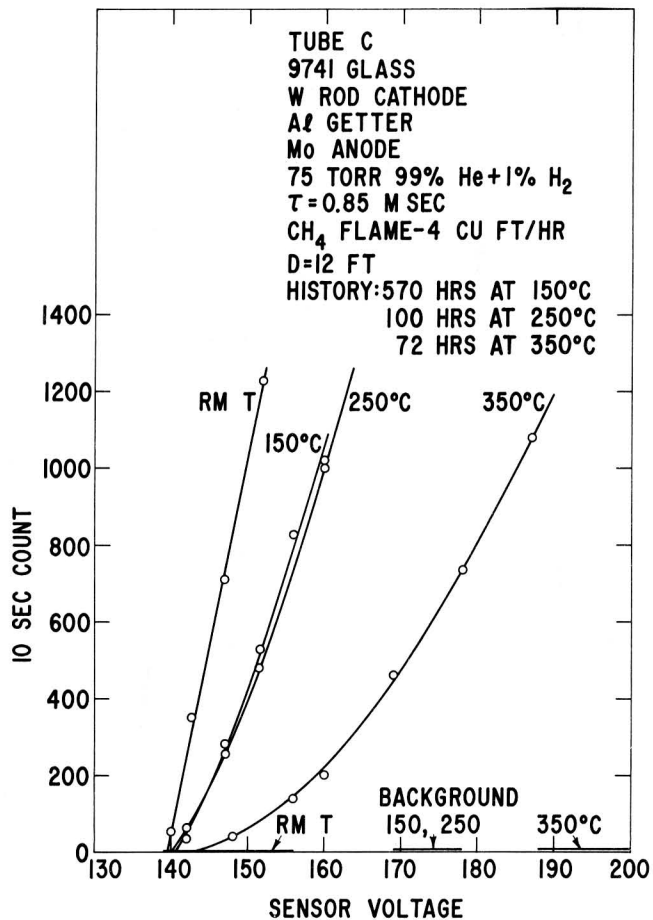
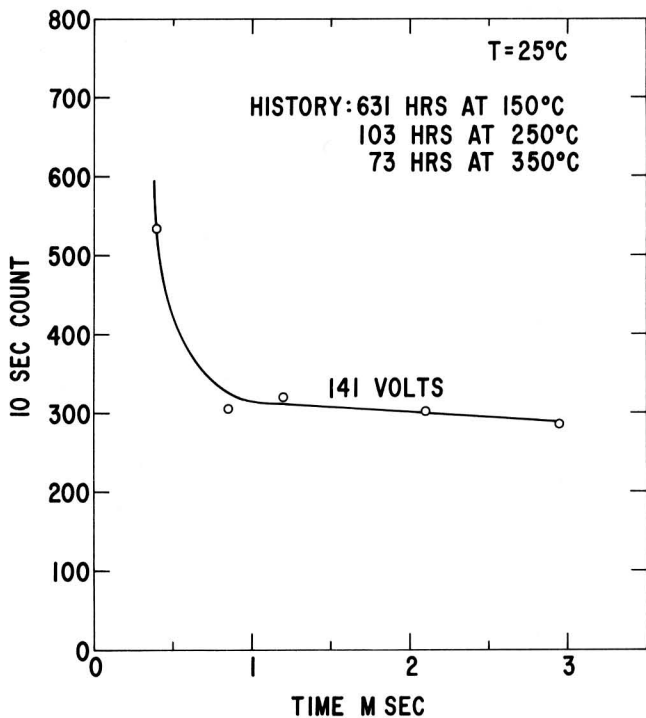


Fig. 6 Ten-second response of tube #C to a standard flame and background vs sensor voltage at different temperatures.



(f)

Fig. 5 (concluded)

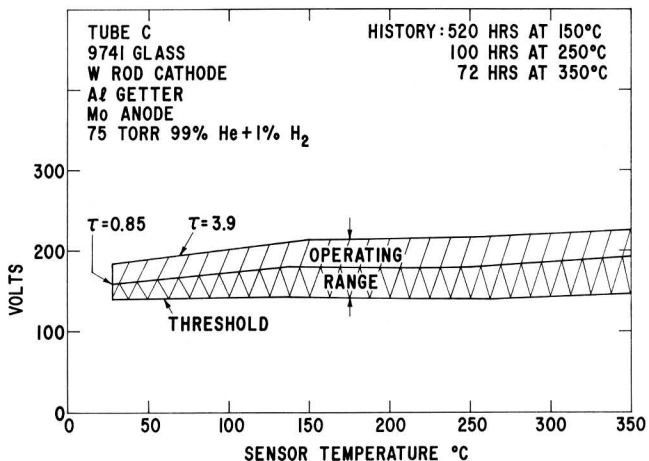


Fig. 7 Useful operating voltage range vs temperature for two different minimum time between counts.

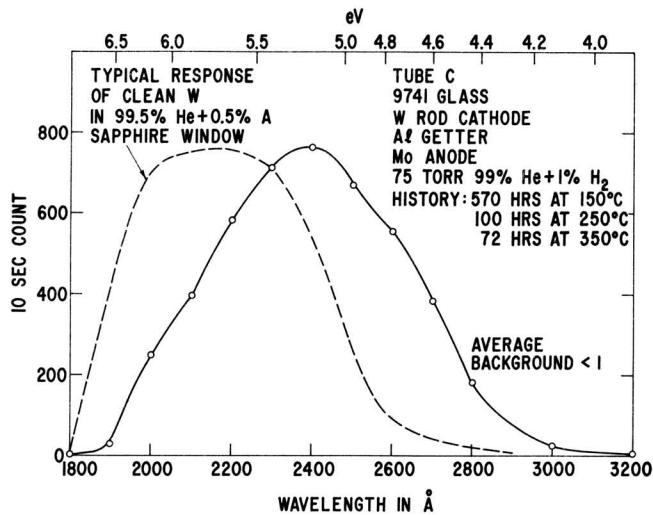


Fig. 8 Comparison of spectral response of titanium-Forsterite-sapphire (99.5% He + 0.5% Ar) and 9741 glass (99% He + 1% H₂).

D. (90% He + 10% CH₄) Fill

Methane appears to be one of the most inert polyatomic gases⁽³⁾ in the temperature range 0 to 400°C. It was tried as an additive to He in the hope of achieving a rapidly recovering gas mixture. The rather large amount of CH₄ was chosen because a finite number of CH₄ molecules are believed to fragment with every discharge⁽¹⁾ so that the total count should be limited by the total number of CH₄ molecules. The sensors with this fill were found to have high thresholds, above 500 volts, and high cathode work functions. Since the useful voltage range decreased as the tube was operated, this sensor was not considered promising and the work was discontinued.

V MINIMUM TIME BETWEEN COUNTS

In terms of operating a flame sensor the practical minimum time between pulses is that value at which the sensor counting rate begins to increase significantly because of a memory effect. This memory effect is due to any excited (or ionized) molecule which provides a free electron, capable of initiating a new discharge, in the process of being deexcited (or neutralized). Metastable atoms are primary offenders since they may yield ultraviolet photons long after the ions have been removed from the gas.⁽⁴⁾ This is illustrated in Fig. 5(f) where 0.9 msec is a reasonable minimum time between counts for a voltage of 141 volts for the tube #C. Use of shorter minimum time between counts results in multiple counts probably due to the presence of a residual population of atoms in metastable states.

By applying a voltage pulse across the sensor it was possible to observe the effect of using too short

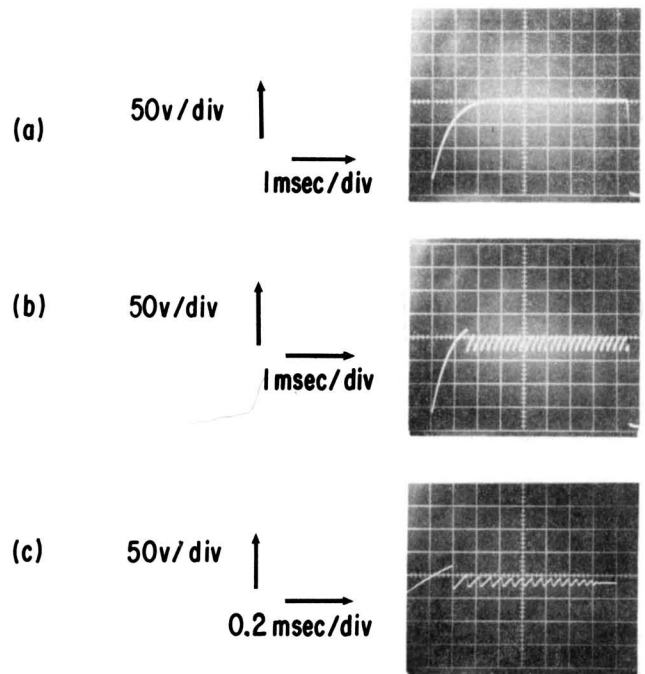


Fig. 9 Voltage across sensor vs time for (99.5% He + 0.5% Ar) filled titanium-Forsterite-sapphire sensor

a minimum time between counts for a given voltage. Figure 9 presents a series of oscilloscope photographs illustrating the effect of decreasing the minimum time between counts for a titanium-Forsterite-sapphire sensor filled with (99.5% He + 0.5% Ar). In Fig. 9(a) the applied pulse voltage, 200 volts, is too low to cause spontaneous breakdown in the tube so that the voltage is sustained until cut off by the circuit after about 6 msec. In Fig. 9(b), spontaneous breakdown occurs at 205 volts and the voltage quickly drops to the extinction voltage, about 152 volts. The voltage across the tube rises again, but this time breakdown occurs at 190 volts, rather than 205 volts, because the tube "remembers" the previous breakdown 0.3 msec earlier. The sensor oscillates between breakdown at 190 and extinction at 152 with a period of 0.3 msec until the voltage is shut off by the circuit. If an attempt were made to operate this sensor at 190 volts with a minimum time between counts of 0.3 msec, it would self-count following an initial response to a UV photon or a background event. For satisfactory operation, either a longer minimum time between counts or a lower voltage (but still above the minimum breakdown voltage) would have to be used. Figure 9(c) illustrates what occurs if the rise time is further shortened. The breakdown voltage decreases and the extinction voltage increases until the sensor goes into continuous discharge terminated only by removing the d-c bias.

By comparing Figs. 9 and 10 it can be seen that (99% He + 1% H₂) is a much faster recovering gas

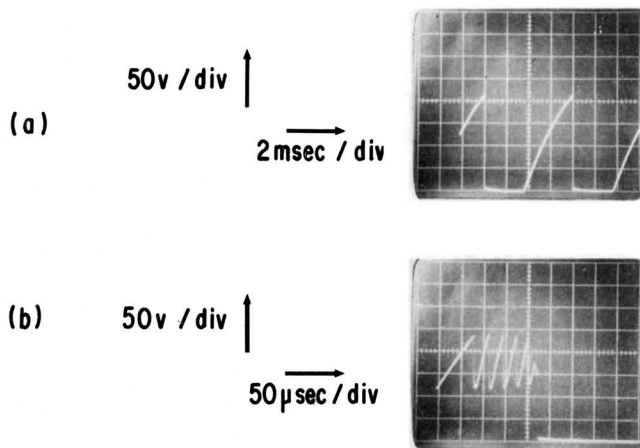


Fig. 10 Voltage across sensor vs time for (99% He + 1% H₂) filled 9741 glass sensor

mixture than (99.5% He + 0.5% Ar). The data presented in Fig. 10 was taken on tube #A which physically differed from tube #C only in having a molybdenum rather than a tungsten cathode. Figure 10(b) shows that even when the time per cycle has been reduced to 35 µsec and the striking voltage and the extinction voltage are slowly beginning to approach each other, very little change occurs in the discharge voltage during the first three cycles. In other words, the tube hardly "remembers" the previous cycle.

VI. CONCLUSIONS

Sensors constructed of 9741 glass were tested up to 400°C. Titanium gettered (99.5% He + 0.5% Ar) filled tubes operated well between 22° and 350°C, but required longer minimum time between counts than did their titanium-Forsterite-sapphire counterparts. Sensors filled with either (99% He + 1% H₂) or (99% Ne + 1% H₂) performed well in the same temperature interval and could operate with shorter minimum time between counts than either type of (99.5% Ar + 0.5% He) filled sensor while having similar operating voltages. All sensors containing H₂ became solar sensitive. This may be due to alkali atoms from the glass so use of a suitable metal-ceramic envelope might avoid this problem. All the sensors (with and without H₂) exhibited a reduction in the width of their usable voltage range as the ambient temperature was reduced below 100°C. The cause of this behavior is not known.

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