United States Patent [19]

Klein

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[54] **ON-LINE DETECTION AND MEASUREMENT OF CONTAMINATING GASES DURING FILLING OF GAS DISPLAY PANELS**

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[73] Assignee: **International Business Machines Corp.**, Armonk, N.Y.

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[21] Appl. No.: **431,812**

[52] **U.S. Cl.** **356/85**

[51] **Int. Cl.** **G01j 3/00**

[58] **Field of Search** 356/85, 86

[56] **References Cited**

FOREIGN PATENTS OR APPLICATIONS

568,974 1/1959 Canada 356/85

OTHER PUBLICATIONS

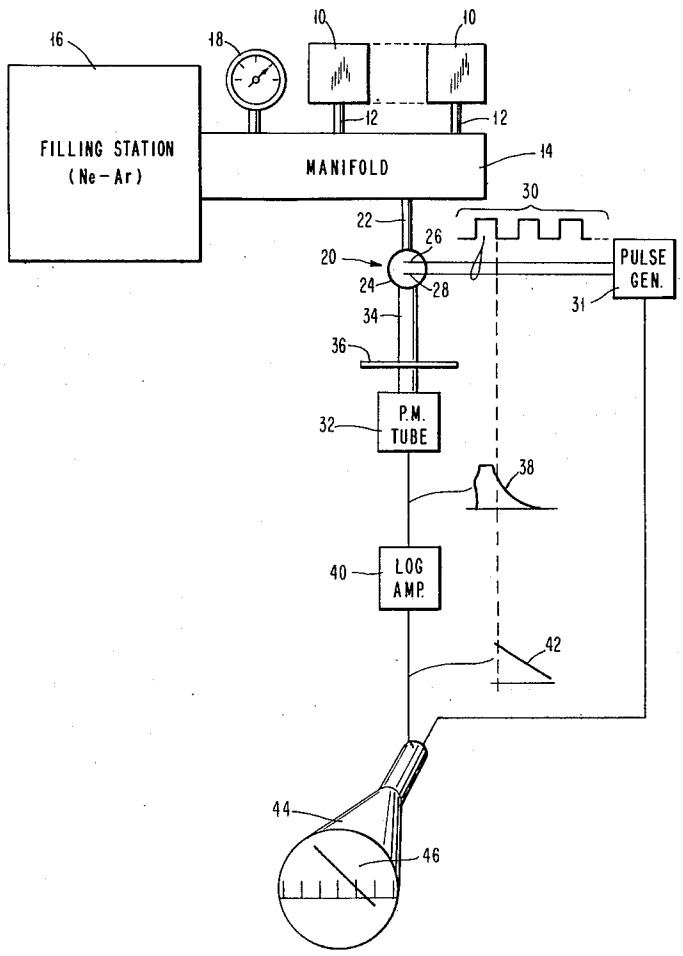
Proceedings of the Fifth International Conference on Ionization Phenomena in Gases, Vol. II, edited by H. Maecker, North-Holland Publishing Co., Amsterdam, 1962, pp. 1356–1358.

Primary Examiner—Ronald L. Wibert
Assistant Examiner—F. L. Evans
Attorney, Agent, or Firm—Sughrue, Rothwell, Mion, Zinn & Macpeak

[57] **ABSTRACT**

The after-glow of argon in a Penning mixture of neon and argon is used to detect and measure the concentration of contaminating gases in the mixture during the filling of gas display panels with the mixture.

15 Claims, 2 Drawing Figures



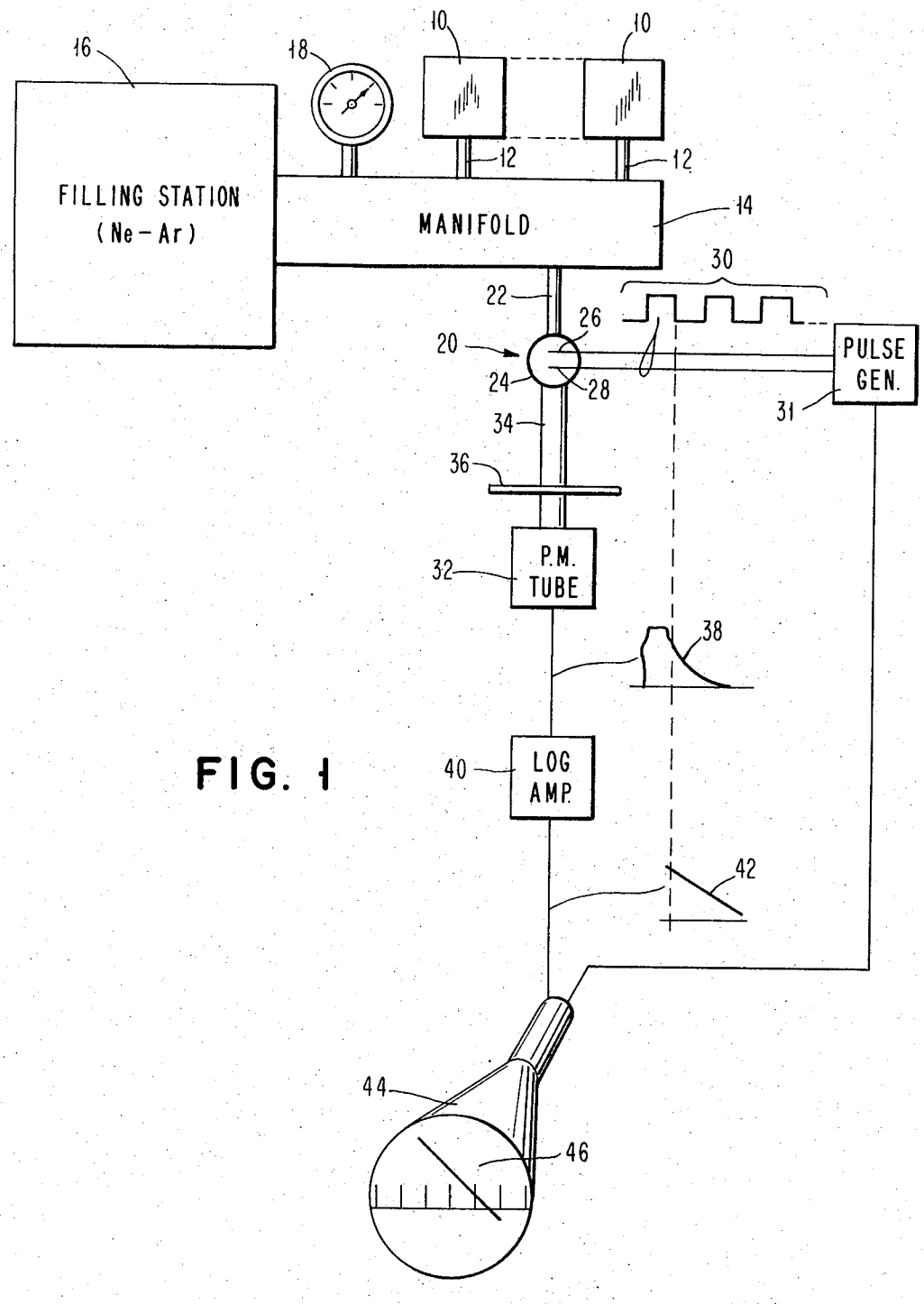
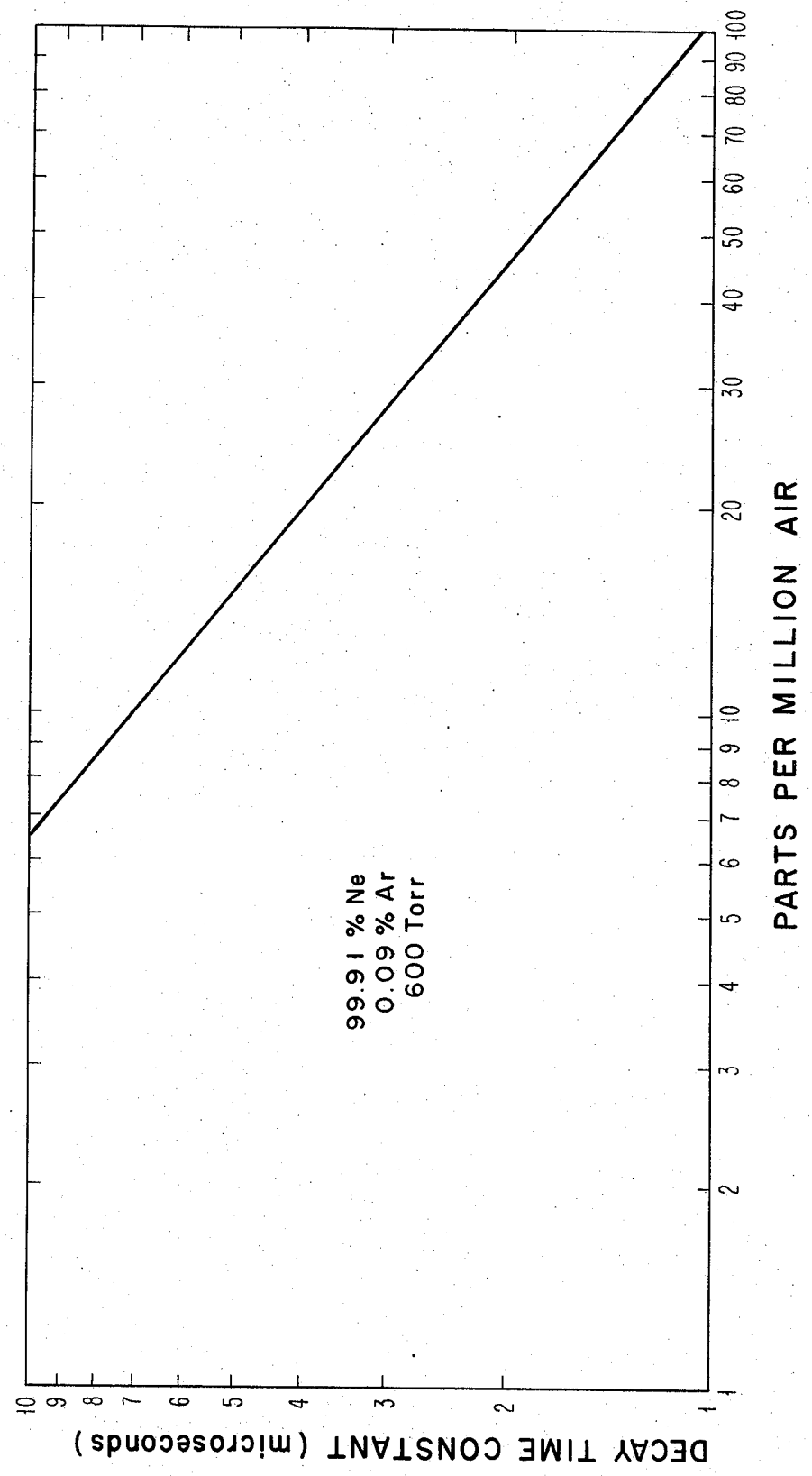

16
18
10
10
12
12
FILLING STATION
(Ne-Ar)
MANIFOLD
14
30
22
26
20
PULSE
GEN.
24
28
31
34
36
P.M.
TUBE
32
38
40
LOG
AMP.
42
44
46

FIG. 1

FIG. 2


DECAY TIME CONSTANT (microseconds)
10
9
8
7
6
5
4
3
2
1
99.91 % Ne
0.09 % Ar
600 Torr
PARTS PER MILLION AIR
1
2
3
4
5
6
7
8
9
10
20
30
40
50
60
70
80
90
100

ON-LINE DETECTION AND MEASUREMENT OF CONTAMINATING GASES DURING FILLING OF GAS DISPLAY PANELS

BACKGROUND OF THE INVENTION

1. Field of the Invention:

This invention relates to the field of gas display panels and, more particularly, to a method and apparatus for detecting and measuring contaminating gases in a gas mixture during the filling of such gas display panels on a production line.

2. Description of the Prior Art:

A gas display panel is illuminated by electrically exciting a discharge in a Penning mixture of neon and argon gas. The mixture is typically approximately 99.9 percent neon and 0.1 percent argon by partial pressures. The Penning mixture may be defined as one in which the ionization potential of the added argon is less than the metastable potential of neon, the parent gas. The presence of undesired contaminating or impurity gases, such as nitrogen, water vapor and others, in concentrations exceeding, for example, 20 parts per million, has a deleterious effect on the operation of the gas panel. During the filling operation in the production of gas panels, a group of gas panels is connected by their tubulations to ports on the manifold of a gas filling station, and the panels are carefully baked out while being subjected to a high vacuum. Then, the panels are filled with the desired gas mixture at a specified pressure. The gas mixture has previously been passed through various purifying devices to eliminate undesired contaminating gases which may be present in the purchased gas or in parts of the filling system. After the panels are filled, the tubulations are sealed off, and the panels are removed from the filling station.

If the filling station is operating correctly, the concentration of contaminating gases will be below a specified level chosen to guarantee correct operation of the panels. However, possible leaks or other faults in the filling system, contaminated gas sources, or mishaps during the seal-off of one of the panels connected to the manifold can introduce unacceptable amounts of contaminating gases. It is important to detect such contamination before the panels are sealed off, because no repair or rework is possible once the panels have been sealed off. What is required, therefore, is a fast simple, on-line measurement of contaminating gas concentration in the gas mixture to allow the operator of the filling system to decide whether to seal off the panels or to troubleshoot them and repeat the filling procedure.

In prior attempts to detect and/or measure impurity gases in the gas mixture during the filling of the gas panels, use has been made of spectrometric methods in which a discharge is excited in the gas mixture, and the intensity ratios are measured for selected spectral lines of neon and of contaminating gases. This method has many disadvantages with respect to use thereof during the actual production of gas panels, i.e., during the filling of the gas panels: the intensity ratios depend strongly on the electrical excitation conditions and on other gases present in the mixture, thus introducing extraneous variables; a monochromator or other high resolution spectroscopic device is required; contaminating gas spectral line signals are weak, thereby requiring signal extraction electronics and, consequently, long observation times; and since data reduction requires computation, results are not available immediately.

The term Penning mixture is well known in the art and may be defined as a mixture of two gases which exhibit the Penning effect or discharge. The Penning effect or discharge may be defined as one which occurs in a mixture of two gases when the gas having the higher ionization potential has a metastable state with a potential higher than the ionization potential of the other gas. The gas forming the larger portion of the mixture is referred to as the parent gas. Typical Penning mixtures are formed by mixing neon (parent) with small quantities of argon, krypton and xenon; argon (parent) with krypton or xenon; or krypton (parent) with xenon. Furthermore, a Penning mixture can be formed by adding mercury vapor to most parent gases. See "Fundamentals of Gaseous Ionization and Plasma Electronics," Essam Nasser, Wiley-Interscience 1971, pages 214 et seq. The Penning mixture of neon and argon may contain from 0.01 to 10 percent of argon; see "Determination of the Townsend Ionization Coefficient Alpha for Mixtures of Neon and Argon," A. A. Kruithof and F. M. Penning, Physica, Vol. 4, Page 430, 1937.

SUMMARY OF THE INVENTION

The object of this invention is to provide an improved method and apparatus for overcoming the above disadvantages of the prior art with respect to the on-line detection and measurement of contaminating gases during the filling of gas display panels.

A more specific object of this invention is to provide such a method and apparatus which utilizes the argon after-glow of a Penning discharge in a neon-argon mixture to detect and measure contaminating gases during filling of gas display panels.

The principle upon which this invention is based may be summarized as follows. During the Penning discharge, some neon atoms are excited to a metastable state which has a long lifetime. De-excitation of the metastable neon atoms can occur by collision of the metastables with argon atoms, thereby resulting in ionization of the argon atoms which then emit characteristic argon radiation. If the discharge is pulsed, neon metastables are present after the electrical excitation has been removed, and they decay at a rate which is determined by their probability of collision with argon atoms. The rate of decay can be followed by observation of the intensity of argon radiation versus time. Experiments have confirmed that the decay is exponential for more than a decade of intensity amplitude for an uncontaminated mixture.

When the Penning mixture is contaminated by gases, such as nitrogen, oxygen, water vapor, etc., the neon metastables can be de-excited by collisions with these molecules as well as by collision with argon atoms. The result is a more rapid decay of the neon metastable concentration as compared to that for the uncontaminated Penning mixture. However, in the contaminated case, the process also can be followed by observation of the intensity of argon radiation as a function of time. Again, the decay of the argon radiation intensity is exponential. However, now the time constant of the decay is a function of the concentration of the contaminating gas. In other words, the after-glow of the argon is utilized to measure the concentration of contaminating gas in the Penning mixture.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic diagram illustrating a preferred embodiment of the method and apparatus of this invention.

FIG. 2 is a graph showing a plot of the decay time constant of the after-glow argon radiation intensity in a Penning mixture of neon and argon versus the parts per million of contaminating air in the mixture.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

FIG. 1 is a schematic block diagram illustrating the apparatus and method of this invention wherein the concentration of contaminating or impurity gases in a Penning mixture is measured using the principle described above. A plurality of gas panels **10** are connected via tubulations **12** to manifold **14** which in turn is connected to a filling station **16** containing a Penning mixture of neon and argon gas in the proportions of approximately 99.9 percent neon and 0.1 percent argon by partial pressures. A pressure gauge **18** is also shown coupled to the manifold **14** to symbolize the fact that in practice a constant pressure is maintained during filling. Typically, this pressure is approximately 600 Torr.

As is well known in the art, the gas panels contain individual discharge areas referred to as cells. A test discharge cell **20** is also coupled to the gas manifold **14** via a conduit **22.** Test cell **20** consists of a glass tube **24** and two sealed-through metal electrodes **26** and **28.** The test cell **20** may be identical to a commercial neon tube in structure.

The test cell is excited by a train of voltage pulses **30** applied to the electrodes by a conventional pulse generator **31** which generates the exciting pulses at a repetition rate of approximately 2 KHz. Typically, each pulse has a duration of approximately five microseconds and a peak voltage of approximately 300 volts.

The resultant light radiation from the excited test cell is transmitted to a conventional photomultiplier tube **32,** such as an RCA C70042R, via a suitable optical coupling **34,** such as lenses, fiber bundles, or a combination thereof. Furthermore, a filter **36** is interposed between the test cell **20** and the photomultiplier **32** for selecting a suitable line of the argon after-glow radiation spectrum while excluding radiation from the neon or contaminating gases. Such a suitable argon wavelength is 7633 Angstroms because it is well isolated from the neon lines.

The output from the photomultiplier **32** is a current pulse **38** having an exponential decay. This current pulse is applied to a conventional logarithmic amplifier **40** whose output voltage **42** has a linear decay as a result of the application of the logarithmic response of the amplifier to the exponentially decaying input pulse.

The output of the amplifier **40** is applied to the deflection circuitry of a conventional oscilloscope **44** so that the output of the logarithmic amplifier is displayed on the face **46** of the oscilloscope. The pulses **30** from pulse generator **31** are applied to the sweep circuitry of the oscilloscope, thereby synchronizing the pulse generator and the oscilloscope. The face of the oscilloscope is provided with a simple calibration and scale so that one can directly observe the time constant of the linear decay of the argon after-glow radiation intensity, i.e., the argon radiation intensity which occurs after the termination of each exciting pulse.

The calibration of this system is accomplished by making measurments of the argon after-glow at the specified operating pressure and with the specified Penning mixture, but with the addition of known amounts of contaminating gas by means of a calibrated leak. One then prepares a calibration curve showing the argon after-glow or radiation intensity decay time constant as a function of the contaminating gas content. Since the most likely contaminating or impurity gas would be air resulting from faults or leaks in the filling system, the preferred calibration would be one made with air.

FIG. 2 is an actual calibration graph for a Penning mixture consisting of 99.09 percent neon and 0.01 percent argon at a filling pressure of 600 Torr. The plot is on a double logarithmic scale for which the ordinate indicates the argon after-glow decay time constant in microseconds and the abscissa the parts per million of air. As shown in the graph, for the conditions used, the method and system illustrated in FIG. 1 is capable of measuring air concentrations in the range from 10 to 100 parts per million. The decay time constant is read from the face of the oscilloscope **44** and the air concentration is then determined by reference to the graph in FIG. 2.

It will be obvious to those skilled in the art that well known electronic and digital techniques may be used to provide a digital read-out either of the time constant or the contamination level. In addition, alarms or other signals could be incorporated in the system. As indicated above, the method and system described herein can be used for Penning mixtures other than neon-argon and, furthermore, have applications other than the on-line measurement and detection of contamination during the filling of gas panels.

In summary, the novel features of this system are: (*a*) the use of the effect of contaminating gases on the metastable decay rate of the parent gas in a Penning mixture to provide a direct indication of the amount of contaminating gas present; (*b*) the use of a pulsed discharge in the Penning mixture to permit observation of metastable decay subsequent to the electrical excitation of the gas for the purpose of measuring contaminating gas concentrations; and (*c*) an apparatus and method that provide a simple direct read-out of a parameter directly related to the contaminating gas concentration.

The specific advantages of the present invention are as follows:

(*a*) the argon after-glow intensity radiation is measured, i.e., the measurement of the argon radiation is made after the electrical excitation of the test discharge cell **20** has been removed, whereby the measurement is substantially independent of the details of the electrical excitation; (*b*) measurement is both fast and direct reading; (*c*) the apparatus is simple and rugged and requires a minimum of operating adjustment; and d) the measuring method and apparatus are well suited to on-line application in a manufacturing environment.

While the invention has been particularly shown and described with reference to a preferred embodiment thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the spirit and scope of the invention.

I claim:

1. A method of detecting the presence of a contaminating gas in a Penning mixture of a first gas and a second gas, the first gas having a higher ionization potential than said second gas and also having a metastable state with a potential higher than the ionization potential of said second gas, comprising the steps of:

a. exciting a sample of the mixture to cause a pulsed discharge therein;

b. removing the excitation; and

c. then detecting the time rate of decay of the radiation intensity of the second gas as an indication of the presence of a contaminating gas, said time rate of decay being faster than that for an uncontaminated Penning mixture of said first and second gases.

2. A method as defined in claim 1 wherein said first gas is neon and said second gas is argon.

3. A method as defined in claim 2 wherein the mixture comprises approximately 0.1 to 10 percent of argon.

4. The method as defined in claim 3 wherein said mixture comprises approximately 99.9 percent neon and approximately 0.1 percent argon.

5. The method as defined in claim 1 further comprising the steps of:

a. plotting a calibration curve for the time constant of the time rate of decay of said radiation versus known concentrations of a contaminating gas; and

b. determining an unknown concentration of the contaminating gas from the detected time rate of decay and by reference to said calibration curve.

6. The method as defined in claim 1 further comprising the step of filling a gas display panel with said mixture of first and second gases and, simultaneously with said filling step, extracting a sample of said mixture and then performing on said sample steps a), b) and c) of claim 1.

7. An apparatus for detecting the presence of a contaminating gas in a Penning mixture of a first gas and a second gas, the first gas having a higher ionization potential than said second gas and also having a metastable state with a potential higher than the ionization potential of said second gas, comprising:

a. electrical pulse generating means for applying to a sample of the mixture an electrical pulse to excite a discharge in the mixture;

b. photoelectric means responsive to the radiation emitted by the second gas after the termination of the pulse for producing an electrical signal proportional to the time rate of decay of the intensity of the radiation; and

c. electro-optical means coupled to said photoelectric means for producing an optical read-out of said signal.

8. The apparatus defined in claim 7 wherein said photoelectric means is a photomultiplier tube, said electro-optic means is an oscilloscope synchronized with said pulse generating means, and the time rate of decay is exponential, and further comprising a logarithmic amplifier connected between said photomultiplier tube and said oscilloscope so that said oscilloscope produces a linear display of the time constant of the decay of the radiation intensity.

9. The apparatus defined in claim 8 further comprising optical filter means for transmitting to said photomultiplier tube only a selected characteristic wavelength of the radiation of said second gas.

10. The apparatus as defined in claim 7 further comprising means for supplying the Penning mixture under a predetermined pressure to a gas panel, and means for extracting said sample from the supplied gas.

11. The apparatus as defined in claim 10 further comprising a test discharge cell for holding the extracted sample, and means for electrically connecting said cell to said pulse generating means.

12. The apparatus as defined in claim 7 wherein said first gas is neon and said second gas is argon.

13. The apparatus as defined in claim 12 wherein the mixture comprises approximately 0.1 to 10 percent argon.

14. The apparatus as defined in claim 13 wherein the mixture comprises approximately 99.9 percent neon and 0.1 percent argon.

15. The apparatus as defined in claim 14 wherein said photoelectric means is responsive to a radiation wavelength of 7633 Angstroms.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,865,489

DATED : February 11, 1975

INVENTOR(S) : Melvin KLEIN

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

IN THE SPECIFICATION:

Column 4, lines 14-15 - delete "99.09 percent neon and 0.01 percent argon" and insert -- 99.91 percent neon and 0.09 percent argon --

Signed and sealed this 6th day of May 1975.

(SEAL)
Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
and Trademarks