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GAS ANALYSIS METHOD

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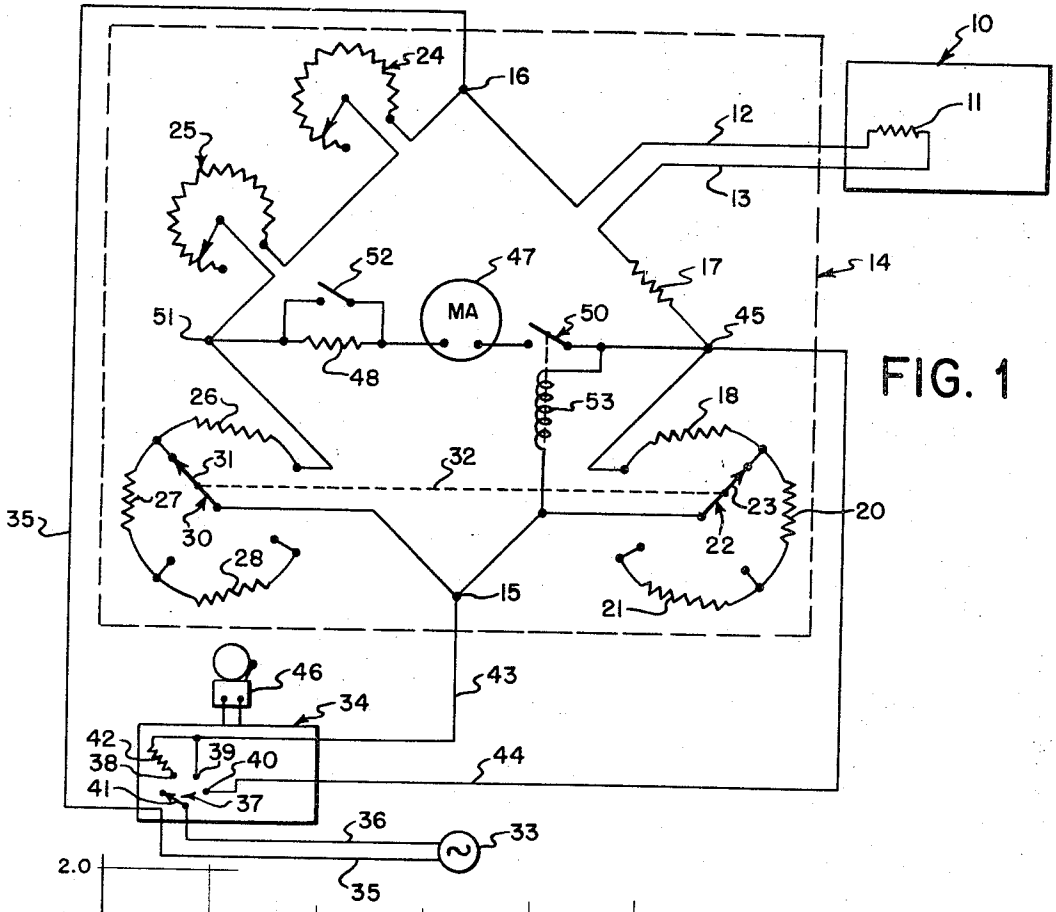


FIG. 1

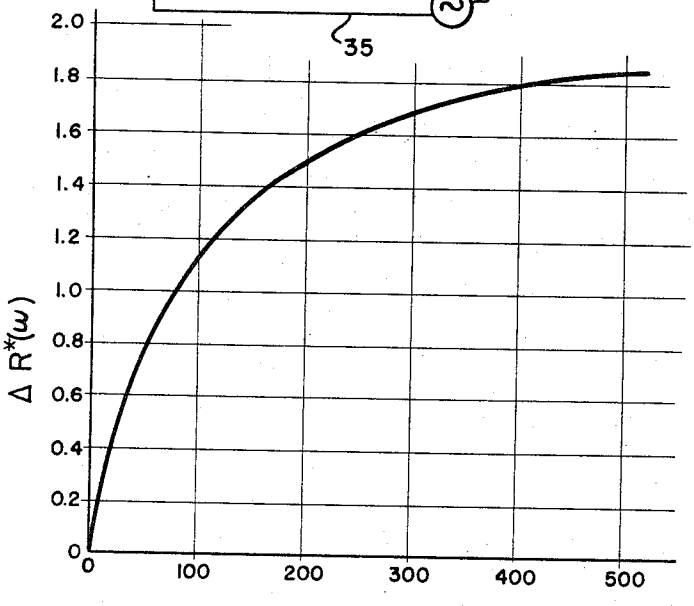


FIG. 2

*ΔR = Increase in filament resistance (ohms) during first minute of exposure at constant current.

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GAS ANALYSIS METHOD

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The present invention relates to a method of detecting the presence of and measuring the concentration of impurities present in a nominally inert gaseous environment. More particularly, the invention provides a novel method by which the presence and concentration of chemically reactive impurities is related to the change in electrical resistance of a filament due to reaction with the impurities in a nominally inert atmosphere.

In recent years there has been a substantial increase in the number and variety of practical applications of materials which are chemically reactive with elements in the normal atmosphere. Of necessity, these materials must be worked in controlled environments in order to preclude undesirable chemical reactions. For example, the welding of refractory materials is usually performed in an impervious enclosure filled with inert elements such as helium or argon. However, it has been found that these inert gases, even though initially pure, often become contaminated with active impurities. In order to minimize the costly deleterious effects of these foreign substances their presence must be promptly detected and their concentrations must be readily and accurately ascertained.

There are known methods and apparatus for making determinations of this kind. For example, a known method includes the step of positioning a metallic filament in the controlled environment, heating the filament and then, with suitable instrumentation, either measuring the time required for the filament to burn through, or measuring the heat generated by the chemical reaction between the filament and the impurities in the gas. In practice, the application of this technique has proved laborious, inconvenient and somewhat inaccurate. In order to simplify and improve the qualitative and quantitative determination of reactive components of a nominally inert gas I have invented an accurate and easily performed method which requires only simple and inexpensive instrumentation.

According to my invention my new method comprises the steps of placing in a nominally inert gaseous atmosphere to be tested a body of a substance which is chemically stable at normal atmospheric temperatures. The substance is then heated by suitable means in order to render the substance relatively unstable. Further, in accordance with my new method, any change in electrical resistance between separated points on the body of the substance is determined as it reacts with the impurities, if any, in the gas being tested. The measured value of the change in resistance of the substance is then related to that value associated with known concentrations of specific impurities in a nominally inert gas.

I have found that functional plots of resistance with respects to time at any given value of heating current have generally the same shape over a substantial range of concentrations of the reactive or impurity component, but the scale is contracted or expanded depending on whether the concentration of the reactive component is large or small. The resistance varies nonlinearly as a function of time, increasing at a greater rate during the initial stages of the heating cycle than subsequently. I have further found that, for a resistive substance of given dimensions and for a given substantially constant value of heating current, the rate of change of resistance with

respect to time in the initial stages of the heating cycle is closely related to the concentration of the reactive or impurity component. Hence, the change in resistance of the filament need only be measured over a relatively short period of time, e.g., one minute, in order to accurately ascertain the concentration of the combining gas in the inert atmosphere.

A feature of my invention is that it may be performed without complex electrical apparatus; rather, my new method may be practiced with several kinds of known electrical circuits and components. I have found that a simple bridge circuit with appropriate rheostats, resistors, relays and timing instruments can be used to practice the method quite adequately. More complex apparatus may be employed if it is desirable to repeat the test of an atmosphere at frequent intervals and if automatic operation is also desirable.

In the following specification I give a detailed description of a particular method according to my invention. In the course of this description reference is made to the accompanying drawing in which:

FIG. 1 is a schematic diagram of electrical circuitry having utility in the practice of a particular method according to my invention, and

FIG. 2 is a graph of changes in resistance plotted against concentrations of water in helium.

Referring now to the drawing, the apparatus selected to illustrate the practice of my new method comprises an enclosure **10** adapted to contain a nominally inert gaseous atmosphere. This enclosure may be a well known, so-called glove box. Within the glove box or other enclosure there are suitable means for supporting a chemically reactive metal filament indicated schematically at **11**. There are provisions for connecting two separated points on the filament to external electrical circuitry as for example, by leads **12** and **13**. A particular means for supporting a filament within the enclosure, including a filament stringing apparatus which is suitable for use in the practice of the present invention, is described in my copending application, Serial No. 203,142, filed June 14, 1962, now Patent No. 3,148,033. It is sufficient to say here that the apparatus described in the copending application is capable of stringing new filaments quickly and efficiently and without any necessity for opening the gas filled enclosure.

As is illustrated schematically within the broken outline **14**, I provide a resistance bridge circuit adapted to be energized from an alternating current source. The reactive metal filament is connected in one leg of this bridge circuit as will be described subsequently. The filament is energized through the bridge circuit and the bridge circuit also serves to detect changes in resistance of the metal filament when it is energized and reacting with impurities in the nominally inert gaseous atmosphere within the enclosure **10**. The particular bridge circuit illustrated in FIG. 1, is specifically arranged to detect impurities in both helium and argon atmospheres as well as to detect leakage of reactive gases into an evacuated enclosure.

The bridge circuit comprises one leg connected between the input terminals **15** and **16** consisting of the filament **11**, fixed resistance **17**, and fixed resistances **18**, **20** and **21** all connected essentially in series between the terminals **15** and **16**. As shown in FIG. 1, resistances **18**, **20** and **21** are arranged on a three position selector switch **22** such that resistance **18** or resistances **18** and **20** or **18**, **20** and **21** may be included in the series circuit simply by setting the movable contact **23** to one or the other of the three fixed contacts. The purpose of this combination of resistances will be made clear in the description of the method.

The second leg of the bridge circuit connected between

the terminals 15 and 16 comprises a variable bias resistor 24, a variable bias trimmer resistor 25 and three fixed resistances 26, 27 and 28 which are arranged on a three position selector switch 30 such that the resistance 26 or the resistances 26 and 27 or the resistances 26, 27 and 28 may be inserted in series with the bias and trimmer resistances 24 and 25 simply by setting the movable contact 31 to any one of the three fixed contacts of the switch 30. As will appear in the description of the method, there are cooperative relations between resistances 18 and 26, resistances 20 and 27 and resistances 21 and 28. Accordingly, for convenience of operation, the movable contact 23 of the switch 22 and movable contact 31 of switch 30 may be ganged together as indicated schematically by the broken line 32.

The particular apparatus illustrated schematically in FIG. 1 is adapted to be energized from any convenient 115 volt source 33 through a program timer 34. One lead 35 from the source 33 is connected through the timer to the input terminal 16 of the bridge. The other lead 36 from the source 33 is connected to the movable contact arm 41 of a three position switch 37, having fixed contacts 38, 39 and 40. The timer is arranged by conventional means to step the movable contact arm from one of the fixed contacts to the other at predetermined intervals as will subsequently be explained in greater detail. The fixed contact 38 is connected through a resistance 42 to a timer output lead 43 and fixed contact 39 is connected directly to output lead 43. The lead 43 is connected at its opposite end to input terminal 15 of the bridge. The third fixed contact 40 of the switch 37 is connected through the output lead 44 to the junction 45 between resistances 17 and 18 in the first leg of the bridge circuit.

The timer is also provided with a suitable visible or audible signaling device, such as bell 46, which is arranged to indicate to the operator of the apparatus the beginning and end of the significant time periods involved in the practice of the method.

It will be obvious to those skilled in the art that the switching functions to be performed in connection with the various steps of the method may be made semiautomatic or wholly automatic simply by arranging the timer to actuate electromechanical or electronic relay devices at the prescribed time. Elaborations of this kind are wholly within the skill of the art and, in the interests of simplicity, will not be described here.

The bridge circuit is also provided with bridge balance detecting means which is, in this particular embodiment, a milliammeter. The meter is connected in series with a resistance 48 and a solenoid actuated switch 50 between the junction 45 of resistances 17 and 18 in the first leg of the bridge and the junction 51 of resistance 25 and resistance 26 in the second leg of the bridge. The solenoid switch may be any suitable type which is spring-biased to the open position when de-energized. The resistance 48 is shunted by a manually operated switch 52. The actuating solenoid 53 of switch 50 is connected between the junction 45 in the first leg of the bridge and the input terminal 15 of the bridge.

Titanium, tantalum, tungsten, niobium and alloys of these metals are typical filament materials. The filament diameter is not critical but should be made as small as is convenient to the end that the rate at which the reactive component affects the filament resistance is maximized. Furthermore, the length of the filament is preferably made short enough so that the resistance of the filament is less than about one tenth of the sum of the resistor 17 and the selected series combination of resistors 18, 20 and 21. This will tend to cause the filament current to remain nearly constant even though the filament resistance may increase considerably during the test.

The resistance values used in the apparatus illustrated in FIG. 1 are selected so that, when the inert gas being tested is helium, the proper ballast resistance comprises the series combination of resistances 17 and 18. Similarly, when the nominally inert gas being tested is argon, the series combination of resistances 17, 18 and 20 provides the proper ballast. The apparatus is also adapted to test evacuated enclosures for in-leakage of reactive gases. For this purpose the series combination of resistances 17, 18, 20 and 21 provide suitable ballast for the filament.

The resistance values of resistors 26, 27 and 28 in the second leg of the bridge are approximately five times the resistances of resistors 18, 20 and 21, respectively, in the first leg. This ratio is not critical, but represents a balance between the cost of the resistance and the sensitivity of the null balance detector.

Variable resistors 24 and 25 in the second leg of the bridge are variable and have maximum values such that the bridge output voltage may be adjusted to zero by variation of the effective portions of these resistors.

The null balance indicator 47, is as previously stated, a milliammeter which, in this particular circuit, reads one milliampere at full scale deflection. Resistance 48 in series with the milliammeter has a value whirh is sufficient to limit the current through the meter to one milliampere at maximum bridge imbalance. Switch 52 short circuits the resistance 48 to provide maximum bridge sensitivity at conditions approaching bridge balance. The solenoid actuated switch 50 is included to protect the meter in case the filament breaks before the end of the test, or was inadvertently not connected before starting the test, either of which conditions would result in a large surge of current through the meter.

Resistance values given in the following table are illustrative only and are suitable for use with a titanium filament one inch long and 0.0035 inch in diameter. I have found that it is advantageous to use resistors having relatively high thermal capacity, i.e. resistors rated at 5 watts or more.

Resistor reference No:	Resistance (ohms)
17	40
18	45
20	82
21	74
24	250
25	20
26	225
27	410
28	370
42	80
48	10^6

My new method for detecting the presence of chemically reactive components, or gaseous impurities, in a nominally inert gas is based upon my observation of a novel relation between the presence and concentration of a reactive component of a gaseous atmosphere and the increase with time of the resistance of a filament which is heated in the presence of the reactive component in order to accelerate the susceptibility of the filament to chemical reaction with such reactive component. By detecting the rate of change of resistance of the filament with respect to time during the initial minutes of the period of heating the filament, as opposed to time periods on the order of hours required by prior methods, I obtain an accurate measure of the concentration of the reactive component. My tests have shown that if the filament current is held constant at an appropriate value, the filament resistance increases with time in a nonlinear fashion, the rate of increase being greatest at the start. The general shape of the curve representing this nonlinear relation between resistance and the time during which the filament is heated is independent of the concentration of the reactive component in the nominally inert gas, but the time scale is contracted or expanded depending on whether the concentration of the reactive component is large or small. As a result, the increase in filament resistance occurring in a predetermined period as short as one minute can be used as a measure of the

concentration of the reactive component of the nominally inert gas. FIG. 2 shows a plot of the increase in filament resistance (in ohms) during the first minute of exposure at constant current, as a function of the concentration of the reactive component.

I will now describe a particular application of my new method as it has been used to determine the oxygen content of a nominally inert gas. The several steps to be performed in this particular application of the method are facilitated by use of the apparatus described above and illustrated in FIG. 1.

The following description assumes that the enclosure **10** contains a nominally inert gas such as helium having some unknown concentration of a reactive component, such as oxygen, which for many purposes would be considered as an impurity in helium. The discussion also assumes that a suitable titanium filament **11** is in place in the enclosure **10** and is connected in the bridge circuit as is shown in FIG. 1.

The test is started by opening shunting switch **52** and then actuating the program timer **34** to connect the source **33** for a short period of time, for example 5 seconds, to the bridge input terminals **15** and **16** through the resistance **42** in the timer. The presence of resistance **42** in the circuit results in an input voltage being applied to the bridge and the filament. This reduced voltage is selected so that the temperature of the filament is raised to about 600° F. to expel any gaseous impurities which may have been adsorbed on the filament surface. At the end of the initial preheat period the timer sounds the bell **46** and switches the contact arm **41** from the contact **38** to the contact **39** where full source voltage is connected to the input terminals of the bridge. With trimmer resistor **25** set at zero, the operator now adjusts bias resistor **24** until the null balance indicator reads zero, first with switch **52** open and then with it closed. At the end of about 15 seconds (20 seconds from the start of the test) which is signaled by the bell **46**, the operator leaves variable resistor **24** as is and then balances any rise in filament resistance by adjusting trimmer resistor **25** to hold the meter at zero. Resistor **25** may conveniently be precision calibrated to have a direct digital read-out of its resistance to any setting.

At the end of 60 seconds (80 seconds from the beginning of the test), again signaled by the sound of the bell, the operator leaves variable resistor **25** at its last setting and opens switch **52**. In five more seconds the timer switches the movable contact arm **41** of switch **37** to the fixed contact **40**. This de-energizes the solenoid operated switch **50** to disconnect the milliammeter **47** and shunts the source voltage around a portion of the first leg of the bridge to the junction **45** which causes a sudden increase in the filament current to a value which causes the filament to melt. The timer then de-energizes the bridge and resets to the beginning of the program.

The final value indicated by resistor **25** is directly proportional to the increase in resistance of the filament during the one minute test period and can be converted to total oxygen content of the inert gas by reference to a predetermined calibration curve.

The method may be repeated at will merely by replacing the filament **11**.

In the event that the inert gas being tested is argon, the gang switches **22** and **30** would be set so that the movable contact arm **23** of switch **22** is connected to the fixed contact at the junction of resistances **20** and **21**, and the movable contact arm **31** of switch **30** is connected to the fixed contact at the junction of resistances **27** and **28**. If the inert atmosphere is nominally a vacuum, the movabel contact arms would be set to the fixed contacts at the remote ends of resistances **21** and **28**, respectively.

The null balancing operation performed by the operator in accordance with the foregoing description, could

be accomplished automatically with commercially available instruments, and the rise in resistance with time could be recorded as a permanent graphic record if desired. If tungsten is used as the filament material, the instrument will also measure the total oxygen content of nitrogen, the latter being used as an inert gas for some purposes. These and other variations in the details of the method and apparatus described in the foregoing specification will occur to those skilled in the art. Accordingly, the scope of the invention is not intended to be limited by these details, rather the invention is defined in the following claims.

In the claims:

1. The method of detecting the presence of and determining the concentration of a gaseous impurity in a nominally inert gaseous atmosphere, comprising the steps of:

(a) introducing an electrically resistive metallic filament into the nominally inert gaseous atmosphere, said filament being chemically reactive with such gaseous impurity;

(b) heating said filament to accelerate the susceptibility thereof to chemical reaction with such gaseous impurity; and

(c) detecting the rate of change of resistance with respect to time of said filament during the initial minutes of the period of heating the filament, wherein said rate of change is related to and indicative of the concentration of such gaseous impurity.

2. The method according to claim **1** and in which said filament is heated during the step of detecting the change of resistance by means of a substantially constant electric current through said filament.

3. The method of detecting the presence of and determining the concentration of a gaseous impurity in a nominally inert gaseous atmosphere, comprising the steps of:

(a) introducing an electrically resistive metallic filament into the nominally inert gaseous atmosphere, said filament being chemically reactive with such gaseous impurity;

(b) preheating said filament to a temperature sufficient to vaporize impurities in the surface of said filament and insufficient to appreciably increase the susceptibility of the filament to chemical reaction with such gaseous impurity;

(c) heating said filament by means of a substantially constant electric current therethrough to a temperature sufficient to accelerate the susceptibility thereof to chemical reaction with such gaseous impurity; and

(d) detecting the rate of change of resistance with respect to time of said filament following said preheating and during the initial minutes of the period of heating the filament, wherein said rate of change is related to and indicative of the concentration of such gaseous impurity.

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