Aug. 15, 1972 A. J. MARTIN ET AL 3,684,454

SOLIDS PYROLYZER

Filed Dec. 18, 1970

Fig. 1.

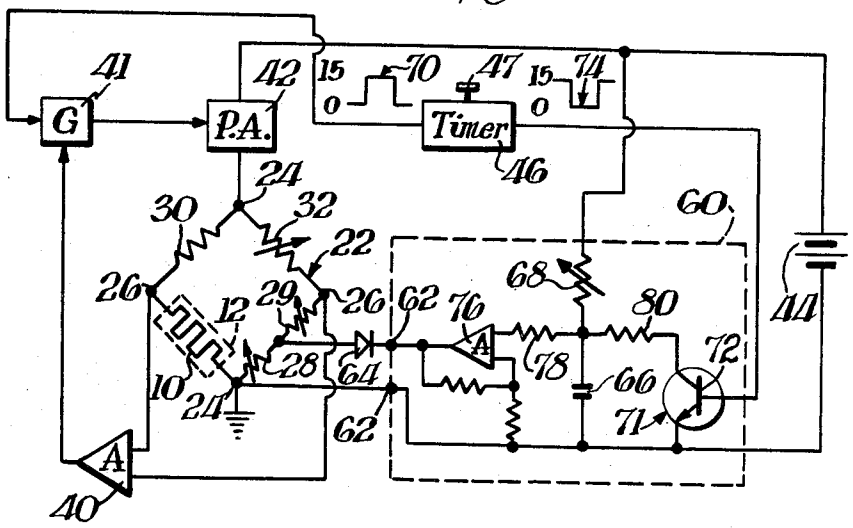


Fig. 2.

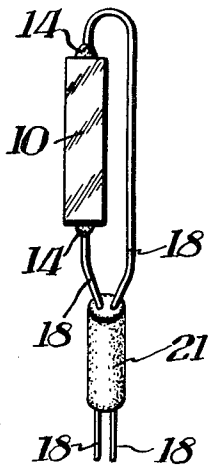


Fig. 4.

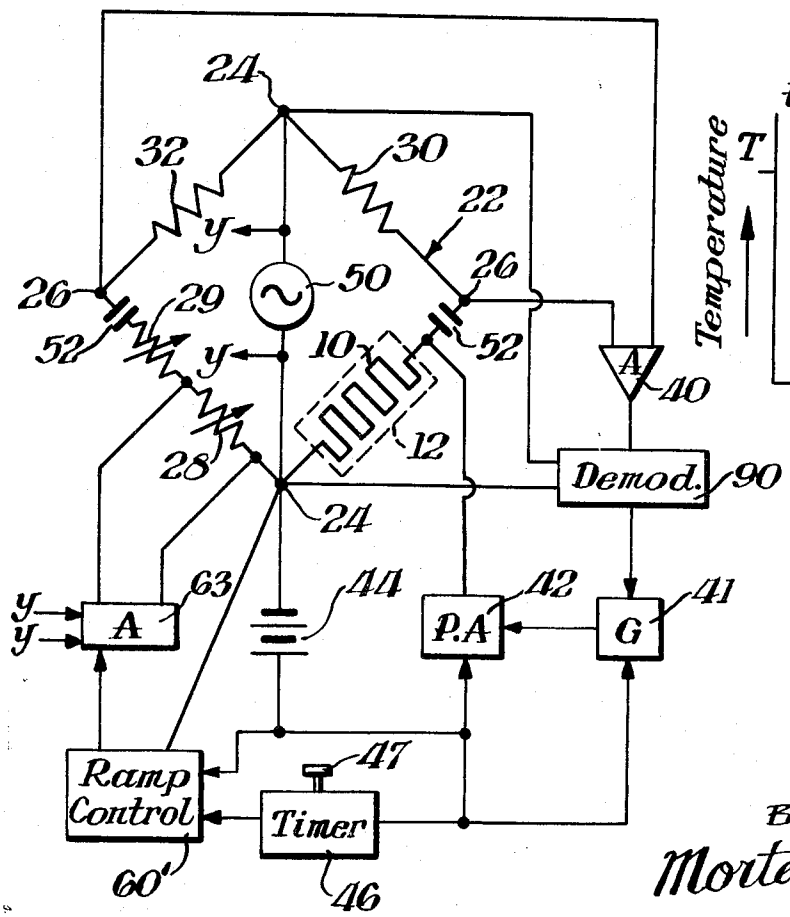
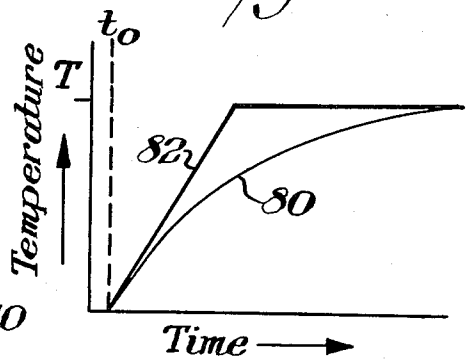


Fig. 3.



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U.S. Cl. 23—253 PC 11 Claims

ABSTRACT OF THE DISCLOSURE

A pyrolyzer, useful in pyrolysis-gas chromatography and other prolysis applications, includes a filament adapted to receive a sample to be pyrolyzed. The filament itself is an element having a positive temperature coefficient of resistance and forms one leg of a bridge circuit. The output signal from the bridge circuit is applied to the control means which varies the electrical power applied to the bridge in accordance with the unbalance condition of the bridge, the pyrolyzing filament functioning both as the heating element and as the temperature sensing element. An automatic clamping impedance circuit controls the bridge imbalance and the rate at which power is applied to the bridge and filament, thereby to improve the reproducibility of the results. The filament itself is constructed of a nickel-chromium alloy, which provides a tensile strength and the alloy is plated with gold which has the advantage of providing an inert material that increases the temperature coefficient of resistance of the filament.

BACKGROUND OF THE INVENTION

This invention relates to a solids pyrolyzer and, more particularly, to an improved pyrolytic apparatus in which the pyrolyzing element functions both as a heating element and as the temperature sensing element to facilitate the accurate control of the heating rate of the element thereby to achieve improved reproducibility of pyrolyses.

Pyrolysis is one of the known techniques of determining the structure of non-volatile materials. One such technique is that described in U.S. Pat. No. 3,057,692 issued Oct. 9, 1962, to William Van Kirk. Van Kirk provides an air-tight chamber and a heating element disposed in a chamber for pyrolyzing a small quantity of the sample to be pyrolyzed. The sample is often prepared for pyrolysis by dipping the heating element into a solution of the sample in a volatile solvent. The filament is then heated or baked to remove the solvent leaving the sample material as a residue.

To determine the structure of the sample, the products of thermal decomposition of the sample material are analyzed and studied using known techniques such as gas chromatography, infrared or ultraviolet spectroscopy, mass spectrometry, etc. It is desirable in performing these pyrolysis studies to pyrolyze a sample at a given temperature without exposing it to elevated temperatures at which the fragments are further decomposed. Because of the possibility of intermediate reactions occurring, the methods of preparing the sample must be specified and the temperature rise time of any pyrolyzer must be measured and specified in order to permit faithful reproducibility of the pyrolysis reaction.

Other methods of pyrolyzing samples known in the prior art include placing the sample in a boat and introducing the boat into a high temperature oven for a set period of time. This method is particularly undesirable since it yields a slow and non-homogeneous, non-repeatable temperature exchange—the products of decomposition are representative of very wide variations of temperature and generally are not reproducible to a high degree of accuracy. Still another method of the prior art involves depositing the sample as a thin film on a wire of a metal

which exhibits a Curie point temperature at which it abruptly changes from a magnetic to a non-magnetic material. This coated material is then introduced into a high frequency electrical field where it absorbs energy and is heated until it reaches the Curie point at which it stops absorbing power. This method is expensive and electrically inefficient and somewhat limited in pyrolysis temperature because of the lack of materials exhibiting such Curie point behavior.

The rates of heat transfer from the heating element to the sample and those within the sample itself are significant factors that must be considered if good reproducibility of the pyrolysis reactions is to be attained. The mechanisms of these heat transfers are extremely complex and will vary from heating element to heating element and sample to sample. Accordingly, it is highly desirable to provide some means of adjustably controlling heating rates of whatever heating elements are used so that different optimum rates may be selected for the different samples to be pyrolyzed. The heating element must be capable of being held at a desired temperature for set periods of time after which it can be cooled. If such conditions are achieved, the thermal decomposition runs are usually more repeatable and hence more easily interpreted and used.

Accordingly, it is an object of this invention to obviate many of the disadvantages of the prior art pyrolyzers.

Another object of this invention is to provide an improved pyrolytic apparatus that is capable of providing more reproducible results.

BRIEF DESCRIPTION OF THE INVENTION

In a preferred embodiment of this invention the pyrolytic apparatus includes an air-tight chamber in which the pyrolysis can be effected. A pyrolyzing filament is adapted to be mounted in the chamber, the filament itself forming one leg of a bridge circuit which both energizes and controls the temperature of the filament to achieve this dual purpose. The bridge error signal is applied to a control means which is responsive to the bridge error signal for varying the electrical power applied to the bridge and hence to the pyrolyzing filament. The remaining resistors forming the legs of the bridge are chosen to dissipate lower power than the pyrolyzing filament, and by selecting such resistors to have a substantially zero temperature coefficient of resistance, their resistance will remain substantially constant. Bridge balance is also controlled by an adjustable ramp voltage generator thereby to control the heating rate of the pyrolyzing filament. This permits the heating rates for different samples to be optimized to enhance the reproducibility of the pyrolysis.

DESCRIPTION OF THE DRAWINGS

The novel features that are considered characteristic of this invention are set forth with particularity in the appended claims. The invention, itself, however, both as to its organization and method, as well as additional objects and advantages thereof, will best be understood from the following description when read in connection with the accompanying drawings, in which:

FIG. 1 is a partial block and partial schematic diagram of a pyrolytic apparatus constructed in accordance with one embodiment of this invention;

FIG. 2 is a pictorial representation of the pyrolyzing filament constructed in accordance with this invention;

FIG. 3 is a temperature plot in which the temperature of the pyrolyzing filament is plotted as the ordinant versus time as the abscissa; and

FIG. 4 is a partial block and partial schematic diagram of a pyrolytic apparatus constructed in accordance with another embodiment of this invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

In FIG. 1 there may be seen a partial block and partial schematic diagram of a pyrolytic heating rate control apparatus constructed in accordance with a preferred embodiment of this invention. In this apparatus the pyrolyzing element or filament **10** which functions both as a heating element as well as the temperature sensor is mounted in an air-tight chamber denoted by the dotted line **12** such as that described by Van Kirk et al. by a ceramic mount **21** (FIG. 2). The pyrolysis filament **10** preferably is in the form of a wire or ribbon that has a chemically inert surface, is relatively strong, has a large surface area, has a relatively high electrical resistance, has a high temperature coefficient of resistance and finally has a low heat capacity to facilitate rapid heating and cooling.

Most of the common metals fail to meet some or all of these requirements. Often, in the prior art, in order to obtain the desired surface area and strength, electrical resistance was decreased to the point where it was difficult to obtain a significant degree of self-heating using reasonable current magnitudes. The requirement of inertness presents a particular problem. Gold is relatively inert at the temperatures employed for pyrolysis, but unfortunately it has low tensile strength and electrical resistance.

In accordance with one aspect of this invention, a solution to this dilemma is obtained by selecting the pyrolysis filament ribbon to be of a metal alloy such as nickel-chromium. The nickel-chromium alloy ribbon is plated with a thin cover of an inert metal such as gold. In this combination, the nickel-chromium alloy provides relatively good strength whereas the ribbon shape provides adequate surface area and the gold covering provides an inert surface having a relatively high temperature coefficient of resistance. Other core metals that may be used for the filament are various alloys such as copper-nickel sold under the trade name Constantan and nickel-iron-chromium sold under the trade name Nichrome, all being alloys of relatively high resistance and low temperature coefficient.

Other outer surface coating metals that may be used for the filament are nickel, cadmium, platinum, silver. In fact, most metals which have a positive temperature coefficient of resistance in the range of 0.2 to 0.7% per degree centigrade are suitable for usage as the outer surface coating so long as the requirements for inertness are met.

The pyrolysis filament **10** is in the form preferably of a straight strip, each end of the filament being connected as by a weld **14** to support wires **18** which are secured in a rigid ceramic insulating member **21**, capable of withstanding the high chamber temperatures, to permit the filament to be inserted into the chamber **12** (FIG. 1). The supports **18** are electrically connected into a bridge circuit **22**. (FIG. 1).

The bridge circuit **22** has a pair of input terminals **24** and a pair of output terminals **26**. The several legs of the bridge are connected respectively between these output and input terminals. Thus, the pyrolysis filament **10** is connected between one of the input terminals **24**, and one of the output terminals **26**. A first adjustable impedance means or resistor **28** and a second adjustable impedance means or resistor **29** are serially connected between the said one input terminal **24** and the remaining output terminal **26**. The adjustable resistors are selected to have a resistance substantially greater than the resistance exhibited by the filament **10** in its operating range.

The remaining legs of the bridge are completed with a fixed resistor **30** and an adjustable resistor **32**. This fixed resistor **30** and the adjustable resistors **28, 29, 32** are selected to have a low or zero temperature coefficient of resistance. The adjustable resistor **32** has one end connected to the second adjustable resistor **29** at the

junction **26** and the remaining end to the upper junction **24** (in the drawing). In like manner, the fixed resistor **30** has one end connected to the upper junction **24** and the remaining end to the heating filament **10** at the junction **26**. The adjustable resistor **32** is selected to have a value significantly greater than the fixed resistor **30** thereby to decrease power dissipation in all elements of the bridge except in the heating filament **10**. In like manner, the heating filament preferably is selected to have a resistance over its operating range slightly greater than that of the fixed resistor **30** so that the filament absorbs more power than the fixed resistor, although this need not be the case.

The output terminals of the bridge are connected to the inputs of a conventional differential amplifier **40**. The output of the amplifier **40**, which provides an error signal varying in amplitude and polarity in accordance with the imbalance of the bridge, is connected through a gate **41** to the control of a power amplifier denoted by the block **42**. This power amplifier may be nothing more than a current control device which is a power transistor or other suitable current control device. The function of the power amplifier **42** is to control the direct current that is applied to the input terminals **24** of the bridge from the source of potential illustrated by the battery **44**. A timer **46** is supplied to initiate the action by opening the gate **41** with a positive going pulse **70** to apply the error signal to the power amplifier **42**. The power amplifier **42** applies the voltage across the bridge for a predetermined period of time—the duration of the pulse **70**—after a start button **47** is depressed. The period of time selected is that necessary to achieve the desired pyrolysis as will be described hereinafter. The timer **46** also supplies a negative-going voltage level or pulse **74** to a ramp voltage generator **60** when the start button **47** is depressed.

In accordance with this invention the ramp voltage generator, which may be of any conventional design, has a pair of output terminals **62** which supply a ramp voltage across the first adjustable resistor **28** through the cathode side of a unidirectional semi-conductor **64**. As will be described, this ramp voltage which has an adjustable slope and cutoff point, permits the heating rate of the filament **10** to be varied.

The ramp voltage generator **60** illustrated includes an RC circuit having a capacitor **66** which is charged through an adjustable resistor **68** by the battery **44**. An NPN transistor **71** has its collector-emitter circuits connected across the capacitor **66** to discharge the capacitor whenever the timer provides a positive voltage to its base, i.e., before and after the filament is heated. The collector-emitter circuit includes a collector resistor **80**. The base **72** of the transistor **71** is connected to receive the negative-going cut off pulse **74** from the timer such that the capacitor is permitted to charge during the occurrence of the pulse **74**. An operational amplifier **76** has its non-inverting input connected through a resistor **78** to the junction between the capacitor **66** and resistor **68**. The remaining input to the operational amplifier is connected to the normal feedback impedance and through the normal input impedance to ground and the two impedances are selected to provide an overall gain of **5**.

When the start button **47** is depressed, direct current voltage is applied to the bridge **22**. The pyrolysis filament **10** at this point is cold with the sample to be pyrolyzed having been deposited thereon using known techniques previously described. At this point, the bridge **22**, depending upon the setting of the first or temperature adjusting resistor **28**, is in the condition of imbalance. Also because of the high voltage level applied to the base of the transistor **72**, the capacitor remains fully discharged and the output of the operational amplifier is essentially clamped to ground. While thus clamped, no voltage can build up across the temperature adjusting resistor **28**, hence the bridge calls for no power to the filament as determined by the balancing resistor **29**.

The balanced condition of the bridge depends upon the ratio of the fixed resistor **30** to the filament **10** being the same as the ratio of the variable resistor **32** to the balancing resistor **29**. When these ratios are identical the bridge is in balance, the error signal is zero and no power is applied to the filament. It will be recalled, however, that the temperature adjusting resistor **28** is adjusted to some value which, but for the clamped junction between resistors **28** and **29**, would cause the filament **10** to be driven to some predetermined high temperature at which electrical balance of the bridge again obtains.

Now the voltage level from the timer **46** applied to the transistor **71** is dropped to zero (pulse **74**) to turn off the transistor **71** and permit the capacitor **66** to begin charging at a rate determined by the charging resistor **68**. As the capacitor continues to charge, a ramp-like positive going voltage is generated at the output of the operational amplifier **76** such that clamping voltage gradually increases until the diode **64** becomes reverse biased and is turned off. At this point the filament temperature will be held constant at the level set by resistor **28**. Prior to this point, with bridge unbalance, an output error signal is derived from the bridge output terminals **26** having a polarity which causes the power amplifier **42** to decrease its resistance and permit the full voltage of the battery and the full current permitted therefrom to be applied to the bridge across the input terminal **24** of the bridge **22**. Because of the higher resistances of the variable resistor **32** and the adjustable resistor **28**, as opposed to the remaining bridge resistors, most of the current flows through the lefthand side of the bridge (in the drawing) and causes the filament **10** to heat. With the heating, the resistance of the filament **10** increases until bridge balance is again attained.

With the increasing voltage drop permitted across the temperature control resistor **28** by the increasing ramp voltage, the filament **10** heats at a rate (function of time) controlled by the charging resistor **68**. Heating continues at this rate until the desired temperature is reached as determined by the resistor **28** at which point the diode is biased off and the increasing ramp voltage has no further effect. After a period of time, established by the timer **46**, sufficient to complete the pyrolysis, the voltage pulse **70** turns off gate **41** and hence power amplifier **42**—the bridge voltage drops to zero—and a high level signal is again applied to the base **72** of the transistor **71**. The charging capacitor is discharged.

The controlled rate of filament heating provided by this invention permits better reproducibility of pyrolysis results. The heat transfer rate from the filament to the sample and that within the sample may be more nearly optimized to attain such reproducibility. With the ribbon type filament design having a rectangular cross section as described, and with the gold plating, the resistance of the gold plate increases at a far more rapid rate than that of the core of the filament so as to provide a reasonable operating range of resistances over the range of temperature in which the filament is to operate.

In a typical circuit constructed in accordance with a preferred embodiment of this invention, a gold plated nickel-chromium alloy ribbon 0.063" wide, 0.0005" thick, and 1.5" long is constructed. This ribbon would have a tensile strength of slightly over 4 pounds and a surface area of about 0.2 square inch. At 100° C. the resistance of this ribbon is about 3.15 ohms and that of the gold plating about 0.25 ohm. On the other hand, at 700° C. the interior of the filament has a resistance of about 4.20 ohms and the gold plate about 0.93 ohm for a total parallel resistance of 0.76 ohm. Hence, it is seen that the gold plate being the lower resistance in each case, provides a rather high temperature coefficient of resistance and permits relatively accurate heat control to be attained.

This adjustable temperature rise characteristic is graphically illustrated in FIG. 3 in which the voltage pulse **74** occurs at the time t_q. Using a conventional circuit without temperature control, the temperature of the filament rises quickly at first as seen by the curve **80** and then approaches the desired temperature T asymptotically. The increase in temperature is such that the total time required for the filament to achieve its final desired operating temperature can be as long as 11 seconds in many cases and in others the rate of increase may greatly exceed the rate of heat transfer to the sample. On the other hand using the circuit of this invention, when the timer is actuated, the temperature of the filament rises, as seen by curve **82**, at a rate determined by adjustable charging resistor **68** until the desired temperature, as determined by the temperature control resistor **28**, is attained at which point the temperature is maintained approximately constant for as long a period of time as required as determined by the timer **46**.

In FIG. 4 there is illustrated an alternative embodiment of this invention in which the bridge **22** is energized by an alternating current source **50**. Other than this change the bridge is substantially identical to that previously described in conjunction with FIG. 1 and accordingly the same corresponding elements have been given the same numbers. The only exception is that this being an alternating current (A.C.) bridge and the energization of the pyrolysis filament **10** being by way of the direct current source such as battery **44**, capacitors **52** are placed in series with the pyrolysis filament **10** and the variable resistor **28** such that the direct current applied to the filament **10** can flow only to the filament and not elsewhere. Since the bridge is an A.C. bridge its output error signal is passed to a synchronous demodulator **90** whose output D.C. signal upon passing through the gate **41** controls the power amplifier **42**. The ramp control circuit **60'** has its output coupled to a paraphase amplifier **63** which inverts and amplifies the A.C. signal from source **50**. The ramp circuit **60'** is the same as shown in FIG. 1 but resistor **78** is connected to the inverting input of the operational amplifier **76** so that the capacitor charge voltage is inverted.

Thus, the bridge provides an output error signal which varies in both phase and amplitude in accordance with the sense and magnitude of the bridge unbalance. This error signal is applied to a differential amplifier **40**, amplified thereby, and then applied to the synchronous demodulator **90**. The demodulator receives a reference A.C. signal from the source **50**. The output of the demodulator, which is a direct current signal, is utilized to control the power amplifier **42** the same as in the case of the circuit of FIG. 1. The ramp voltage which is inverted and decreasing in amplitude with time, is used to control the amplification of the paraphase amplifier **63**. Initially the paraphase amplifier applies the full amplitude alternating current signal such as is necessary to in effect cancel the A.C. voltage drop across the resistor **28**. This A.C. signal decreases in amplitude with the decrease in ramp voltage until resistor **28** is again allowed to function fully in its bridge balancing control application. This later occurs when the A.C. signal from the paraphase amplifier **63** drops to zero. Thus the ramp voltage controls the rate of filament temperature increase.

The pyrolysis filament **10** performs the dual function of a sensing element as well as the heating element. This facilitates accurately controlling the rise times to insure reproducible pyrolysis results. In still another alternative embodiment of the invention, not shown, the ramp control **60'** may control a variable impedance that parallels the resistor **28** such that initially the combined parallel impedance is zero, but as the ramp voltage varies with time the variable impedance is increased to a high value such that the effective impedance (parallel) is that of the resistor **28**.

There has thus been described a relatively simple yet efficient pyrolysis apparatus that is capable of providing temperature rise times of controllable rates. Such temperature rise times permit reproducible accurate pyrolysis

results not usually attainable with the prior art. The filament employed in such circuits is a plated filament which provides many advantages for this particular application.

It is obvious that many embodiments may be made of this inventive concept, and that many modifications may be made in the embodiments hereinbefore described. Therefore, it is to be understood that all descriptive material herein is to be interpreted merely as illustrative, exemplary and not in a limited sense. It is intended that various modifications which might readily suggest themselves to those skilled in the art be covered by the following claims.

What is claimed is:

1. Pyrolytic apparatus for reproducibly pyrolyzing a test sample comprising, in combination:

a bridge circuit means adapted to be connected to a source of electrical power for producing an error signal that is indicative of the electrical balance condition of said bridge means,

control means responsive to said error signal for varying the electrical power applied to said bridge means,

said bridge circuit means including an electrical resistance element having a positive temperature coefficient of resistance for heating said sample and sensing the resistance of said resistance element,

said bridge circuit means also having an adjustable impedance means for adjusting the electrical balance of said bridge circuit means and hence the temperature of said electrical resistance element, and

ramp means coupled to said adjustable impedance means for varying the effective impedance thereof as a function of time, thereby to vary the temperature rise time of said resistance element.

2. An apparatus according to claim **1** wherein said ramp means includes clamping means connected across said adjustable impedance means, said clamping means having a reference voltage source that varies in amplitude in accordance with said function of time.

3. An apparatus according to claim **1** wherein said ramp means includes means to vary said function of time.

4. An apparatus according to claim **1** wherein said ramp means includes:

clamping means connected across said adjustable impedance means, said clamping means having a reference voltage source that varies in amplitude in accordance with said function of time, and

means to vary said function of time.

5. An apparatus according to claim **1** wherein said first material is plated with a second substantially inert material having a temperature coefficient of resistance exceeding that of said first material.

6. An apparatus according to claim **5** wherein said first material is a nickel-chromium alloy and said second material is gold.

7. An apparatus according to claim **1** wherein said ramp means includes:

a ramp voltage generator for generating voltage, and

means coupled between said adjustable resistance means and said generator for clamping the voltage developed across said adjustable resistance means to said ramp voltage generator voltage,

and wherein said bridge circuit means includes:

first, second, third and fourth legs, each including an impedance element,

said first leg including said electrical resistance element, and

said second leg including said adjustable impedance means.

8. An apparatus according to claim **7** wherein

said bridge circuit is adapted to be connected to an alternating current source of electrical power, whereby said error signal varies in phase and amplitude in accordance with the sense and magnitude of bridge imbalance,

said first and second legs each include a series connected capacitor,

and which also includes a source of direct current power,

said control means being connected in series with said source of direct current power and said electrical resistance element and responsive to the phase and amplitude of said error signal for varying the direct current power applied to said electrical resistance element, thereby to vary the direct current power applied to said electrical resistance element in accordance with said error signal.

9. An apparatus according to claim **8** wherein said control means includes:

a demodulator for converting said error signal to an amplitude varying direct current error signal, and

current control means responsive to said direct current error signal for varying the current from said source of direct current power applied to said electrical resistance element.

10. An apparatus according to claim **9** wherein said first material is plated with a second substantially inert material having a temperature coefficient of resistance exceeding that of said first material.

11. An apparatus according to claim **10** wherein said first material is a nickel-chromium alloy and said second material is gold.

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U.S. Cl. X.R.

23—230 PC, 232 E, 254 E, 255 E; 219—499, 505