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APPARATUS FOR DETERMINING THERMAL STABILITY OF MATERIALS

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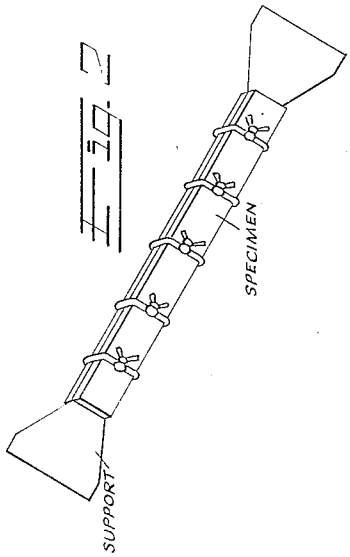

FIG. 2

FIG. 1

INVENTOR.
Howard R. Moore

BY M. A. Hayes

ATTORNEY

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APPARATUS FOR DETERMINING THERMAL STABILITY OF MATERIALS

Howard R. Moore, Drexel Hill, Pa.

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This invention relates to an apparatus for measuring the thermal stability of materials, and more particularly the minimum temperatures required to effect permanent changes in the physical properties of organic and inorganic materials in the solid state.

The apparatus is used to make determinations of the threshold burning temperatures of organic compounds and resinous polymers of the most diversified character. It is useful in determining the melting points of inorganic compounds, such as oxides and silicates. The thermal stability of synthetic inorganic pigments similar to ultramarine blue can be investigated with its aid.

An object of the invention is to provide a plurality of metal supports of different resistivities and designs to serve as substrata for the solid materials to be tested.

Another object is to provide electrical power sources capable of furnishing controlled and uniform sources of heat to metal supports of different resistivity and design so that the materials tested are in immediate contact with flat metal surfaces having temperatures of 100 to 3300° C.

Another object is to provide a finished apparatus comprising parts essential to effective utilization of the principle of transforming electrical energy into heat energy for measuring accurately and in a reproducible fashion the fire-resistant properties of organic raw materials and finished products of the most diversified character.

The foregoing objectives are realized with the assembly of parts and combinations hereinafter set forth and claimed.

The principles of operation and type of data obtained with this device are most conveniently illustrated by its application to determinations of the burning tendencies of organic materials. Visible burning occurs when the rate of combustion of materials attached to the metal supports is sufficiently rapid to give visible flames at normal pressures and temperatures.

An immediate use of the apparatus is to provide quantitative data on the burning properties of the following classes of finished products subjected to a controlled source of heat for definite periods of time: surface coatings, plastic sheeting, linoleum, cements, adhesives, electrical insulation, silicone resins, phonographic discs, decorative materials (chemically treated), film base (non-flammable), wood preservatives, water-proofing materials, textile preservative compounds, floor waxes, gasket materials, sheet materials fabricated from neoprene and other synthetic rubbers.

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Heretofore, in the art of measuring the fire retardance of solid organic materials, it has been customary to employ gas burners or blast lamps for the direct application of heat to the specimens. Electric muffle furnaces have also been used, in which the backs of sheet-metal supports for test material have been substituted for the furnace doors. None of these methods is satisfactory, since they fail to furnish a source of heat that is sufficiently uniform, rapid and intense to meet the severe service conditions required of fire-resistant materials.

Temperatures in excess of 1800° F. rarely can be obtained by methods hitherto used. Furthermore, older methods are inherently deficient in providing a source of heat that is constant in a series of tests, so that it is impossible to secure reproducible results.

As a consequence of the foregoing defects, the use of older methods does not insure the heating of solid materials to sufficiently high temperatures, with sufficient speed, to prevent the loss of volatile combustible ingredients by vaporization or by gaseous diffusion out of the organic matrix. Owing to these basic effects, the older methods give misleading results and higher ratings for fire retardance than the various compositions are entitled to receive. A unique feature of the new method is its capacity to supply heat of the requisite intensity, very rapidly, to ignite combustible ingredients in the materials tested.

The older sources of heat derived from sources external to the supports for the test specimen are all inferior to the method developed in my invention which depends on the generation of heat within a metallic support and the test material attached thereto by the preferred method of utilizing the heating effect of an electric current in metal strip supports of special design. High frequency induction can also be used to secure controlled rates of heating and temperatures

short of fusion but this method is not as convenient or cheap as the preferred method.

The basic principle of my invention is an application of the principle of the transformation of electrical energy into heat energy to provide a uniform source of heat, applied at a controlled rate, to individual metallic substrata for the various materials tested. Flammability characteristics are then defined in terms of the minimum quantity of electric current that ignites specimens affixed to the test strip and produces the first detectable evidence of luminous flames. Alternatively, flammability is defined in terms of the minimum lengths of time required to ignite test specimens in direct contact with different metal substrata heated by constant currents.

The validity of the application of the fundamental equation for the transformation of electrical into heat energy to this invention is confirmed in a semi-quantitative manner by comparing the calculated temperature increases of the metallic strip substrata with the observed values determined by means of the optical pyrometer. These calculations verify the application of the familiar equation

$$H=\frac{E^2}{r}\times\frac{t}{4.18}$$

to this invention. Estimates of the heating effect in calories, H, can be used to calculate the degrees temperature rise from published data on the heat capacity of the metal as a function of temperature, the mass, length and cross section of the strip, the specific heat and specific resistivity of the metal under consideration.

In order to make the invention more clearly understood, there is shown in the diagram, Fig. 1, means for carrying out the invention into practical use. This arrangement of essential parts is given as a means of illustration only and does not limit the construction of a finished test unit to this particular construction. Thus, the essential elements comprising the unit can be varied in proportion and in arrangement without departing from the basic principles and scope of the invention as defined in the appended claims.

Fig. 2 shows a special adaptation, in perspective, of the test specimen.

A practical embodiment of the thermoelectric principle is also given in Navy Department Specification 27–L–12, under date of March 1, 1945, for battleship linoleum, fire retardant. The invention includes a gas burner to ignite any combustible gases released by the ⅛-inch-thick linoleum specimens tested. The gas burner provides a non-luminous flame by the burning of gas such as commercial propane gas. The gas flame is adjusted to be about one inch from the test specimen, and to extend lengthwise approximately parallel to the specimen for a distance of about five inches. A suction blower is also provided to remove smoke and fumes evolved during a run. The foregoing specification gives further information on operating details and thermal stability properties ascertained with the thermoelectric apparatus, as a means of insuring the procurement of a suitable grade of fire-resistant linoleum for ships.

The separate items of equipment and parts of the assembly, as illustrated schematically by Fig. 1, are:

(1) An A. C. or D. C. power supply.

(2) An auxiliary 110 volt, 60 cycle, current supply to operate the contactors (circuit breakers) and timer.

(3) Switch C manually operated to start and stop the flow of current into the test specimen.

(4) Contactor A to function as a means of safely delivering currents as high as 600 amperes to the test specimen.

(5) Contactor B to function as a means of starting and stopping the timer on the auxiliary circuit.

(6) Electric timer T totalizing time in minutes, seconds and fractions of a second, and provided with an electric or manual reset.

(7) Ammeters for measuring the current flowing through the specimen, utilizing a suitable shunt for the D. C. power source and a current transformer for the A. C. power supply.

(8) A. C. and D. C. voltmeters for measuring the voltage drop across the specimen depending on the power supply.

(9) Copper or brass terminal bars with jaws and clamps for affixing the metallic test specimen, one bar to be fixed and the other movable to allow for expansion and contraction of the support.

(10) A metallic test support, with or without material subjected to test.

The steel support shown in Fig. 2 is cut from hot or cold rolled strip stock 13 inches x 3 inches in size with a constriction 6 inches long by 1 inch wide for application of the test material. Linoleum or other plastic sheet materials are affixed with wires to this narrow constriction which attains a uniform temperature over its entire 6 inch length because of its higher resistivity. Peak temperatures of 2600° F. are obtained with steel specimens 0.017 ± 0.003 inch in thickness, although still higher temperatures of 2900 to 3000° F. are obtained with specimens ranging from 0.0123 to 0.0139 inch in thickness.

In practice it has been found that thin sheet stock of steel or ferrous alloy sheets can be used only if provision is made in the design of the terminal bars to accommodate a pulling device to keep the piece perfectly straight as it expands on heating. This device can take the form of a combination of a stationary terminal bar and a movable head. The movable head is controlled with a spring or air cylinder which gradually draws the piece over as it expands. In this manner, it is possible to allow for thermal expansion during heating. An air-cylinder device is preferred since it provides an automatic release to permit contraction of the specimens after the current is turned off at the conclusion of a run.

A further desirable modification of the apparatus consists of an automatic graphic recorder of time, current and voltage substituted for the indicating meters and contactor listed as items 5–8, inclusive. A suitable recorder for this purpose is manufactured by the Esterline Angus Company.

The power supply comprises a single-phase 60-cycle A. C. welding transformer having the following preferred specifications:

(*a*)	Open-circuit voltage	75–80 volts.
(*b*)	Welding-current rating	600 amperes.
(*c*)	Kilowatts at rated load	20 kva.
(*d*)	Primary voltage	220 to 440 volts.
(*e*)	Primary current	91 to 182 amperes at rated load.

(*f*) A manually operated current regulator.

Alternately, a suitable D. C. power supply com-

prises a welding generator with a current rating of 600 amperes, the current delivery of which is capable of regulation in small increments or in a continuous manner.

The specifications for the power source required by this invention are a direct function of the type of material chosen for the metal support and its dimensional characteristics. The design illustrated by Fig. 2 is preferred for the majority of tests, although it is recognized that more compact, inexpensive and readily operated power sources can be utilized with supports of reduced length and cross sectional area.

In operating the test unit with either power source, the procedure after inserting a "blank" metal specimen is as follows:

(1) Adjust the current regulating device, provided with either the A. C. or D. C. power supply, to deliver a moderate amount of current corresponding to 150 to 275 amperes. These quantities of current import a fairly uniform temperature to steel specimens 0.017 inch thick for a period of at least three minutes.

(2) Commence the test by turning switch C to the "on" position, thereby actuating contactor A which starts timer T due to closing of contactor B. Contactor B is normally open, but closes due to the voltage drop in the test circuit.

(3) Observe the ammeter and voltmeter at the instant of throwing switch C in order to obtain the "zero time" starting current and voltage drop across the specimen.

(4) Obtain the "workability range" of the test specimen for different current regulator settings by recording the current and voltage readings at 10 to 20 second intervals over a period of 3 to 4 minutes. As pointed out, supra, these data are most conveniently obtained with an automatic graphic recorder which gives permanent continuous records of the current and voltage readings at definite time intervals.

(5) Open the test circuit by turning switch C to the "off" position, an operation which demagnetizes the coils of contactors A and B and stops timer T and the flow of current through the test specimen. The same operations occur by fusing the specimen.

Current and voltage readings are useful in computing the electrical resistance of the test supports at any time after closing switch C. These data are plotted as reference curves for estimating the amount of heat supplied experimental materials in repeat tests.

The same procedure is repeated in determining the fusion times of "blank" specimens for starting currents in excess of 275 amperes. Fusion times thus obtained for starting currents in excess of 275 amperes flowing through test specimens 0.017 inch thick are given by Table 1.

Table 1

"Zero Time" Starting Currents, Amperes	Time in Seconds Required for Fusion
275	greater than 180
300	85–90
350	47–49
400	31–33
420	17–18
475	10–11
520	7–8

For all practical purposes, the voltage drops for starting currents ranging from 150 to 275 amperes show only very small increases after the current is allowed to flow through the test supports for a period of 90 seconds. In other words, the resistivity corresponding to these "constant currents" is practically unaffected as the strip is continuously heated, and a condition of substantially uniform temperature is set up. On the other hand, starting currents of 300 to 600 amperes produce constantly increasing temperatures as the specimens are heated until fusion occurs. Nevertheless, operation of the device at these higher currents is indispensable for the evaluation of surface coatings and other materials such as plastic sheeting whose thickness does not exceed $\frac{1}{32}$ inch, because the sudden acquisition of high temperatures ignites any solid combustible materials present or volatile decomposition products before they can escape by vaporization or diffusion.

Temperature data preferably should be obtained with a photoelectric recording potentiometer similar and equal to the instrument manufactured by the General Electric Company. The use of such an instrument to provide the data for time-temperature curves is especially advantageous since instantaneous readings over the range of 400 to 3000° F. can be readily obtained with a platinum-platinum rhodium thermocouple attached to the support. Other devices such as the radiation pyrometers coupled with "Micromax" recorders manufactured by the Leeds and Northrup Company can be used, but are not favored because of time lag and the dependance of readings on the distance of the pyrometer from the strip and variable areas selected for observation.

The use of platinum-platinum rhodium thermocouples in conjunction with the recording photoelectric potentiometer is superior to radiation and optical pyrometers since it permits simultaneous readings of the temperature of the metal support beneath the test material. This procedure is followed with organic materials exceeding 0.01 inch in thickness when it is incorrect to assume that the temperature of the strip is identical with the value given by the time-temperature reference curve for uncoated, or "blank," metal supports. The higher temperatures usually obtained under these circumstances for the same current, voltage and time readings are due to the thermal insulating properties of the test material. These temperature differences are proportional to the thickness of the materials tested and inversely proportional to their thermal conductivity.

Table 2 gives time-temperature reference data for uncoated supports in degrees Fahrenheit and the times in seconds which corresponds to various starting or "zero time" currents for mild or cold-rolled steel specimens averaging 0.017 inch in thickness. These data were obtained with the assistance of an optical pyrometer for different "zero time" starting currents. The results are valuable in illustrating the principles of the invention, although it is recognized that more accurate data are obtainable with thermocouples and a suitable recording instrument with negligible time lag for starting currents in excess of 275 amperes, as explained above. All such improvements in applying the best available instrumentation for recording the basic data of temperature, current, voltage and time are considered within the scope of this invention.

Table 2

"Zero Time" Starting Currents, Amperes	Temperature, Degrees Fahrenheit, Time, Seconds								
	7	10	12	15	30	40	60	80	100
200	160	230	270	350	700	900	1,230	1,400	1,400
220	360	500	600	730	1,240	1,450	1,600	1,600	1,600
250	460	640	740	810	1,460	1,670	1,770	1,770	1,770
275	800	1,040	1,180	1,340	1,830	1,940	1,940	1,940	1,940
300	1,040	1,250	1,380	1,540	2,020	2,170	2,330	2,420	2,430* at 86 sec.
325	1,300	1,540	1,680	1,800	2,220	2,320	2,460	2,500* at 74 sec.	
350	1,450	1,660	1,880	2,040	2,420	2,500	2,540* at 48 sec.		
375	1,560	1,900	2,040	2,200	2,500	2,620* at 45 sec.			
400	1,700	2,080	2,280	2,400	2,680* at 32 sec.				
420	1,770	2,200	2,500	2,660	2,740* at 18 sec.				
475	1,880	2,600	2,810* at 11 sec.						
520	2,560	2,890* at 8 sec.							

NOTE.—Fusion temperatures are indicated by asterisks.

The rapidity with which the support is heated to temperatures of 1700° F. and above with starting currents in excess of 400 amperes explains the success of this method in securing flammability data on single coats of paint not exceeding 1 mil. in thickness. Hitherto, with previous methods, it was necessary to use 4 to 5 mils., or a 4 to 5 coat system of the same paint, to detect flammability. The rapid heating of the substratum which permits ignition of the thermal decomposition products of the solid organic binder, in situ, before they can be driven off by heat, is an outstanding feature of this invention.

In practice, the majority of determinations are made by the "constant-current technique" which insures steady temperatures of 200 to 2000° F. for heating periods of 3 minutes or more without fusion of the support. In this method, organic materials affixed to the metal strip are subjected to a substantially constant heat source, and the minimum time required for visible burning to take place and the duration of burning recorded. This technique affords a uniform source of heat of sufficient intensity for the majority of organic materials of thickness varying from 0.0005 inch for surface coatings to 0.125 inch for battleship linoleum.

The results obtained with "blank" specimens further show that the test unit also includes provisions for determining fire retardance as a function of the first visible detection of burning when starting currents of 300 to 600 amperes are impressed on the test specimens. In procuring data by this procedure, the "zero time" currents are gradually increased from 300 amperes to the critical or "threshold" current minimum that just permits ignition of the experimental material. These critical current values and the duration of burning after the current is turned off comprise the criteria of flammability by this method.

The foregoing technique for determining threshold currents is intended for surface coatings and thin sheets of plastics and other organic materials designed to meet the most severe requirements for fire resistance. The upper limit of thickness of dried organic surface coatings or other organic materials of the most refractory character, as exemplified by the silicone resins, evaluated by this procedure is in the neighborhood of 0.01 inch. Fire-retardant materials exceeding this thickness can be more conveniently evaluated by the "constant current technique."

The threshold current technique is also used to determine the varying degrees of solvent retention by surface coatings. The procedure is to measure displacements of the minimum currents required for burning to higher values as the thinner is gradually eliminated by longer periods of air drying or by baking. Several tests must be made of the same coating applied to different strips and allowed to air dry or bake for various times in order to secure significant results.

It will be noted that the results obtained by both techniques, "constant" and "threshold" currents, are frequently expressed in terms of the starting or "zero time" values obtained at the instant of closing switch C, Fig. 1. But the use of an automatic graphic recorder of time, current and voltage as described, supra, is preferable since the instrument charts give the true currents flowing at the time burning is first noticed. Expression of flammability in terms of the actual current flowing at the critical instant of first burning constitutes a more accurate criterion of comparative fire-retardant characteristics than the various "zero time" current settings obtained with the current regulator control furnished with the power supply.

The most vital factors of this invention are the kinds of metal strips selected for prescribed temperature ranges and their dimensional characteristics. These considerations govern the specifications of the electric power sources required to insure maximum heat, short of fusion, of the various kinds of metal strips required for different temperatures.

The general design of strip having a constriction for the high-resistance heated area, illustrated by Fig. 2, is essential. Investigations with powdered materials require that the longitudinal edges be upturned one eighth of an inch to retain these materials when the support is placed in a horizontal position.

The geometry of the test strip should be apportioned to the maximum load or "duty cycle" of the available electrical power supply.

Thus a power supply with a maximum current rating of only 200 amperes suffices to heat a steel test strip 0.012 inch thick if the width and length of the constricted area is reduced to 0.75 and 4.00 inches, respectively. This strip has only one third the volume of the 6 inch long x 1 inch wide, 0.017 inch thick support used to procure the data of Table 2. A strip having these dimensions for the constricted portion requires a much less ex-

pensive power source, although the observation area is appreciably less.

Other variations in the design of the test strip are useful in obtaining special information on the ignition and burning characteristics of organic materials. For example, horizontal or vertical fins originating from the constricted area and covered with the test material are useful in measuring the amount of horizontal or vertical propagation of flame after ignition occurs and the current is turned off.

An essential qualification of the type of sheet metal chosen for fabrication of the test specimen supports of this invention is that it possess high temperature coefficients of resistivity, so that sufficiently high temperatures can be readily obtained for evaluating the most refractory materials without taxing the current source. A second requirement is that it be inexpensive since thermal expansion and surface oxidation reactions usually render the same specimens unsuitable for more than one test run. Annealed hot or cold-rolled steel specimens are favored for this purpose, because their resistivity increases ninefold to tenfold in the range of 2500 to 2600 degrees Fahrenheit.

While steel specimens are preferred because they can be economically discarded after each test run, nichrome sheet specimens also can be used for repeat runs at temperatures below 1800° F. where expansion and surface chemical effects are less objectionable. Nichrome and other high-resistance alloys have the outstanding advantage of permitting a large number of repeat runs with the same specimen below certain critical temperatures when allowance is made for expansion effects. The occurrence of surface oxidation reactions resulting in the formation of fire scale and the accompanying changes in resistivity prevent the use of steel for repeat runs for temperatures exceeding 900° F.

Platinum supports can be used advantageously for a large number of tests, particularly for inorganic compounds and pigments. The same specimen can be used repeatedly in this case. However, the use of platinum is not recommended for evaluating organic materials since carbonaceous gases, such as carbon monoxide resulting from the incomplete combustion, have a deleterious effect on the metal.

The effect of exceptionally high temperatures, in the range of 2000 to 3000 degrees centigrade, on various oxides, silicates and other inorganic compounds can be investigated with the aid of metal supports consisting of sheet molybdenum, tantalum of tungsten. Tungsten sheet stock is only presently available as ¼ inch ribbon, however. Tests with these metals must be carried out in a reducing atmosphere of hydrogen or other inert gas. At the conclusion of such tests, the heat treated powders can be scraped off the supports and investigated for chemical changes that might have occurred.

It is to be understood that various modifications and changes can be made in the above exemplification of this invention without departing from the spirit and scope thereof as set forth in the appended claims.

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

What is claimed is:

1. An apparatus for testing the thermal stability of specimens comprising a metal support for the specimen, said support having a constricted portion serving as a high electrical resistance area, a fixed electrically conductive terminal contact for securing one end of said support, an electrically conductive, yieldingly movable head contact for yieldingly securing the other end of said support to accommodate changes in the length of said support, a temperature indicator adjacent said support for indicating the temperature of said support, means for providing a non-luminous flame adjacent said support, a suction blower adjacent said support, a main electrical circuit adapted for connection to an electrical power source and including said terminal contact and said movable head contact in series, a voltmeter connected in parallel with said contacts, an ammeter connected in series with said contacts, a switch in said circuit, an auxiliary circuit including a relay for operating said switch, a timer connected in parallel with said relay, a switch in series with said timer, a relay in said main circuit in parallel with said contacts for operating said timer switch.

2. An apparatus for testing thermal stability of a specimen, said apparatus comprising a metal support adapted to have a specimen mounted thereon, an electrical circuit adapted for connection to a power source and including said support in series, electrical instruments in said circuit for indicating the electrical energy supplied to said support, an electrical timer in said circuit, means adjacent said support for maintaining a non-luminous flame, and a temperature indicator adjacent said support.

3. An apparatus for testing the thermal stability of a specimen, said apparatus comprising a metal support adapted to have a specimen mounted thereon, an electrical circuit adapted for connection to a power source and including said support in series, igniting means spaced slightly from said support, and a temperature indicator adjacent said support.

4. An apparatus for testing the thermal stability of a specimen, said apparatus comprising a metal support adapted to have a specimen mounted thereon, an electrical circuit adapted for connection to a power source and including said support in series, means adjacent said support for maintaining a non-luminous flame, and a temperature indicator adjacent said support.

5. An electrical system for heating an object comprising a metal resistor adapted to support the object, a main electrical circuit adapted for connection to an electrical power source, said main circuit including said resistor in series, a voltmeter connected in parallel with said resistor, an ammeter connected in series with said resistor, a switch in said main circuit, an auxiliary circuit including a relay for operating said switch, a timer connected in parallel with said relay, a switch in series with said timer, and a relay in said main circuit in parallel with said resistor for operating said timer switch, said relay being connected in said main circuit between said resistor and said main circuit switch.

6. An electrical system for heating an object comprising a metal resistor adapted to support the object, a main electrical circuit adapted for connection to an electrical power source, said main circuit including said resistor in series, electrical instruments in said main circuit for indicating the electrical energy supplied to said resistor, a switch in said main circuit, an auxiliary circuit including a relay for operating said switch,

a timer connected in parallel with said relay, a switch in series with said timer, and a relay in said main circuit in parallel with said resistor for operating said timer switch, said relay being connected in said main circuit between said resistor and said main circuit switch.

7. An apparatus for testing the thermal stability of a specimen, said apparatus comprising an electrical resistor adapted for support a specimen, an electrical circuit for energizing said resistor to cause heating of the resistor and specimen, and means adjacent said support for maintaining a non-luminous flame.

8. An apparatus for testing the thermal stability of a specimen, said apparatus comprising

an electrical resistor adapted to support a specimen, an electrical circuit for energizing said resistor to cause heating of the resistor and specimen, and igniting means adjacent said resistor for igniting gases from the heated specimen.

HOWARD R. MOORE.

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