

Feb. 19, 1957

S. S. PRENTISS

2,782,103

ANALYZER FOR GASEOUS MIXTURES

Filed Oct. 12, 1951

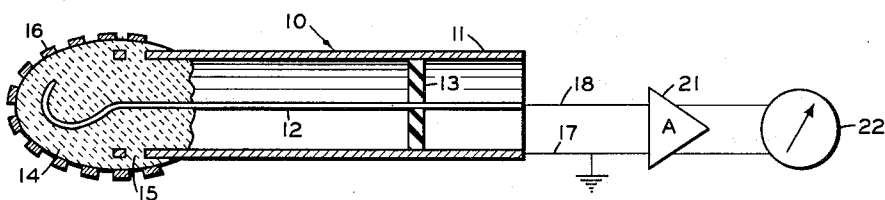


FIG. 1

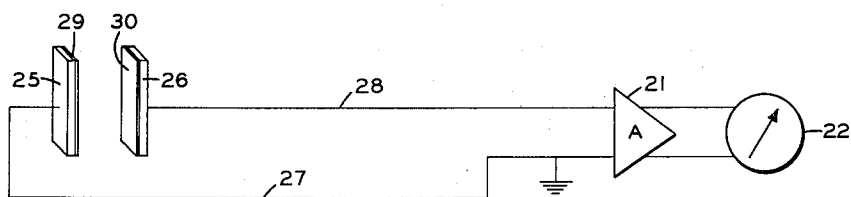


FIG. 2

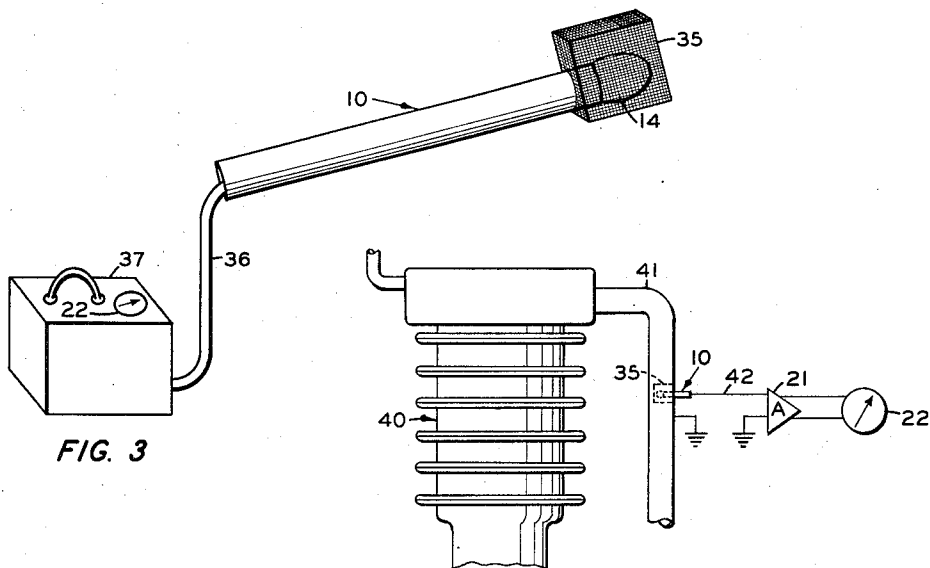


FIG. 3

FIG. 4

INVENTOR.
S. S. PRENTISS

BY *Hudson & Young*

ATTORNEYS

1

2,782,103

ANALYZER FOR GASEOUS MIXTURES

Spencer S. Prentiss, Bartlesville, Okla., assignor to Phillips Petroleum Company, a corporation of Delaware

Application October 12, 1951, Serial No. 251,115

1 Claim. (Cl. 23—255)

This invention relates to the analysis of gaseous mixtures. In another aspect it relates to the detection of explosive and combustible gaseous mixtures.

In many diversified fields of present day industry there is a need for rapid and safe methods of analyzing gaseous mixtures. This is particularly true in those industries wherein explosive vapors are likely to be encountered, such as in mines and around petroleum and chemical processing plants, for example. Efficiency studies of internal combustion engines, jet engines, and the like often require an analysis of the exhaust gases therefrom or of the fuel-air ratio of the input feed mixture. In petroleum exploration and drilling operations it is desirable to analyze soil and mud particles, since the detection of changes in the combustible gas contained therein often gives valuable information as to oil bearing strata. From the foregoing illustrations, which obviously include only a few of the many applications of combustible gaseous mixture analysis, it should be apparent that there is a widespread need for efficient analyzers.

For some time it has been known quite generally that certain substances, in the presence of a combustible fluid mixture, have the property of promoting combustion along their surfaces which results in the combustible constituents of the fluid mixture uniting with any air or oxygen which may be present. An example of such a substance is platinum which is a catalyst of combustion under certain temperature conditions. When a combustible material is brought together with air or oxygen in the presence of such a catalyst of combustion, the temperature of the latter is increased by an amount depending upon the proportion of combustible constituents present. By measuring this increase in temperature there is provided an indication of the percentage of combustibles present in the mixture. In accordance with this principle, apparatus has been provided for detecting combustion of a gaseous mixture on the surface of a heated platinum filament. Heat generated by the oxidation of the gas increases the temperature of the filament thereby resulting in an increase in the electrical resistance of said filament. This change in resistance is measured by means of a Wheatstone bridge circuit wherein the platinum filament constitutes one of the resistance arms of said bridge. Another known method of gaseous analysis based upon this catalytic property of platinum employs a strip of platinum wire positioned around the bulb of a thermometer device. Any increase in temperature of the platinum due to combustion taking place on its surface is indicated by the reading of the thermometer. While these various known devices operate in a satisfactory manner under certain conditions, most of these devices lack the desired degree of portability and rigidity which is needed in many testing operations. A further limitation is that these devices usually require that the gaseous mixtures under analysis be maintained within an analysis chamber.

It is toward providing an improved form of gaseous

2

analyzer and detector that the present invention is directed. In accordance therewith, a catalytic agent is disposed upon the surface of a flame detecting device which can be positioned directly in the region of a mixture under analysis. The improved form of flame detecting device employed in this manner is essentially of the form described in the copending application of D. R. De Boisblanc, Serial No. 220,113, filed April 9, 1951, entitled "Detecting Device."

Accordingly, an object of this invention is to provide means for safely and accurately indicating the presence of an explosive or gaseous mixture.

Another object is to provide means for analyzing gaseous mixtures to determine the proportions of combustible components present therein.

A further object is to provide means for analyzing the fuel-air ratio of feed streams to internal combustion and other type engines.

A still further object is to provide apparatus for carrying out the above-mentioned objects which is simple to construct, easy to operate, and which is capable of giving rapid reliable results.

Various other objects, advantages, and features of this invention should become apparent from the following detailed description taken in conjunction with the accompanying drawings illustrating a preferred embodiment of this invention in which:

Figure 1 is a schematic view of a combustible gaseous mixture detecting probe together with suitable electrical indicating circuitry;

Figure 2 illustrates a second form of the testing apparatus;

Figure 3 shows a modification of the apparatus of Figure 1 especially adapted to detect the presence of explosive vapors; and

Figure 4 illustrates an application of this analysis instrument for studying the fuel-air input mixtures to internal combustion engines.

An improved form of combustion detecting device recently has been developed which relies upon the principle that in any given electrical resistance element having two electrodes connected thereto, one of which is grounded, there exists a constant distribution of potential at all points throughout said element. If an electrically charged particle is brought into contact with the surface of this element electrical current will flow therein until all points within the element are once again at zero or ground potential. During the time when current is flowing, the region of the element in the neighborhood of the ungrounded electrode exhibits a potential variation which is dependent upon the magnitude of the charge of the particles striking said element, the electrical resistance of the element, and the geometric relation of the ungrounded electrode with respect to the second grounded electrode. By measuring this potential variation through the use of a suitable amplifying circuit there is obtained an indication of the presence of the electrically charged particles striking the element. Since it is known that ionized gases occur in the region of a flame this method of measuring potential variation provides an effective means for determining the presence of flame in the region of said detecting element. In the aforementioned copending De Boisblanc application there is described appropriate apparatus which can be used in this manner for flame detection.

Referring now to the drawings in detail and to Figure 1 in particular, there is shown a combustion detecting element 10 comprising a cylindrical metallic casing 11 having a metallic electrode 12 positioned therein and electrically insulated from casing 11 by means of suitable insulating support such as 13. A ceramic refractory tip

3

14, into which, while plastic, is inserted the hook-shaped end of electrode 12, is positioned across one end of casing 12 and anchored thereto by suitable holes 15 drilled near the end of casing 11. Tip 14 preferably is constructed of a baked and hardened refractory material such as aluminum oxide. Electrode 12 is fitted somewhat loosely into casing 10 so as not to work loose from tip 14 due to thermal expansion at elevated temperatures. Upon the surface of refractory tip 14 there is formed a partial coating of suitable combustion promoting catalytic material such as, for example, thin strips 16 of platinum or other combustion supporting materials which are discussed fully hereinafter. Electrical leads 17 and 18 are attached to casing 11 and electrode 12, respectively, to connect combustion detecting element 10 into the associated electrical circuitry which comprises an alternating current amplifier 21 and an output indicating device or meter 22.

The operation of the flame detecting probe per se, which is not the subject of the present invention, can be explained in the following manner. Assuming that tip 14 is positioned in the region of a flame, then the ions contained within said flame will bombard the surface of tip 14 and in so doing generate electrical voltage fluctuation across said tip. Each ion that strikes tip 14 introduces a small burst of current therein. It is believed that the voltage fluctuations generated between casing 11 and electrode 12 by the individual bursts of current have a statistical fluctuation in magnitude over a wide frequency range. However, these electrical signals must be amplified many fold by amplifier 21 before being of sufficient magnitude to give a readable signal on meter 22.

The present invention, however, is directed to the addition of a suitable combustion supporting catalyst such as platinum strips 16 to tip 14. When probe 10 is inserted into the region of a combustible mixture there is a tendency for combustion to take place upon the surface of said element even though the temperature is not high enough to normally initiate combustion. This surface combustion in turn provides the ions required to actuate the flame detecting probe. In this manner the reading on meter 22 is indicative of the presence of a combustible mixture in the region surrounding probe 10.

In Figure 2 there is illustrated a second form of detecting device which comprises a pair of spaced opposing electrodes 25 and 26 connected in circuit arrangement with amplifier 21 by means of connecting leads 27 and 28, respectively. The output of amplifier 21 is indicated on meter 22. Partial coatings 29 and 30 of combustion supporting catalytic material are formed on the opposing surfaces of electrodes 25 and 26, respectively. The operation of this second form of detecting device is essentially the same as that of the probe in Figure 1, it having been found that the air gap between electrodes 25 and 26 serves essentially the same function as the ceramic noise resistance element 14 positioned between casing 11 and electrode 12 in Figure 1, and that coatings 29 and 30 serve the same function as coating 16 on element 14.

In Figure 3 there is shown a portable combustion detecting unit which is particularly adapted to determine the existence of an explosive mixture such as may be encountered in mines, for example. Probe unit 10 contains an elongated casing 11 which can serve as a handle for conveniently carrying the probe unit into a region containing what may be an explosive atmosphere. Tip portion 14, upon which combustion readily takes place due to platinum coating 16 thereon, is completely enclosed within a screen 35 of an effective heat conducting material such as copper wire. Screen 35 serves to prevent any flame which may be initiated upon the surface of tip 14 from escaping outward therefrom, said screen 35 forming essentially a Davy's safety lamp. Probe 10 is connected by means of a flexible conduit 36 to a portable indicating unit 37 which contains amplifier 21 and output meter 22. In place of, or in addition to, output meter 22, a suitable warning device such as a bell or buzzer can

4

be inserted therein. Wire screen 35 thus allows combustion detecting probe 10 to be used in atmospheres of explosive vapors without danger of any flame initiated on tip 14 escaping into the region of the explosive vapors.

In Figure 4 there is illustrated an application of this combustion detecting element for use in efficiency studies of internal combustion engines. Such an engine is illustrated schematically at 40 as being supplied with a fuel-air input mixture through intake manifold 41. Inserted within manifold 41 is a probe element 10 surrounded by a protecting wire screen 35. Electrode 12 is connected to the input of amplifier 21 by an electrical lead 42, the input circuit being completed by a grounded lead which can be applied directly to a manifold 41. The input fuel-air mixture which enters engine 40 thus surrounds probe 10 which is employed to initiate combustion of a portion thereof. Protective screen 35 prevents this combustion from taking place throughout manifold 41. Since the reading on output meter 22 is indicative of the degree of combustion taking place upon probe 10, this meter reading can be calibrated to give an indication of the proper fuel-air mixture entering engine 40. This is true because the degree of combustion is influenced by the ratio of fuel to air supplied engine 40. In addition to its use as an indicating device, the output signal of amplifier 21 can be applied to suitable control mechanism to regulate the fuel-air input supplied by the carburetor, not shown. In this manner engine 40 can be operated at the condition of maximum efficiency by proper regulation of its fuel-air input ratio. Approximately the same results can be obtained by positioning the combustion detecting probe 10 within the exhaust fumes of engine 40. By measuring the combustible content of the output exhaust fumes, a similar indication is obtained of the efficiency of the engine. Again, suitable control mechanism can be employed in response to the signal from amplifier 21 to control the initial fuel-air input ratio. In addition to studies of internal combustion engines, other types of engines such as turbo-jets, for example, can be studied with this probe in like manner.

In addition to the above-mentioned platinum coating, various other materials can be employed as combustion supporting catalytic agents. It has been found that even the stablest organic substances when mixed with air and passed over suitable catalytic surfaces will commence to oxidize at quite moderate temperatures. Particularly active in this respect are the various metals of the platinum group which include platinum, palladium, iridium, rhodium, osmium and ruthenium. In addition, the oxides of iron, cobalt, nickel, chromium, copper, manganese, silver, and cerium are catalytic in somewhat the same manner. Platinum black, platinum sponge and the corresponding forms of palladium also are quite active as well as the metallic elements themselves. For the detection of carbon monoxide, the catalyst "Hopcalite" is particularly effective. Hopcalite is a mixture of the following approximate composition: cupric oxide, 30 percent; manganese peroxide, 50 percent; cobaltic oxide, 15 percent; and silver oxide, 5 percent.

The detecting elements of this invention can be constructed in various manners; one of which comprises depositing a coating of the catalytic active material upon a portion of the surface of the probe element itself. This coating can be in the form of thin strips or wires of the catalytic material disposed either directly on the surface of the probe or protruding therefrom like whiskers. A second mode of construction comprises mixing a quantity of the catalytic material with the material of which the probe tip is formed, the latter procedure resulting in catalytic points being formed on the surface of the probe which serves to isolate the combustion at said individual points. In this embodiment the magnitude of the combustion taking place is not as large as if the catalytic material is coated on the entire surface. However, such a probe

has a greater safety factor when used in the detection of explosive vapors.

In constructing the probe element of Figure 1 various ceramic refractory materials can be used in addition to aluminum oxide to form the tip element 14. Examples of these substances which have been found effective include the oxides of calcium, magnesium, zirconium, beryllium, and thorium; and the carbides of titanium, zirconium, columbium, tantalum, silicon, tungsten, and hafnium. The probe element itself can be constructed in various configurations as illustrated in the copending application of R. S. Marsden, Jr., Serial No. 220,116, filed April 9, 1951, entitled "Electrical Noise Element." As therein illustrated casing 11 can be formed of a ceramic material as can electrode 12; in addition two electrodes can be positioned within casing 11 thereby eliminating casing 11 as one of the output electrodes. A still further example comprises a mass of ceramic material having two metallic electrodes positioned therein.

Amplifier 21 can be any conventional alternating current amplifier adapted to pass a wide band of frequencies. Since the detected noise signals are of relatively small amplitude amplifier 21 must have high gain and should have little electrical noise introduced therein in order that a maximum signal can be transmitted thereby. The output of amplifier 21 can be indicated on any suitable metering device such as a thermocouple voltmeter or can be rectified to actuate any direct current control or recording mechanism.

While this invention has been described in conjunction with present preferred embodiments thereof, it should be apparent that various changes in details of the apparatus can be made without departing from the scope of the invention; and, further, that the theory set forth, although believed to be accurate, is not considered as the sole basis of the operativeness of this invention. This apparatus does operate successfully and effectively whether or not upon the principles described herein.

Having described my invention, I claim:

Apparatus for indicating the presence of a combustible gaseous mixture comprising a metallic casing having an electrode positioned within and electrically insulated from the casing, a tip of electrically conductive refractory ma-

terial positioned between and electrically connecting said casing and said electrode, a catalytically active agent positioned on said tip, said agent being capable of initiating combustion of a gaseous mixture to be analyzed, alternating current amplifying means having the input terminals thereof connected to said electrode and said casing, respectively, and means to indicate the output signal of said amplifying means which is representative of electrical voltage fluctuations that are generated by combustion of the mixture to be analyzed taking place in the region of said tip.

References Cited in the file of this patent

UNITED STATES PATENTS

15	262,054	Kitsee	Aug. 1, 1882
	1,421,720	Toberts	July 4, 1922
	1,880,941	Erickson	Oct. 4, 1932
	2,219,540	Miller	Oct. 29, 1940
	2,285,866	Markle	June 9, 1942
20	2,298,288	Gerrish et al.	Oct. 13, 1942
	2,363,478	Boeke	Nov. 28, 1944
	2,437,720	Ackley	Mar. 16, 1948
	2,508,588	Waltman	May 23, 1950
25	2,511,177	Richardson	June 13, 1950
	2,577,435	Siebenthaler	Dec. 4, 1951
	2,581,812	Page	Jan. 8, 1952
	2,583,930	Cotton	Jan. 29, 1952
	2,617,716	Hartline	Nov. 11, 1952
30	2,688,648	McIlvaine	Sept. 7, 1954

FOREIGN PATENTS

	11,101	Great Britain	July 16, 1890
	398,722	Great Britain	Feb. 1, 1933
35	591,808	Great Britain	Aug. 29, 1947

OTHER REFERENCES

	Cook et al.:	"Physical Review,"	vol. 74, No. 11, Dec. 1, 1948, pages 1714-1719. (Copy in Scientific Library.)
		"Chem. Engineering,"	vol. 57, No. 8, page 149, August 1950, item 149A. (Copy in Scientific Library.)
40	Garrison et al.:	"Review of Scientific Instruments,"	vol. 20, No. 11, November 1949, pages 785-794. (Copy in Scientific Library.)