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[54] **METHOD OF MANUFACTURE OF AN EXHAUST GAS SENSOR FOR AN AIR-FUEL RATIO SENSING SYSTEM**

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Related U.S. Application Data

[63] Continuation of Ser. No. 198,515, Nov. 15, 1971, abandoned.

[52] **U.S. Cl.** ..... **29/592;** 23/232 E; 23/254 E; 29/625; 156/89

[51] **Int. Cl.** **G01n 29/02**

[58] **Field of Search** ..... 23/232 E, 254 E, 255 E; 204/195 P, 195 M, 195 S; 73/27 R, 26; 338/34, 249, 254, 255, 256, 314; 29/592, 610, 612, 613, 614, 625, 627; 156/89, 228, 242, 246

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[57] **ABSTRACT**

A titanium dioxide ceramic disc having two spaced electrodes embedded therein is located in the exhaust passage of a reciprocating internal combustion engine. The electrical resistance across the electrodes is proportional to the equilibrium oxygen pressure of the exhaust gases and thus represents the air-fuel ratio of the mixture supplied to the engine.

6 Claims, 3 Drawing Figures

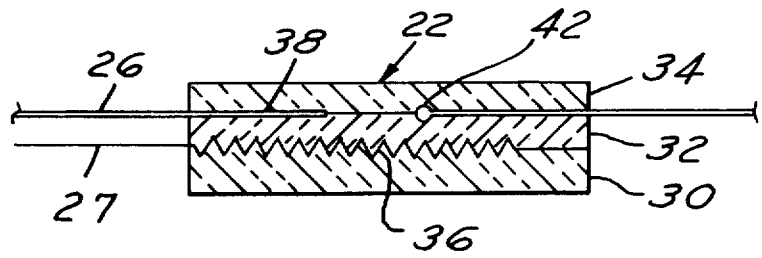
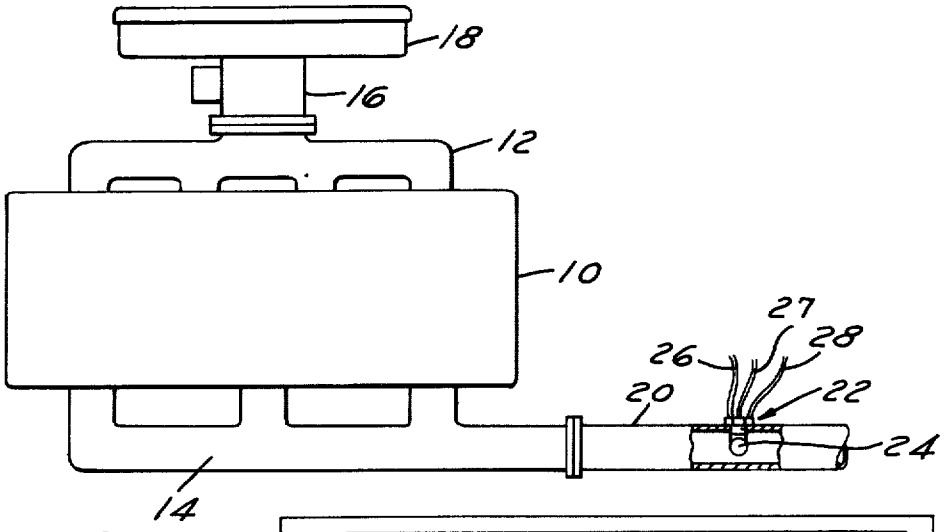


FIG.1



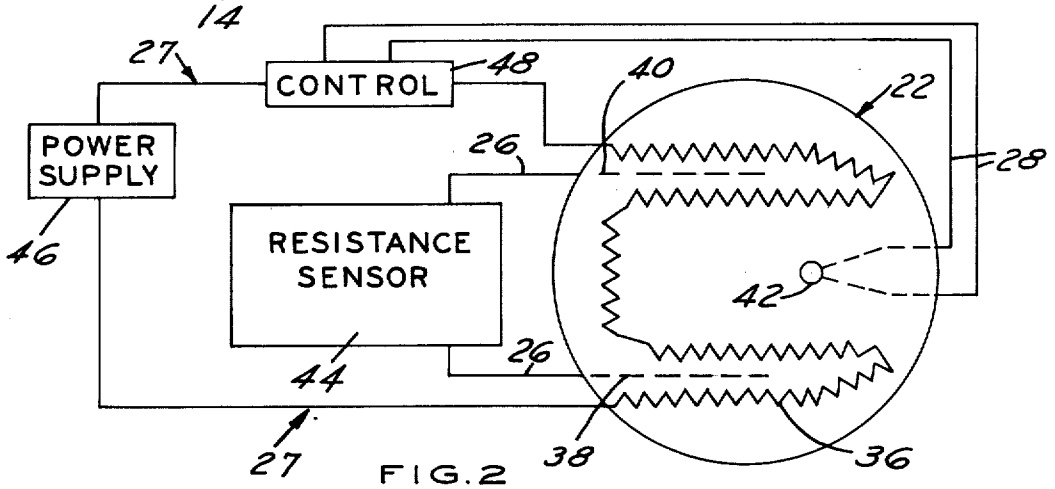


FIG.2

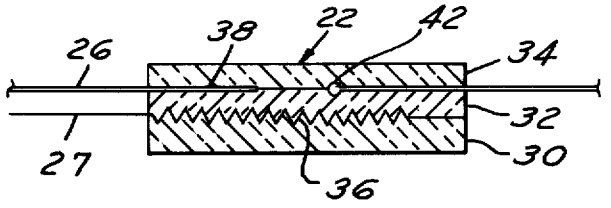


FIG.3

METHOD OF MANUFACTURE OF AN EXHAUST GAS SENSOR FOR AN AIR-FUEL RATIO SENSING SYSTEM

This is a continuation of application Ser. No. 198,515, filed Nov. 15, 1971, now abandoned.

SUMMARY OF THE INVENTION

The temperature of the exhaust gases leaving the combustion chambers of reciprocating internal combustion engines is proportional to the amount of combustion taking place within the engine and this relationship has been used in aircraft for indicating the air-fuel ratio of the combustible mixture being supplied to the engine. Subsequent investigations showed that the thermal conductivities of various exhaust gas components could be used to indicate the proportion of such components in the exhaust gases. These investigations produced systems of the resistance bridge type that compared the thermal conductivity of the exhaust gases with known gas mixtures to indicate either air-fuel ratio or the combustion efficiency of the engine.

Recent interest in improving the environment by diminishing the quantity of undesirable components in the exhaust gases of automotove engines has accentuated investigations into systems for monitoring continuously the air-fuel ratio of combustible mixtures. These investigations have led to numerous refinements of the thermal conductivity system. For example, it was found that thermal conductivity varies almost linearly with the carbon dioxide content of the exhaust gases and carbon dioxide content in turn is proportional to the air-fuel ratio. Subsequently it was found that the thermal conductivity of the exhaust gases is a function of both the carbon dioxide content and the hydrogen content. Other approaches involved combining thermal conductivity devices with exhaust gas temperature devices.

This invention provides a system for determining the air-fuel ratio of the mixture supplied to a combustion mechanism by detecting directly the oxidation-reduction characteristics of the exhaust gases. The system comprises a sensing member made of a metal compound containing oxygen atoms and having at least two metal oxidation states of approximately equal energies that is located in contact with either the air-fuel mixture supplied to the combustion mechanism or the exhaust gases leaving the mechanism. Two electrodes spaced apart from each other by at least a portion of the sensing member are attached to the member and to an electrical or electronic device for sensing the electrical resistance across the electrodes. The electrical resistance is proportional to the equilibrium oxygen pressure of the gaseous mixture in contact therewith and resistance measurements can be converted directly into the air-fuel ratio of the mixture supplied to the combustion mechanism.

Equilibrium oxygen pressure is the partial pressure of the oxygen in a gaseous mixture when the mixture is brought to complete chemical equilibrium. The system of this invention measures equilibrium oxygen pressure of a gaseous mixture even though the gaseous mixture is not at chemical equilibrium, i.e., even though the actual partial pressure of the oxygen exceeds the partial pressure that would be present at equilibrium.

Useful metal compounds containing oxygen atoms and having at least two oxidation states of the metal of approximately equal energies include transition metal

oxides such as titanium dioxide, vanadium oxide, chromium oxide, manganese oxide, iron oxide, nickel oxide, cobalt oxide, and rare earth metal oxides such as cerium oxide, praseodymium oxide, etc. Oxides of the metals are preferable because the ceramic properties thereof provide relatively long useful lives at higher operating temperatures and of the inherent presence of oxygen atoms. Other compounds and mixtures of the oxides with each other and with the other compounds also can be used. Energies of the two oxidation states of the metals must be sufficiently close to permit reversal by changes in the equilibrium oxygen pressure of the gases at operating temperature. Simple empirical tests can be used to determine the required relationship.

Sensing members made from the metal compounds preferably are located in the exhaust gases leaving the combustion mechanism because the exhaust gases approximate more closely the desired operating temperatures of the members and do not contain any unvaporized fuel. The system of the invention is useful particularly in measuring and controlling the air-fuel ratio of the combustible mixture being supplied to an internal combustion engine.

The sensing member preferably is a relatively thin plate made from sintered particles of the desired metal compound. Such plates typically have a density of about **80–95** percent of theoretical; plates of lower density operate effectively but tend to be frangible while plates of higher density, including theoretical density, exhibit decreasing response times. Particle size affects response time only; a wide variety of particles sizes can be used. The electrodes are attached to a surface of the plate or embedded within the plate. One preferred construction involves sandwiching the electrodes between two green ceramic plates and firing the assembly into a unitary structure.

Maintaining the sensing member within a relatively broad temperature range, typically about **600°–900°C.**, produces adequate indications of the air-fuel ratio supplied to an engine despite the fact that temperature variations change the resistance between the electrodes. Temperatures below **600°C** tend to coat the member with soot and other particulate impurities while temperatures above **900°C** tend to decrease overall life. Accuracy improvements are achieved by associating a controlled electrical heater with the sensing member to maintain its temperature within a narrower range. A highly useful structure involves a sandwich made of three green ceramic plates with the electrodes between an outer plate and the middle plate and an electrical resistance wire between the middle plate and the other outer plate. A thermocouple for temperature control can be embedded with either the electrodes or the resistance wire.

It is believed that the metal ions of the metal compounds are reduced or oxidized from one oxidation state to the other in proportion to the reducing or oxidizing nature of the exhaust gases. In the case of titanium dioxide molecules, for example, reduction frees an electron that conducts current much more readily and thereby reduces the resistance of the portion of the ceramic material located between the electrical leads.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a schematic illustration of a reciprocating internal combustion engine showing the installation in

the exhaust pipe of a sensing member of this invention.

FIG. 2 is a schematic plan view of a disc-shaped sensing member of this invention showing the electrical connections thereto.

FIG. 3 is a sectional elevation of the disc-shaped sensing member of FIG. 2 showing the disposition of the electrodes, an electrical resistance heating wire, and a thermocouple in a sandwich construction.

DETAILED DESCRIPTION

Referring to FIG. 1, a reciprocating internal combustion engine 10 includes an intake manifold 12 for delivering an air-fuel mixture to the engine combustion chambers (not shown) and an exhaust manifold 14 for removing the combustion products from the combustion chambers. A carburetor 16 is attached to the intake manifold and an air cleaner 18 is attached to the air inlet of carburetor 16. Carburetor 16 receives fuel from a fuel source (not shown), produces an air-fuel mixture and supplies the air-fuel mixture to intake manifold 12.

Exhaust manifold 14 is connected to an exhaust pipe 20. Threaded into the wall of exhuast pipe 20 is a plug-shaped member 22 comprising a disc-shaped ceramic sensing member 24. Three sets of electrical leads 26, 27 and 28 extend from the top of plug-shaped member 22.

Turning to FIGS. 2 and 3, sensing member 22 comprises a sandwich of three thin ceramic plates 30, 32 and 34. A length of electrical resistance wire 36 is sandwiched between plates 30 and 32. Two electrodes 38 and 40 and a thermocouple 42 are sandwiched between plates 32 and 34. Electrodes 38 and 40 are spaced apart a considerable distance as shown in FIG. 2. The entire sandwich is fired into a unitary structure by conventional ceramic firing techniques.

Electrical leads 26 connect electrodes 38 and 40 to an electrical resistance sensor 44 as shown in FIG. 2. Leads 27 connect the ends of resistance wire 36 to an electrical power supply 46 and leads 28 connect thermocouple 42 to a control circuit 48 located between the power supply and one end of the resistance wire.

Each of plates 30, 32 and 34 consists essentially of titanium dioxide. Each plate has a final thickness of about 0.008 inch and a diameter of about 0.25 inch. The plates are made by a cast tape process that comprises casting a titanium dioxide slurry onto a plastic carrier tape, evaporating the vehicle from the slurry, stripping the plastic tape and punching discs from the remaining green ceramic layer. Titanium dioxide powder having a particle size of −325 mesh is used to make the slurry although subsequent grinding steps might reduce the final particle size.

Resistance wire 36 typically is made of platinum alloyed with about 13% rhodium and is about 0.008 inches in diameter. Electrodes 38 and 40 typically are made of platinum and are about 0.008 inches in diameter. Thermocouple 42 is a gold-palladium-platinum and gold-palladium combination. The green plates, resistance wire, electrodes and thermocouple are sandwiched together as shown and pressed at about 10,000 psi. After pressing, the assembly is fired at about 2300°–2500°F. for 1–2 hours.

The resulting disc is installed in the exhaust conduit of a reciprocating internal combustion engine where exhaust gases will heat the disc to about 700°C. When the engine is supplied with an air-fuel mixture of about 13:1, the resistance across the electrodes is about 2000 ohms. Changing the air-fuel ratio to 14:1 without changing any other engine parameters increases the resistance to about 7000 ohms. An air-fuel ratio of 15:1 produces a resistance of 20,000 ohms. Other embodiments produce resistances ranging from 100 ohms at an air-fuel ratio of 11:1 to 500,000 ohms at a ratio of 16:1.

Actual values of electrical resistance of course depend also on the distance between the electrodes and temperature, but these factors shift the entire resistance vs. air-fuel ratio curve without affecting significantly the shape of the curve. Resistance changes rapidly in the vicinity of the stoichiometric air-fuel ratios and considerable temperature variations can be tolerated when measurements are being made in that vicinity.

A wide variety of materials can be used to make the elctrodes, resistance wire and thermocouple used in the sensing member. The sensing member also can be formed in a wide variety of sizes and shapes including cylinders, squares, rectangles, etc.

Thus this invention provides a system for rapidly and accurately measuring the air-fuel ratio of combustible mixtures supplied to combustion mechanisms. The system is useful not only for analytical purposes but also as an element in a control loop for automatically controlling air or fuel supplies to produce or maintain desired air-fuel ratios.

We claim:

1. A process for preparing an exhaust gas sensing member comprising the steps of

forming a slurry of a major portion of particles of a transition metal oxide;

drying the slurry into a sheet;

forming plates from the dried slurry;

sandwiching spaced electrodes between a pair of said plates; and

firing the sandwiched plates into a unitary structure.

2. The process of claim 1 including the step of sandwiching an electrical heating means between a third plate and one of said pair of plates prior to the step of firing.

3. The process of claim 1 wherein the slurry is formed of particles of the transition metal oxide capable of being fired to achieve a density of from about 80% of theoretical to about 95% of theoretical.

4. The process of claim 3 wherein the slurry is formed of −325 mesh particles of the transition metal oxide.

5. The process of claim 3 wherein the sandwiched plates are fired at a temperature of from about 2300°F to about 2500°F for a period of time less than about two hours.

6. The process of claim 1 wherein the step of sandwiching comprises the steps of: placing a pair of plates in confronting relation on opposite

sides of a pair of spaced electrodes; and pressing said plates together under a pressure of about 10,000 psi.

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