Chapter 3

Catalytic Combustible Gas Sensors

Fig. 1 A Catalytic Bead Sensor

Catalytic bead sensors are used primarily to detect combustible gases. They have been in use for more than 50 years. Initially, these sensors were used for monitoring gas in coal mines, where they replaced canaries that had been used for a long period of time.

The sensor itself is quite simple in design and is easy to manufacture. In its simplest form, as used in the original design, it was comprised of a single platinum wire. Catalytic bead sensors were produced all over the world by a large number of different manufacturers, but the performance and reliability of these sensors varied widely among these various manufacturers. A catalytic bead sensor is shown in Figure 1.

Principle of Operation

Combustible gas mixtures will not burn until they reach an ignition temperature. However, in the presence of certain chemical media, the gas will start to burn or ignite at lower temperatures. This phenomenon is known as a *catalytic combustion*. Most metal oxides and their compounds have these catalytic properties. For instance, volcanic rock, which is comprised of various metal oxides, is often placed in gas burning fireplaces. This is not only decorative, but it also helps the combustion process and results in cleaner and more efficient burning in the fireplace. Platinum, palladium, and thoria compounds are also excellent catalysts for combustion. This explains why the automobile exhaust system is treated with platinum compounds and is called a catalytic converter. This kind of gas sensor is made on the basis of the catalytic principle, and therefore is called the *catalytic gas sensor.*

A gas molecule oxidizes on the catalyzed surface of the sensor at a much lower temperature than its normal ignition temperature. All electrically conductive materials change their conductivity as temperature changes. This is called the *coefficient of temperature resistance* (Ct). It is expressed as the percentage of change per degree change in temperature.

Platinum has a large Ct in comparison to other metals. In addition, its Ct is linear between 500°C to 1000°C, which is the temperature range at which the sensor needs to operate. Because the signal from the sensor is linear, this means that the concentration of gas readings are in direct proportion to the electrical signal. This improves the accuracy and simplifies the electronic circuitry. Also, platinum possesses excellent mechanical properties. It is physically strong and can be transformed into a fine wire which can be processed into small sensor beads.

Furthermore, platinum has excellent chemical properties. It is corrosion resistant and can be operated at elevated temperatures for a long period of time without changing its physical properties. It is capable of producing a constant reliable signal over an extended period of time.

The electrical circuit used to measure the output of catalytic sensors is called a *Wheatstone bridge,* in honor of English physicist and inventor Sir Charles Wheatstone (1802-75). Wheatstone bridges are commonly used in many electrical measurement circuits. As shown in Figure 2, four circuit branches are arranged

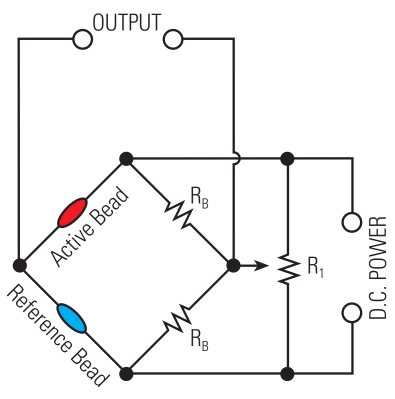

Fig. 2 A catalytic bead sensor Wheatstone bridge–a circuit for measuring an unknown resistance by comparing it with known resistances.

in a square. The source of the electrical current is connected, and between the other pair of opposite corners, the output measurement circuit is connected.

In operation, R_1 is the trim resistor that keeps the bridge balanced. A balanced bridge has no output signal. Resistor value R_B and trim pot R_1 are selected with relatively large resistance values to ensure proper function of the circuit. When the gas burns on the active sensor surface, the heat of combustion causes the temperature to rise, which in turn changes the resistance of the sensor. As the bridge is unbalanced, the offset voltage is measured as the signal. It is important that the reference sensor or bead maintains a constant resistance during the exposure to the combustible gas; otherwise, the measured signal will be inaccurate.

Evolution of the sensor. The original catalytic sensor was a coil-shaped platinum wire. The coiled shape, illustrated in Figure 3, was used to obtain a compact geometry for efficient heating and to produce a strong enough signal to function as a gas sensor. Unfortunately, despite the excellent physical and chemical properties of platinum, it is a poor catalyst for combustion of hydrocarbon gases.

Fig. 3 Hot Wire Sensor

For the proper detection of hydrocarbon gases, the sensor requires a heated surface temperature between 900°C and 1000°C so that the sensor can properly react with gases at a sufficiently high and stable rate. At this temperature, however, the platinum starts to evaporate. The evaporation rate increases as the gas molecules start to react with the sensor and as the sensor temperature increases. This causes a reduction in the cross-section of the platinum wire, and, as a result, the resistance increases. This affects the sensor's operating temperature, which shows up as *zero* and *span drifts.*

The reference wire ideally should be the same as the active wire, with the same geometry and operating temperature, but should be nonreactive with the gas. This is not practically possible, however. A compromise is made by operating the reference wire at a temperature that is substantially lower so that no oxidation takes place in the presence of hydrocarbons. In addition, the reference wire is chemically treated to reduce the catalytic property of the platinum. This may also be achieved by coating platinum wire with a non-catalytic metal, such as gold.

Another problem with hot platinum wire is that it becomes very soft at a temperature of 1000°C. Therefore, it is difficult to maintain its coil shape. Also, the coefficient of thermal resistance becomes less linear as the temperature increases. This situation also results in poor zero and span quality of the sensor, as well as a relatively short operating life.

One way to improve stability of the sensor is to coat the platinum wire with suitable metal oxides. Thus, the final step is to treat the finished sensor or bead with a catalyst, such as platinum, palladium or thoria compounds. Figure 4, shows the sensor bead.

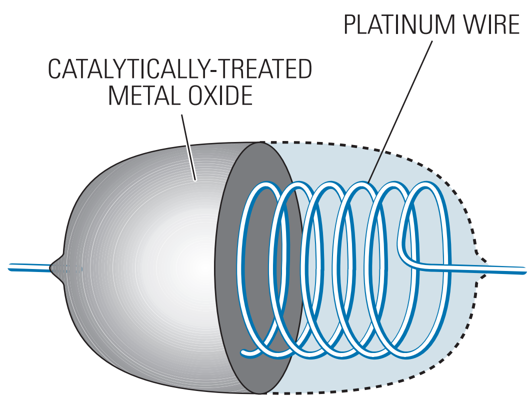

Fig. 4 A Catalytic Bead Sensor

The construction of the catalytic sensor bead is analogous to constructing a building by using reinforced concrete. The coating makes the sensor physically very rugged. The sensor becomes a very small mass which helps make it resistant to shock and vibrations. Most importantly, the catalyst coating reduces the temperature needed to achieve a stable signal for hydrocarbons between 400°C and 600°C.

The use of fine diameter wire not only reduces the size of the sensor, but it also increases the signal, because finer wire has a higher magnitude of resistive value and the signal output is the percentage change of total wire resistance. This also reduces power consumption.

The reference sensor can be constructed in the same way as the active sensor, with the exception that the catalyst chemical is eliminated. The bead can be further treated with chemicals, such as potassium, to prevent the reference bead from reacting with the gas. A near perfectly compensated pair of sensors is now possible. The sensor is called a "catalytic" sensor because the use of the catalyst is the main ingredient involved in the proper functioning of the sensor. The catalytic sensor is stable, reliable, accurate, and rugged, and has a long operating life. The output is linear because the platinum wire has a good linear coefficient of thermal resistance.

Characteristics

The sensor's output is directly in proportion to the rate of oxidation. The maximum output of the signal occurs at about the stoichiometric[1] mixture of the gas, or it is based on the theoretical combustion reaction formula. Methane, for example:

$$CH_4 + 2O_2 + 8N_2 \rightarrow CO_2 + 2H_2O + 8N_2$$

It takes 10 moles of air for one mole of methane to complete the reaction, assuming there is one part of oxygen and four parts of nitrogen in air.

Therefore, for a theoretical combustion to take place, one part of methane will require 10 parts of air

[1] Pertaining to substances that are in the exact proportions required for a given reaction.

to complete the combustion, or theoretically 9.09% of methane in a mixture of air.

For a sensor to detect methane, the signal output will respond linearly from 0–5% of methane (which is 100%LEL). As the concentration reaches close to the stoichiometric value of 9%, the signal increases very rapidly and peaks at around 10%. The signal starts to drop slowly as the concentration of gas passes approximately 20%; after 20% it drops straight down to a level that reflects no output as the concentration of gas reaches 100%. Figure 5, illustrates this effect.

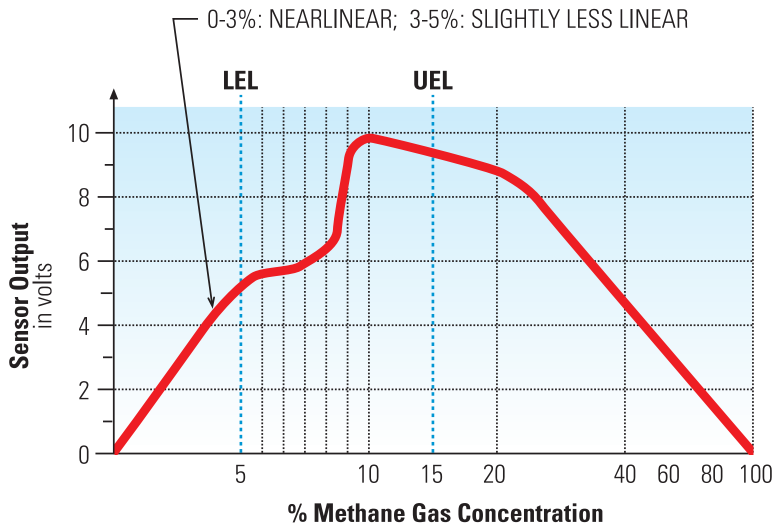

Fig. 5 Sensor Output vs. Gas Concentration

Consider another example, propane. The reaction formula for propane is:

$$C_3H_8 + 5O_2 + 20\ N_2 \rightarrow 3CO_2 + 4H_2O + 20N_2$$

or one part of propane per 25 parts of air for theoretical combustion of propane. The actual theoretical combustion concentration for propane is 3.85%.

The LEL for methane is 5% and for propane is 2.1%. This value is near half of the theoretical combustion value. There is a safety factor of 2 added to ensure safety.

Sensor Operation Factors

There are several factors affecting the operation of the catalytic sensor.

1. Catalyst Poisoning: There are chemicals which will deactivate the sensor and cause the sensor to lose sensitivity and eventually become totally nonresponsive to gases. The most common chemicals that can poison catalytic sensors are those that contain silicon, such as the common oil and lubricants with silicon compounds used as additives in machinery. Sulfur compounds, which are often released with gases, chlorine, and heavy metals also cause the poisoning of the sensor.

The exact cause of this poisoning is very difficult to identify. Some chemicals, with very small concentrations, will totally destroy the sensor. There have been instances in which the silicon contained in simple hand lotions has caused problems with catalytic sensors.

2. Sensor Inhibitors: Chemicals such as halogen compounds, which are used in fire extinguishers and Freon used in refrigerants, will inhibit the catalytic sensor and cause it to temporarily lose the ability to function.

Normally, after 24 or 48 hours of exposure to ambient air, the sensor starts to function normally. These are just a few typical chemicals that inhibit the sensor performance and are by no means to be considered as the sole possible inhibitors.

3. Sensor Cracking: The sensor, when exposed to excessive concentration of gases, excessive heat, and the various oxidation processes that take place on the sensor surface, may eventually deteriorate. Sometimes this will change the zero and span setting of the sensor.

4. Correction Factors: Catalytic sensors are most

Relative Sensitivity

As an example for a typical sensor calibrated for 100% LEL methane gas, the relative sensitivity to other gases is as follows:

Gas	Reading
Methane	*100%*
Propane	60%
n-Butane	60%
n-Pentane	50%
n-Hexane	45%
Methanol	100%
Ethanol	70%
iso-Propyl Alcohol	60%
Acetone	60%
Methyl Ethyl Ketone	50%
Toluene	45%

commonly calibrated to methane for 0-100% LEL full scale range.

The manufacturers generally provide a set of *correction factors* that allow the user to measure different hydrocarbons by simply multiplying the reading by the appropriate correction factor to obtain the reading of a different gas. The reason for using methane as the primary calibration gas is that methane has a saturated single bond that requires the sensor to operate at the highest temperature in comparison to other hydrocarbons. For instance, a typical catalytic sensor for methane gas may require a 2.5-volt bridge voltage to obtain a good signal, while the same sensor will only need 2.3 volts for butane gas. Therefore, if the sensor is set to read butane, it will not read methane properly.

In addition, methane gas is a very common gas and is often encountered in many applications. Furthermore, it is also easy to handle and has the ability to be mixed into different concentrations easily. However, it should be noted that the correction factors are a set of numbers that should be used with great care. The correction factors can vary from sensor to sensor, and they can even change on the same sensor as the sensor ages. Therefore, the best way to obtain precise readings for a specific gas is to actually calibrate the sensor to the gas of interest directly.

5. Percent LEL for Mixtures of Hydrocarbons: For combustion to take place, the following requirements must be present:

a. Combustible mixture

b. Oxygen

c. Ignition source

This is sometimes referred to as the combustion triangle. But in real life, the process of igniting a combustible mixture is much more complicated. The environmental conditions, such as pressure, temperature, temperature of the ignition source, and even humidity can have an affect on the combustible mixture concentration.

If two or more chemicals are involved, it is not even possible to calculate and determine the combustion range of the mixture. Therefore, it is best to consider the worst-case scenario and calibrate the sensor accordingly. Furthermore, a sensor calibrated at a percentage LEL for one gas cannot necessarily be used for other gases. Many instruments on the market today have a scale unit as a percentage of LEL without indicating that the unit is calibrated on methane. Therefore, if the unit is used for some other gas or mixture of gases, the data can be totally meaningless.

For example, a catalytic sensor calibrated on methane produces lower readings when exposed to hydrocarbons of higher carbon content, while infrared instruments will produce much higher readings if exposed to a higher carbon content gas. This is a very common mistake made by many users of gas detection equipment.

Summary

A catalytic sensor is relatively easy to manufacture. However, the quality of the sensor varies quite drastically from one manufacturer to another.

The overall technology of making a sensor for the market is more of an art than a predictable scientific event. This is particularly true in selecting, preparing and processing all the chemicals needed to make the final sensor. There are too many variables in the process that inhibit the making of a predictable final product. Therefore, most users of catalytic sensors select their sensors based on the reputation of the manufacturer.

Typical Specifications for Catalytic Sensors

Sensor Type: Diffusion catalytic bead

Temperature Range: –40°C to +60°C

Response Time: 10 to 15 sec. to 90% of reading

Accuracy: ±5%

Repeatability: 2%

Drift: 5–10% per year

Life Expectancy: Up to 3 years; depending on application

Sensors can be remotely mounted up to 2,000-3,000 meters, depending on the manufacturer and cable size used to wire the sensor.