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(74) Agents: **GRIFFIN, Patrick, M.** et al.; Delphi Technologies, Inc., Legal Staff MC 480-410-202, P.O. Box 5052, Troy, MI 48007-5052 (US).

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(71) Applicant (*for all designated States except US*): **DELPHI TECHNOLOGIES, INC.** [US/US]; Legal Staff - MC 480-410-202, 5825 Delphi Drive, Troy, MI 48098 (US).

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(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **BLOINK, Raymond. L.** [US/US]; 5094 Mark David Drive, Swartz Creek, MI 48473 (US). **CLYDE, Eric, P.** [US/US]; 605 Nebobish Avenue, Bay City, MI 48708 (US). **JAIN, Kailash, C.** [US/US]; 1939 Spiceway Drive, Troy, MI 48098 (US).

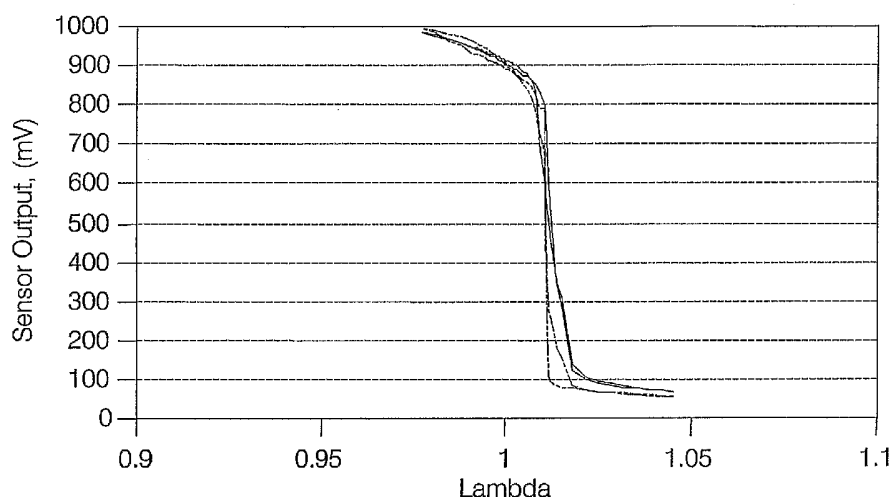
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(54) Title: METHODS FOR FORMING CONICAL SENSORS AND SENSORS FORMED THEREFROM

Co-fired sensors with DAZ1269 Porous Coating:
370C Heated Sensor S Curves, Both Directions



(57) Abstract: One method for coating a conical sensor (10) comprises: disposing a green ceramic coating (36) on a conical sensor element to form a coated-sensor (10), wherein the green ceramic coating (36) comprises a first ceramic powder having a first sintering temperature, a second ceramic powder having a second sintering temperature, a fugitive filler material, and a binder, wherein the conical sensor element comprises an inner electrode (32) disposed on an inner surface (14) of a conical electrolyte body (12), and an outer electrode (34) disposed on an outer surface (16) of the conical electrolyte body (12), and heating the coated-sensor to a firing temperature equal to or greater than the second sintering temperature and below the first sintering temperature.

METHODS FOR FORMING CONICAL SENSORS AND SENSORS FORMED THEREFROM

BACKGROUND OF THE INVENTION

The present disclosure relates to a coating for a sensor, and to its method
 5 of manufacture. More specifically, the disclosure relates to a method for co-firing a sensor element and a coating, and to the conical sensor formed therefrom.

Oxygen sensors are used in the automotive industry to sense amounts of oxygen present in exhaust gases relative to a reference gas, such as air. A switch type oxygen sensor, generally, comprises an ionically conductive solid electrolyte material,
 10 a sensing electrode, which is exposed to the exhaust gas, and a reference electrode, which is exposed to the reference gas. It operates in potentiometric mode, where oxygen partial pressure differences between the exhaust gas and reference gas on opposing faces of the electrochemical cell develop an electromotive force, which can be described by the Nernst equation:

$$E = \left(\frac{RT}{4F} \right) \ln \left(\frac{P_{O_2}^{ref}}{P_{O_2}} \right)$$

15 where: E = electromotive force
 R = universal gas constant
 F = Faraday constant
 T = absolute temperature of the gas
 $P_{O_2}^{ref}$ = oxygen partial pressure of the reference gas
 20 P_{O_2} = oxygen partial pressure of the exhaust gas

The large oxygen partial pressure difference between rich and lean exhaust gas conditions creates a step-like difference in cell output at the stoichiometric point; the switch-like behavior of the sensor enables engine combustion control about stoichiometry. Stoichiometric exhaust gas, which contains unburned hydrocarbons,
 25 carbon monoxide, and oxides of nitrogen, can be converted very efficiently to water, carbon dioxide, and nitrogen by automotive three-way catalysts in automotive catalytic converters. In addition to their value for emissions control, the sensors also provide improved fuel economy and drivability.

Further control of engine combustion can be obtained using amperometric mode exhaust sensors, where oxygen is electrochemically pumped through an electrochemical cell using an applied voltage. A gas diffusion-limiting barrier creates a current limited output, the level of which is proportional to the oxygen content of the exhaust gas. These sensors typically consist of two or more electrochemical cells; one of these cells operates in potentiometric mode and serves as a reference cell, while another operates in amperometric mode and serves as an oxygen-pumping cell. This type of sensor, known as a wide range, lambda, or linear air/fuel ratio sensor, provides information beyond whether the exhaust gas is qualitatively rich or lean; it can quantitatively measure the air/fuel ratio of the exhaust gas.

The solid electrolyte commonly used in exhaust sensors is yttria-stabilized zirconia. This material is an excellent oxygen ion conductor under various exhaust conditions. The electrodes are typically platinum-based and are porous in structure to enable oxygen ion exchange at electrode/electrolyte/gas interfaces. These platinum electrodes may be co-fired. Co-fired electrodes are often used in planar type sensors, in which the electrodes may reside between laminated layers, where many secondary processes are not accessible. In this case, a thick film paste may be screen printed onto unfired (green) ceramic tape and dried. The screen-printed tapes are then stacked, laminated, cut, and fired to make sensors.

The materials and processes used to fabricate sensors often provide a source for contaminant impurities that degrade the performance of the electrochemical cell. These impurities, especially silicon-based impurities, tend to migrate by diffusion, for example in the firing process, creating a barrier to oxygen ion conduction at the electrode/electrolyte interface.

Many oxygen and other gas sensors include an electrolyte body comprising an electrolytic material of a known type formed in a thimble-like or conical shape. The electrolyte body typically includes electrodes on the interior and exterior thereof. It is desirable to protect the electrolyte body with a coating that allows the gas being sensed to pass through while preventing other gases or particulate material from reacting with the surface of the electrode and electrolyte body. Ideally, the coating should act as a diffusion barrier, limiting the gas exchange rate to or from the electrolyte body.

Typically, applying the coating includes flame spraying or plasma spraying magnesia-alumina spinel on the surface of the electrolyte body and/or the outer electrode. A problem with such methods is the requirement for several complex and expensive steps in the manufacturing process of the conical sensor. These methods are also high investment, high maintenance and both have considerable variation inherent to them. One method to resolve the multi-step conical sensor manufacturing process includes providing a coating that can be processed along with the electrolyte body as a secondary ceramic layer. The secondary ceramic layer could be sintered simultaneously with the electrolyte body and electrodes, such that formation of an entire functioning sensor element is obtained in the same sintering process. Application of such coatings, however, creates problems if the amount of shrinkage of the coating during the sintering is different from that of the electrolyte body. Such a difference in shrinkage, can result in stress between the different ceramic layers, giving rise to warping, cracking and/or peeling of the sensor.

SUMMARY OF THE INVENTION

Disclosed herein are methods for coating conical sensors, and sensors formed therefrom. In one embodiment, the method for coating a conical sensor comprises: disposing a green ceramic coating on a conical sensor element, wherein the green ceramic coating comprises a first ceramic powder having a first sintering temperature, a second ceramic powder having a second sintering temperature, a fugitive filler material, and a binder, dip-coating the conical sensor element into the green ceramic coating to form a coated-sensor element, and heating the coated-sensor element to a firing temperature equal to or greater than the second sintering temperature and below the first sintering temperature. The conical sensor element comprises an inner electrode disposed on an inner surface of a conical electrolyte body, and an outer electrode disposed on an outer surface of the conical electrolyte body.

In another embodiment, the method for coating a conical sensor comprises: disposing a green ceramic coating on a conical sensor element, dip-coating the conical sensor element into the green ceramic coating to form a coated-sensor element, and heating the coated-sensor element to the firing temperature, wherein the first sintering temperature is less than the second sintering temperature. The green ceramic coating comprises a first ceramic powder having a first sintering temperature

that is about 85% to about 95% of a firing temperature, and a second ceramic powder having a second sintering temperature that is greater than or equal to about 97% of the firing temperature. The conical sensor element comprises an inner electrode disposed on an inner surface of a conical electrolyte body, and an outer electrode disposed on an outer surface of the conical electrolyte body.

The above described and other features are exemplified by the following figures and detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

Referring now to the figures, which are exemplary embodiments, and wherein the like elements are numbered alike:

Figure 1 is a side elevation sectional view of an embodiment of a gas sensor 10;

Figure 2 is a linear graph depicting diffusion limited current measurements generated from a sensor wherein the sensor's coating was applied by a plasma spray method, and from another sensor wherein the other sensor's coating was applied by the method disclosed herein;

Figures 3 and 4 show representative data for Lambda switching curves for a from groups of more than about 10 each of heated and unheated sensors at initial test;

Figure 5 is a SEM micrograph of a co-fired sensor element;

Figure 6 is a SEM micrograph of a co-fired sensor element where the coating was employed on a bisque electroded zirconia electrolyte body; and

Figure 7 shows the Lambda switching curves for two heated sensors.

DESCRIPTION OF THE PREFERRED EMBODIMENT

A coating for sensors, in particular for conical sensors ("sensor"), is formed by a method of dip coating a coating onto a sensor element and then co-firing the resulting coated-sensor element. Although described in connection with an oxygen sensor, it is to be understood that the coating can be employed with any type of sensor, such as a nitrogen oxide sensor, a hydrogen sensor, a hydrocarbon sensor, and the like.

The sensor element typically comprises an electrolyte body, having an inner surface, an outer surface, and a cavity opening and a cavity terminus located at

opposing ends of the electrolyte body. A reference gas (inner) electrode may be disposed on the inner surface, and an exhaust gas (outer) electrode may be disposed on the outer surface to form an electrochemical cell.

The electrolyte body can be solid or porous, can comprise any material capable of permitting the electrochemical transfer of oxygen ions, preferably has an ionic/total conductivity ratio of about 1, and can withstand temperatures up to about 1,200°C. The electrolyte body can comprise any material typically employed as sensor electrolytes, including, but not limited to, zirconia, and the like, which may optionally be stabilized with calcium, barium, yttrium, magnesium, aluminum, lanthanum, cesium, gadolinium, and the like, as well as oxides, alloys, and combinations comprising at least one of the foregoing materials, with a zirconia/yttria/alumina mixture preferred. Additives that can be incorporated into the electrolyte body include, but are not limited to, binders, waxes, and organic powders. The foregoing additives can also be added to improve the performance characteristics of the sensor. Typically, the electrolyte, which can be formed by, for example, die pressing, roll compaction, tape casting techniques, and the like, has a thickness of up to about 500 micrometers or so, with a thickness of about 25 micrometers to about 500 micrometers preferred, and a thickness of about 50 micrometers to about 200 micrometers especially preferred.

The inner and outer electrodes are preferably disposed in ionic contact with the electrolyte body. These electrodes can comprise any catalyst capable of ionizing oxygen, including, but not limited to, platinum, palladium, osmium, rhodium, iridium, gold, ruthenium, zirconium, yttrium, cerium, calcium, aluminum, silicon, and the like, and oxides, mixtures, and alloys comprising at least one of the foregoing catalysts. The outer and inner electrodes can be formed using numerous techniques, including sputtering, painting, chemical vapor deposition, screen printing, spraying, stenciling, ink striping, and the like.

The thickness of the inner electrode can be up to about 15 micrometers, with a thickness of about 8 to about 12 micrometers preferred to optimize the performance and catalytic activity and therefore reduce an optional heater's wattage requirements. In contrast to the inner electrode, the outer electrode preferably has a thickness of about 5 micrometers to about 20 micrometers. Within this range, a thickness of less than or equal to about 15 micrometers is preferred, with a thickness of less than or equal to about 12 micrometers more preferred. Also within this range, a

thickness of greater than or equal to about 8 micrometers is also preferred, with a thickness of greater than or equal to about 10 micrometers even more preferred.

The coating disposed on the surface of the sensor element, which is capable of being co-fired with the sensor element body and electrodes to form the sensor, may optionally be used to coat the entire sensor element or a portion thereof. The coating can be applied to at least a portion of the outer electrode and/or to at least a portion of the outer surface of the electrolyte body to provide regulated exhaust gas diffusion and protection from poisons contained in the exhaust gas. It is preferable to coat only a portion of the element for fit versus function reasons. Functionally, only the electrode needs to be covered unless the sensor being produced is an isolated ground sensor, in which case the conductive path from the sensing electrode to the assembly interface must be covered as well to isolate the element from the case in the final assembly. With regards to fit, the body of the element is formed by mold and grind techniques which are more precise than dipping or spraying (plasma and flame). The precision of the mold and grind provides far better tolerance fits with the final assembly package, and the Zr body is much better for electrical connections because it is harder and more durable with contact connectors and can have conductive paths printed onto it.

Preferably the coating has a similar degree of shrinkage as that of the outer surface of the electrolyte body and/or the outer electrode on which the coating is disposed. To accomplish this, the coating can preferably comprise a ceramic material capable of sintering at a predetermined sintering temperature. Preferably, then, the ceramic material comprises at least two ceramic powders, the first of which does not sinter to full density at the predetermined firing temperature and the second of which sinters to or near to full density at the predetermined firing temperature. For the first powder, the firing temperature (i.e., the processing temperature; the temperature at which the element will be processed to sinter the powders) should be about 85% to about 95% of the powder's sintering temperature (i.e., the temperature at which the powder sinters to full density). Within this range, a sintering temperature of less than or equal to about 93% of the firing temperature is preferred. Also within this range, a firing temperature of greater than or equal to about 90% of the powder's sintering temperature is also preferred. With respect to the second powder, the firing temperature is preferably greater than or equal to about 97% of the powder's sintering

temperature, with greater than or equal to about 98% of the powder's sintering temperature preferred, and greater than or equal to about 99% of the powder's sintering temperature more preferred, and about 100% of the powder's sintering temperature especially preferred.

5 The first ceramic powder preferably resists shrinkage and the second ceramic powder preferably increases shrinkage during firing. Thus, the ratio of the first and second ceramic powders can be adjusted to adjust the amount of shrinkage of the coating during sintering at the predetermined temperature. The first ceramic powder can comprise an alumina (e.g., alpha alumina or the like), such as those commercially
10 available from Aluminum Company of America (ALCOA); and the second ceramic powder can also comprise an alumina (e.g., alpha alumina, or the like) such as those commercially available from ALCOA, or a milled, partially stabilized zirconia body such as those commercially available from SEPR Corp., with the milled partially stabilized zirconia body preferred. The particular alumina and/or zirconia powders
15 chosen are based upon the firing temperature to be employed and their sintering temperature. A powder's sintering temperature is related to the powder's median particle size and surface area. For example, for a firing temperature of about 1,500°C, the first ceramic powder may have a median particle size of about 1 micrometer to about 1.5 micrometers (with about 1.3 micrometers preferred) and a surface area of
20 about 3 m²/g to about 5 m²/g (e.g., about 3.5 m²/g). Likewise, the second ceramic powder can have a median particle size of about 0.25 micrometers to about 1 micrometer, (e.g., about 0.5 micrometers), with a surface area of about 6 m²/g to about 12 m²/g. For an alumina second powder, a surface area of about 7 m²/g to about 12 m²/g (e.g., about 9 m²/g) is preferred for this firing temperature, while for a zirconia
25 powder a surface area of about 6 m²/g to about 9 m²/g (e.g., about 7.5 m²/g) is preferred for this firing temperature. Preferably, the particles sizes and the surface areas of the first ceramic powder and the second ceramic powder are not equal.

 In order to increase the percentage porosity based upon the total volume of the coating, the coating may further comprise a fugitive filler material. As used
30 herein, a "fugitive filler material" is a material that will occupy space until the coating is co-fired with the sensor after which the fugitive filler material decomposes thereby leaving additional porosity in the coating. The type and amount of fugitive filler material used preferably achieves a substantially uniform pore diameter (i.e., about

90% of the pore volume is within ± 0.1 micrometer of the median diameter, as determined by mercury porosimetry analysis), of about 0.05 to about 1.5 micrometers. Within this range, the median pore diameter is preferably less than or equal to about 1.0, with less than or equal to about 0.5 more preferred. Also within this range, the pore diameter is preferably greater than or equal to about 0.07, with greater than or equal to about 0.1 preferred. The porosity is preferably controllable for particular applications. Porosity may be controlled by the amount of fugitive filler material provided relative to the first and second ceramic powders. Preferably, sufficient fugitive material is employed to attain the desired porosity. Although a porosity of up to about 50% or so based upon the total volume of the coating, can be attained, a porosity of about 10% to about 20% is typically preferred. The amount of fugitive material can be about 10 volume percent (vol%) to about 95 vol% based upon the coating volume (i.e., the combined volume of first ceramic powder, the volume of second ceramic powder, and the volume of the fugitive material). The fugitive filler material may comprise carbon (e.g., carbon black, graphite, and the like), non-soluble organics, and/or other appropriate materials that decompose to leave the desired porosity in the finished coating.

Additionally, the coating may further comprise binder. The binder may include any agents suitable for improving the adhesion between the coating and the sensor, especially during the period prior to firing. A preferable binder system includes poly(vinyl butyral) together with butyl benzyl phthalate. Some other possible binder systems include: ethyl cellulose/diethyl oxalate, polyethylene/butyl stearate, polyvinyl alcohol/glycerine, and the like, as well as combinations comprising at least one of any of the binders mentioned in this paragraph.

When forming the coating, a slurry (e.g., suspension) is preferably prepared. The formation of the slurry may comprise combining the ceramic materials, binder, and fugitive filler material in a solvent wherein the solvent may comprise xylene, ethanol, and the like, and combinations comprising at least one of the foregoing. Additionally, a dispersant may be added to the slurry, wherein the dispersant may include fish oil(s) (e.g., Z-3 fish oil or the like), phosphate ester dispersant(s), and the like. Other dispersants having chemical compatibility with the powder(s) and the solvent.

The slurry (e.g., powder suspension) may comprise about 10 wt% to about 80 wt% of the ceramic material, with about 20 wt% to about 50 wt% preferred; about 1 wt% to about 20 wt% binder, with about 3 wt% to about 15 wt% preferred; about 1 wt% to about 20 wt% of the fugitive filler material, with about 3 wt% to about 15 wt% preferred; about 0.5 wt% to about 2.0 wt% dispersant, with about 0.75 wt% to about 1.75 wt% preferred; and about 20 wt% to about 70 wt% solvent, with about 25 wt% to about 60 wt% preferred. As used herein, weight percent is based on the total weight of the slurry. Within the above range, the powder suspension preferably comprises less than or equal to about 15 wt% of the fugitive filler material, with less than or equal to about 10 wt% more preferred. Also within this range, the powder suspension preferably comprises greater than or equal to about 3 wt% of the fugitive filler material, with greater than or equal to about 5 wt% more preferred based upon the total weight of the slurry. The powder suspension may further comprise about 5 wt% to about 30 wt% of the first ceramic powder. Within this range, the powder suspension preferably comprises less than or equal to about 25 wt% of the first ceramic powder, with less than or equal to about 20 wt% preferred. Also within this range, the powder suspension preferably comprises greater than or equal to about 8 wt% of the first ceramic powder, with greater than or equal to about 10 wt% more preferred. The powder suspension may still further comprise about 5 wt% to about 50 wt% of the second ceramic powder. Within this range, the powder suspension preferably comprises less than or equal to about 45 wt% of the second ceramic powder, with less than or equal to about 42 wt% more preferred. Also within this range, the powder suspension preferably comprises greater than or equal to about 8 wt% of the second ceramic powder, with greater than or equal to about 10 wt% more preferred. As used herein, weight percent is based on the total weight of the slurry.

Prior to adding the binder, the powder suspension may optionally be milled for up to 24 hours. The binder may then be added to the powder suspension to form the completed slurry. The completed slurry may comprise about 1 to about 20 wt% of binder based upon the total weight of the slurry. Preferably the completed slurry comprises, within this range, less than or equal to about 18 wt% binder, with less than or equal to about 13 wt% more preferred. Also within this range, the completed slurry may preferably comprise greater than or equal to about 5 wt% of

binder, with greater than or equal to about 8 wt% more preferred. As used herein, weight percent is based on the total weight of the slurry.

The completed slurry may be mixed, milled, shaken, stirred, or otherwise agitated using any mechanism for mixing solutions for a time sufficient to dissolve the binder. For instance, the completed slurry may be milled at about 110 revolutions per minute (rpm) for at least an hour and then left to sit for up to or exceeding about 16 hours without agitation. Prior to coating the sensor, the completed slurry may be shaken for about two minutes and given a final milling for a period of time sufficient to fully mix and uniformly distribute the materials within the suspension.

The completed slurry may then be vacuum de-aired or slow rolled to eliminate air bubbles that would cause defects in the coating. At this point, the completed slurry may be applied to the sensor to form a green ceramic coating. More particularly, the green ceramic coating is preferably applied to the outer electrode of the sensor and, optionally, over the area where the conductive path on the element contacts the assembly case in the "hip" region (coverage to approximately between where the numbers 22 & 37 are on Figure 1. As used herein, "green ceramic coating" is used generally to refer to the coating before it is co-fired (sintered) with the sensor element.

Preferably, the green ceramic coating is applied to the sensor element after the sensor element has been bisque-fired. Bisque firing is a binder burn-out and partial sintering of the molded and ground green ceramic element body. Bisque firing allows co-firable electrodes and coatings to be applied to the element prior to sintering. For example, when a slurry is used to form the coating, the sensor element can be immersed in the slurry, which is preferably stirred at a constant speed, and then withdrawn from the slurry. The amount of coating deposited on the sensor element depends upon the physical and chemical properties of the slurry, such as viscosity and pH, as well as the withdrawal rate. For example, about 150 milligrams (mg) to about 350 mg of coating can adhere to the sensor element (via wet pickup) by manipulating the withdrawal rate. About 200 mg to about 300 mg of wet pickup (or about 120 mg to about 190 mg of calcined pickup) is preferred.

After coating, the formed coated-sensor element may be sintered (co-fired) at temperatures of up to about 1,200°C, with up to about 1,500°C preferred, for up to about 2 hours, or so, to form the sensor, e.g., to densify the ceramic body as well

as the porous ceramic coating, to form the electrodes, and to burn off the fugitive filler material.

Although a multi-layered coating can be employed, the porous coating (final sintered coating) is preferably a single layer having an overall thickness of about 100 micrometers to about 300 micrometers. Within this range, a thickness of less than or equal to about 250 micrometers is preferred, with less than or equal to about 200 micrometers more preferred. Also within this range, a thickness of greater than or equal to about 110 micrometers is preferred, with greater than or equal to about 120 micrometers more preferred.

After sintering, a secondary poison protective coating may be applied. Various other coatings can be applied over the porous coating for poison protection and the like. Possible coatings are porous and typically comprise metal oxide(s) and have a thickness of less than or equal to about 200 micrometers. For example this protective coating can be formed from metal oxide(s) and fugitive filler material(s). Possible metal oxides can include zirconia, alumina, magnesia, titania, and the like, as well as mixtures, alloys, and combinations comprising at least one of the foregoing metal oxides, with a coating comprising alpha alumina, gamma alumina, or delta alumina, as well as combinations comprising at least one of these aluminas preferred.

Referring now to Figure 1, the sensor is shown generally at 10. Sensor 10 typically comprises an electrolyte body 12 having an inner surface 14, an outer surface 16, a cavity opening 18 located at one end of electrolyte body 12, and a cavity terminus 20 located at an opposing end of electrolyte body 12. An inner electrode 32 is disposed on inner surface 14, and an outer electrode 34 is disposed on outer surface 16. A coating 36 is disposed over outer electrode 34. The coating 36 is deposited on and extends over the active area of sensor 10, (e.g., the area below a lower shoulder 26 extending to the cavity terminus 20; to form a case-ground sensor). Optionally, the coating 36 may extend over the protrusion 22 (over the upper shoulder 24; to form and isolated ground sensor), but preferably does not extend to the end to near the opening 18.

Sensor 10 can be formed in any generally cylindrical shape and is preferably tapered from cavity opening 18 to cavity terminus 20. A protrusion 22 is typically formed on sensor 10 at a point intermediate cavity opening 18 and cavity terminus 20 to define an upper shoulder 24 and a lower shoulder 26 that preferably

extends completely around the circumference of electrolyte body 12. Protrusion 22 is generally configured and dimensioned to engage a surface within a shell portion (not shown) of the gas sensing apparatus into which sensor 10 is received, thereby causing the inactive portion of the sensor 10, e.g., the portion above and including the lower shoulder 26, to extend out of the shell portion while the active portion extends into the shell portion to contact the exhaust gas.

Still referring to Figure 1, the sensor 10 may be incorporated into a gas sensing apparatus (not shown). The upper portion 30 of the sensor 10 may be disposed in electrical communication with a wiring harness assembly (not shown); and a lower portion 37 of the sensor 10 may be disposed within a subassembly (not shown). A heater may be inserted into a cavity 28 of the sensor 10, adjacent to the inner electrode 32. Additionally, the gas sensing apparatus may include an upper shield (not shown) disposed around the wiring harness assembly; and a shell (not shown) disposed around the subassembly, wherein a first end of the shell is concentrically disposed within an end portion of the upper shield.

Example 1 (co-fired coating #1)

Table 1 below details the types and amounts of agents used to form an exemplary green ceramic coating suitable for co-firing with a sensor element.

Table 1		
Co-fired Coating Preparation		
Description	Ingredient	Weight Percent
Solvent/Dispersant	xylenes	17.988
	¹ Z-3 Fish Oil	0.923
	ethanol	17.988
Powders	² A-152SG alumina	17.46
	² A-16SG alumina	23.18
	³ Ultra Pure Thermax C	10.277
Binders	⁴ Santicizer 160	6.092
	⁵ Butvar B-98	6.092

¹commercially available from R. E. Mistler, Inc.

²commercially available from Aluminum Company of America (ALCOA)

³carbon black

⁴butyl benzyl phthalate, commercially available from Monsanto Corp.

⁵poly(vinyl butyral), commercially available from Monsanto Corp.

Here, a dispersant solution was first prepared in which 0.923 wt% of Z-3 fish oil was dissolved in 17.988 wt% of xylene and 17.988 wt% of ethanol. The powder suspension was then formed by adding 10.277 wt% of Ultra Pure Thermax carbon black, 17.46 wt% A-152SG alumina, and 23.18 wt% A-16SG alumina to the dispersant solution.

5 The powder suspension was milled for 2 hours on a roller mill at 110 rpm with milling media. 6.092 wt% of Santicizer 160 and 6.092 wt% of Butvar B-98 was then added to the powder suspension to form the completed slurry. The completed slurry was mixed by rolling on a mill roller for 4 hours. The completed slurry was then allowed to sit without agitation overnight at room temperature. Prior to coating the sensor, the
10 completed slurry was shaken for 5 minutes and rolled without milling media for 2 hours at room temperature (approximately 22°C). The completed slurry was then vacuum de-aired and applied to the outer electrode of the sensor by dipping the sensor into the slurry. However, prior to applying the completed slurry, the sensor was first bisque fired at 1,100°C for 2 hours and electrodes were applied. After applying the green
15 ceramic coating, the coated sensor element was fired at 1,500°C for 2 hours to form the sensor. The fired porosity of this coating was 29.1% with a median pore diameter of 0.51 micrometers, as measured by mercury porosimetry.

Figure 2 depicts diffusion limited current measurements obtained from a plasma sprayed-coating (hatched line) formed according to known methods and from a
20 co-fired coating obtained according to the method detailed above in Example 1. Diffusion Limited Current is a test method where sensor temperature and gas composition are controlled such that the diffusion rate of gas through the porous coating is the only limiting factor to sensor output current. Figure 2 shows the co-fired porous coating is more porous than the plasma sprayed coating. The increased porosity
25 is desirable for exchange of gases between the exhaust and the electrode, provided the electrode with coatings over it is sufficiently durable.

Table 2 depicts test data from a gas blending bench test, which shows that the co-fired coating provides appropriate porosity for the sensor to function as well as, if not better than, flame sprayed parts. The results were obtained by applying an
30 offset voltage of 450 millivolts (mV), heating the sensor to 400C, and flowing rich and lean gases across the sensor coated with the porous coating formed according to Example 1 (co-fired coating), and across a sensor coated with a porous coating formed

by flame spray by known methods. The two groups of sensors had approximately the same coating thicknesses (thickness described in preferred method). The data shown is the sensor output under the described conditions.

Under the test conditions, "lean" refers to that point where the air/fuel (A/F) ratio is greater than 14.7; "rich" refers to that point where the A/F ratio is less than 14.7. "Response time" refers to the time it takes the sensor to adjust to the new condition, and is measured in milliseconds (ms). Lean and Rich voltages are the voltages generated by the sensor when the gas stream is Lean and Rich respectively, as described. Each of the 6 co-fired coating elements shown in Table 2 differ only in electrode treatments, similarly the flame sprayed elements differ from each other only in the condition of the electrodes. The porous coating affects the diffusion of gases to the electrode, and thus effects output voltages and response times for a given electrode. In the data shown in Table 2, the co-fired coatings are the same. From the low lean voltages (less than 150 mV) as well as the high rich voltages (greater than 800 mV), it can be concluded that the co-fired porous coating is allowing access for exhaust gases to the sensing electrode in a manner comparable with flame spray coatings. Part to part differences are not believed to be due to coatings. Based upon the Diffusion Limited Current data previously shown and the gas bench data shown in Table 2, the co-fired porous coating provides a sufficient diffusion layer for the element electrode.

Table 2				
Audit Test Standard Results: Conical Elements, Unheated, 400°C				
Element Coating Description	Lean Voltage (mV)	Rich Voltage (mV)	Lean to Rich Response Time (ms)	Rich to Lean Response Time (ms)
co-fired coating #1	79.4	896.1	26.6	261.5
flame spray	101.6	840.4	61.6	1034.2
co-fired coating #1	79.9	826.9	235.7	452.4
co-fired coating #1	68.2	888.5	39.3	246.7
co-fired coating #1	74.4	902.8	27.2	184.9
co-fired coating #1	65	902.5	25.5	165.5
flame spray	94.6	847.1	63.5	996.3
co-fired coating #1	71.9	853.9	32.2	541.8

Table 3: Engine Test Results from sensors produced with co-fired coating #2 (from Example 2 below). Test data is at 3 different exhaust temperatures, with engine perturbation frequencies of 0.5 and 1.5 hertz (Hz), and Air/Fuel perturbations of ± 0.3 from stiochiometry.

Table 3												
Description	Lean Voltage (mV)			Rich Voltage (mV)			Lean to Rich Response Time (ms)			Rich to Lean Response Time (ms)		
	260°C 0.5Hz, 0.3 A/F	450°C 1.5Hz, 0.3 A/F	595°C 1.5Hz, 0.3 A/F	260°C 0.5Hz, 0.3 A/F	450°C 1.5Hz, 0.3 A/F	595°C 1.5Hz, 0.3 A/F	260°C 0.5Hz, 0.3 A/F	450°C 1.5Hz, 0.3 A/F	595°C 1.5Hz, 0.3 A/F	260°C 0.5Hz, 0.3 A/F	450°C 1.5Hz, 0.3 A/F	595°C 1.5Hz, 0.3 A/F
Co-Fired Sensor with porous coating, heated												
Number	12	6	3	12	6	3	12	6	3	12	6	3
Average	59.7	75.8	78.3	884.8	828.3	787.3	42.2	20.3	18.7	60.8	24.8	20.3
Std. Dev.	7.62	2.93	2.89	9.20	6.80	1.53	11.78	2.50	3.51	13.22	5.27	0.58
Min	47	71	75	873	823	786	20	17	15	41	19	20
Max	71	80	80	901	838	789	61	23	22	80	33	21
Co-Fired Sensor with porous coating, unheated												
Number		7	4		7	4		7	4		7	4
Average		151.6	73.8		884.3	858.5		11.6	6.3		56.4	13.8
Std. Dev.		10.13	2.50		8.79	3.00		2.57	1.89		3.51	0.96
Min		137	71		871	857		9	5		52	13
Max		161	77		896	863		16	9		61	15

- 5 The engine test data shown in Table 3 demonstrates the activity of the working sensors under a range of engine exhaust temperatures and conditions. The data is comparable with other sensors and meets the specification requirements for most applications. Figures 3 and 4 show Lambda switching curves for heated and unheated sensors at initial test. An ideal sensor switches from Rich (greater than 450 mV with a 450 mV offset voltage applied) to Lean (less than 450 mV with a 450 mV offset voltage applied) at Lambda of 1.000 (the stiochiometric point of a given fuel, commonly 14.7 A/F, but this value changes depending on the exact composition of the fuel). The 3rd graph which follows demonstrates the rich voltage for sensors during a durability test called Hot-Rich. During this test the sensors are run continuously at high temperatures with the air/fuel ratio skewed rich, this is meant to accelerate the aging
- 10
- 15

process in an engine and is considered a rigorous durability test. Each 100 hours of Hot-Rich Testing is the equivalent of 50,000 miles. The data indicates the co-fired sensors are durable for at least 100,000 miles.

Example 2 (co-fired coating #2)

Table 4 below details the types and amounts of agents used to form a second exemplary green ceramic coating suitable for co-firing with a sensor element.

Table 4		
Co-fired Coating Preparation		
Description	Ingredient	Weight Percent
Solvent/Dispersant	Xylenes	12.568
	Z-3 Fish Oil	0.641
	Ethanol	12.568
Powders	A-152SG Alumina	12.907
	A-16SG Alumina	22.018
	Ultra Pure Thermax C	4.110
Additional Solvent	Xylenes	17.138
	Ethanol	17.138
Binders	Santicizer 160	4.260
	Butvar B-98	4.260

Here, a dispersant solution was first prepared in which 0.641 wt% of Z-3 fish oil was dissolved in 12.568 wt% of xylene and 12.568 wt% of ethanol. The powder suspension was then formed by adding 4.110 wt% of Ultra Pure Thermax carbon black, 12.907 wt% A-152SG alumina, and 22.018 wt% A-16SG alumina to the dispersant solution.

The powder suspension was milled for 2 hours on a roller mill at 110 rpm with milling media. 17.138 wt% of additional xylene and 17.138 wt% of additional ethanol was then added to the powder suspension to dilute it. 4.260 wt% of Santicizer 160 and 4.260 wt% of Butvar B-98 was then added to the powder suspension to form the completed slurry. The completed slurry was mixed by rolling on a roller mill for 4 hours. The completed slurry was then allowed to sit without agitation overnight at room temperature. Prior to coating the sensor, the completed slurry was shaken for 5 minutes and rolled without milling media for 2 hours at room temperature (approximately

22°C). The completed slurry was then vacuum de-aired and applied to the outer electrode of the sensor by dipping the sensor into the slurry. However, prior to applying the completed slurry, the sensor was first bisque fired at 1,100°C for 2 hours and electrodes were applied. After applying the green ceramic coating, the coated sensor element was fired at 1,500°C for 2 hours to form the sensor. The fired porosity of this coating was 22.3% with a median pore diameter of 0.27 microns, as measured by mercury porosimetry.

Example 3 (co-fired coating #3)

Table 5 below details the types and amounts of agents used to form a third exemplary green ceramic coating suitable for co-firing with a sensor element.

Table 5		
Co-fired Coating Preparation		
Description	Ingredient	Weight Percent
Solvent/Dispersant	Xylenes	12.294
	Z-3 Fish Oil	0.873
	Ethanol	12.294
Powders	A-152SG Alumina	11.532
	¹ zirconia body	40.374
	Ultra Pure Thermax C	2.004
Additional Solvent	Xylenes	6.147
	Ethanol	6.147
Binders	Santicizer 160	4.168
	Butvar B-98	4.168

¹milled partially stabilized zirconia body made using ZR2 commercially available from SEPR Corp.

Here, a dispersant solution was first prepared in which 0.873 wt% of Z-3 fish oil was dissolved in 12.294 wt% of xylene and 12.294 wt% of ethanol. The powder suspension was then formed by adding 2.004 wt% of Ultra Pure Thermax carbon black, 11.532 wt% A-152SG alumina, and 40.374 wt% milled SEPR zirconia body to the dispersant solution. The powder suspension was milled for 2 hours on a roller mill at 110 rpm

with milling media. 6.147 wt% of additional xylene and 6.147 wt% of additional ethanol was then added to the powder suspension to dilute it. 4.168 wt% of Santicizer 160 and 4.168 wt% of Butvar B-98 was then added to the powder suspension to form the completed slurry. The completed slurry was mixed by rolling on a roller mill for 4
5 hours. The completed slurry was then allowed to sit without agitation overnight at room temperature. Prior to coating the sensor, the completed slurry was shaken for 5 minutes and rolled without milling media for 2 hours at room temperature (approximately 22°C). The completed slurry was then vacuum de-aired and applied to the outer electrode of the sensor by dipping the sensor into the slurry. However, prior
10 to applying the completed slurry, the sensor was first bisque fired at 1,100°C for 2 hours and electrodes were applied. After applying the green ceramic coating, the coated sensor element was fired at 1,500°C for 2 hours to form the sensor. The fired porosity of this coating was 19.7% with a median pore diameter of 0.26 microns, as measured by mercury porosimetry.

15 In the figures, Figure 5 is a SEM micrograph shows virtually inseparably bonded alumina/zirconia porous coating obtained by co-firing on a zirconia electrolyte oxygen sensor body. Figure 6 is a SEM micrograph shows alumina/zirconia porous coatings obtained by co-firing on bisque electroded zirconia electrolyte body. In Figure 7, the gas bench data with standard gas feed stream (similar to automobile exhaust)
20 shows the Lambda switching curves for two heated sensors. This data shows that the sensors with coatings as described herein are suitable for engine control applications. High sensor amplitude, $V_{\text{rich}} - V_{\text{min}}$, and low hysteresis between lean to rich and rich to lean transitions indicates symmetrical response of the sensor.

The sensors formed from the coatings described herein have several
25 advantages over other sensors. First, the coating is ideally suited for a conical sensor. Because the coating may be co-fired with the sensor, traditional methods for applying a coating, such as, flame spray or plasma spray, need not be used. This is particularly beneficial in that flame spray and plasma spray methods are extremely high economic investments, and require technical maintenance processes subject to considerable
30 variations in their operability. Additionally, the coating disclosed herein is easier to manufacture than are tapes, and eliminates many of the materials used to form the tape, and tapes cannot be used to coat conical sensors. In addition, the coating is very strong,

and well adhered to both the electrolyte and the electrode materials, e.g., it is not possible to selectively remove the coating after co-firing without destroying the sensor.

The disclosed coating also has a greater porosity than traditional coatings, i.e., than do plasma sprayed coatings (as is evidenced by the diffusion limited
5 current data), without sacrificing efficiency. Therefore, the porosity is sufficient to balance the two competing interests in designing a coating for a sensor; namely to protect against sensor degradation due to extreme exhaust conditions and poisons, and to provide sufficient gas residence time at the outer electrode to allow reactions to proceed to completion.

10 Therefore, the dip-coating method used to coat the sensor is an improvement over currently used materials, as the dip process is more easily controlled than either flame spray or plasma spray to provide consistent coverage thickness and porosity. The dip process is also a significant cost savings over either flame spray or plasma spray and can be processed much faster and easier than either of these
15 traditional methods.

Previously, conical sensors were plasma or flame sprayed in order to obtain the desired porosity in conjunction with the necessary adhesion of the coating to the outer electrode. Previously, dip coatings were used only for secondary poison protective coatings and were not co-fired as the diffusion coating. With the flame and
20 plasma spraying, the coating could be applied to an electrode to obtain a desired porosity and adhesion. With the present combination of ceramic materials, the desired shrinkage (e.g., a shrinkage of less than or equal to about 5% of the shrinkage of the element body and electrode preferred), the desired porosity, and the desired adhesion was obtained. For example, if the electrode shrinkage is 10%, the coating shrinkage
25 should be about 9.5% to about 10.5%. The desired amounts and/or types of each ceramic powder can be chosen to attain the desired shrinkage.

While the invention has been described with reference to exemplary embodiments, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted for elements thereof without departing
30 from the scope of the invention. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from the essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiment disclosed as the best mode contemplated for

carrying out this invention, but that the invention will include all embodiments falling within the scope of the appended claims.

CLAIMS

1. A method for coating a conical sensor (10) comprising:
disposing a green ceramic coating (36) on a conical sensor element to form a coated-sensor (10), wherein the green ceramic coating (36) comprises a first ceramic powder having a first sintering temperature, a second ceramic powder having a
5 second sintering temperature, a fugitive filler material, and a binder, wherein the conical sensor element comprises an inner electrode (32) disposed on an inner surface (14) of a conical electrolyte body (12), and an outer electrode (34) disposed on an outer surface (16) of the conical electrolyte body (12); and
heating the coated-sensor to a firing temperature equal to or greater than
10 the second sintering temperature and below the first sintering temperature.
2. The method of Claim 1, wherein the fugitive filler material has an average particle size of up to about 1 micrometer.
3. The method of Claim 1, wherein relative amounts of the first and the second ceramic powders are adjusted to have a green ceramic coating (36) shrinkage that is less than or equal to about $\pm 5\%$ of a shrinkage of the outer surface (16).
4. The method of Claim 1, wherein the first ceramic powder further comprises alumina having a first median particle size of about 1.0 micrometers to about 1.5 micrometers, and wherein the second ceramic powder further comprises at least one of alumina and zirconia having a second median particle size of about 0.25 micrometers
5 to about 0.95 micrometers, and wherein the first median particle size does not equal the second median particle size.
5. The method of Claim 4, wherein the first ceramic powder has a first surface area of about $3 \text{ m}^2/\text{g}$ to about $5 \text{ m}^2/\text{g}$, and wherein the second ceramic powder has a second surface area of about $6 \text{ m}^2/\text{g}$ to about $12 \text{ m}^2/\text{g}$, and wherein the first surface area does not equal the second surface area.

6. The method of Claim 5, wherein second ceramic powder comprises the alumina, and wherein the second surface area is about 7 m²/g to about 12 m²/g.

7. The method of Claim 6, wherein second ceramic powder comprises the zirconia, and wherein the second surface area is about 6 m²/g to about 9 m²/g.

8. The method of Claim 1, wherein the binder includes butyl benzyl phthalate, poly(vinyl butyral), and combinations comprising at least one of the foregoing.

9. The method of Claim 1, further comprising bisque firing the conical sensor element prior to the dip-coating (36).

10. The method of Claim 1, wherein the first sintering temperature is about 85% to about 95% of the firing temperature.

11. The method of Claim 1, wherein disposing the green ceramic coating (36) on a conical sensor element further comprises dip-coating the conical sensor element.

12. The method of Claim 11, wherein the dip-coating further comprises dipping the conical sensor element into a slurry comprising about 10 wt% to about 80 wt% combined first ceramic material and second ceramic material; about 1 wt% to about 20 wt% binder; about 1 wt% to about 20 wt% of the fugitive filler material; about 0.5 wt% to about 2.0 wt% dispersant; and about 20 wt% to about 70 wt% solvent, based on the total weight of the slurry.

13. The method of Claim 12, with about 20 wt% to about 50 wt% ceramic material, about 3 wt% to about 15 wt% binder; about 3 wt% to about 15 wt% fugitive filler material; about 0.75 wt% to about 1.75 wt% dispersant; and about 25 wt% to about 60 wt% solvent.

14. A method for coating (36) a conical sensor (10) comprising:
disposing a green ceramic coating (36) on the conical sensor element to
form the conical sensor (10), wherein the green ceramic coating (36) comprises a first
ceramic powder having a first sintering temperature that is about 85% to about 95% of
5 a firing temperature, and a second ceramic powder having a second sintering
temperature that is greater than or equal to about 97% of the firing temperature,
wherein the conical sensor element comprises an inner electrode (32) disposed on an
inner surface (14) of a conical electrolyte body (12), and an outer electrode (34)
disposed on an outer surface (16) of the conical electrolyte body (12), and wherein the
10 first sintering temperature is less than the second sintering temperature; and
heating the coated-sensor (10) element to the firing temperature.

15. The method of Claim 14, wherein relative proportions of the first
and the second ceramic powders are adjusted to have a green ceramic coating (36)
shrinkage that is less than or equal to about $\pm 5\%$ of a shrinkage of the outer surface
(16).

16. The method of Claim 14, wherein the first ceramic powder
further comprises alpha alumina having a first median particle size of about 1.0
micrometers to about 1.5 micrometers, and wherein the second ceramic powder further
comprises at least one of alpha alumina and zirconia having a second median particle
5 size of about 0.25 micrometers to about 0.95 micrometers, and wherein the first median
particle size does not equal the second median particle size.

17. The method of Claim 16, wherein the first ceramic powder has a
first surface area of about $3 \text{ m}^2/\text{g}$ to about $5 \text{ m}^2/\text{g}$, and wherein the second ceramic
powder has a second surface area of about $6 \text{ m}^2/\text{g}$ to about $12 \text{ m}^2/\text{g}$, and wherein the
first surface area does not equal the second surface area.

18. The method of Claim 17, wherein second ceramic powder
comprises the alpha alumina, and wherein the second surface area is about $7 \text{ m}^2/\text{g}$ to
about $12 \text{ m}^2/\text{g}$.

19. The method of Claim 17, wherein second ceramic powder comprises the zirconia, and wherein the second surface area is about 6 m²/g to about 9 m²/g.

20. The method of Claim 14, further comprising bisque firing the conical sensor (10) element prior to the disposing the green ceramic coating (36) on the conical sensor element.

21. The method of Claim 14, wherein the green ceramic coating (36) further comprises at least one of a fugitive filler material and a binder.

22. The method of Claim 14, wherein disposing a green ceramic coating (36) on the conical sensor element further comprises dip-coating.

23. The method of Claim 22, wherein the dip-coating further comprises dipping the conical sensor (10) element into a slurry comprising about 10 wt% to about 80 wt% combined first ceramic material and second ceramic material; about 1 wt% to about 20 wt% binder; about 1 wt% to about 20 wt% of the fugitive filler
5 material; about 0.5 wt% to about 2.0 wt% dispersant; and about 20 wt% to about 70 wt% solvent, based on the total weight of the slurry.

24. The method of Claim 23, with about 20 wt% to about 50 wt% ceramic material, about 3 wt% to about 15 wt% binder; about 3 wt% to about 15 wt% fugitive filler material; about 0.75 wt% to about 1.75 wt% dispersant; and about 25 wt% to about 60 wt% solvent.

25. A conical sensor (10) formed from the method of Claim 1.

26. A conical sensor (10) formed from the method of Claim 14.

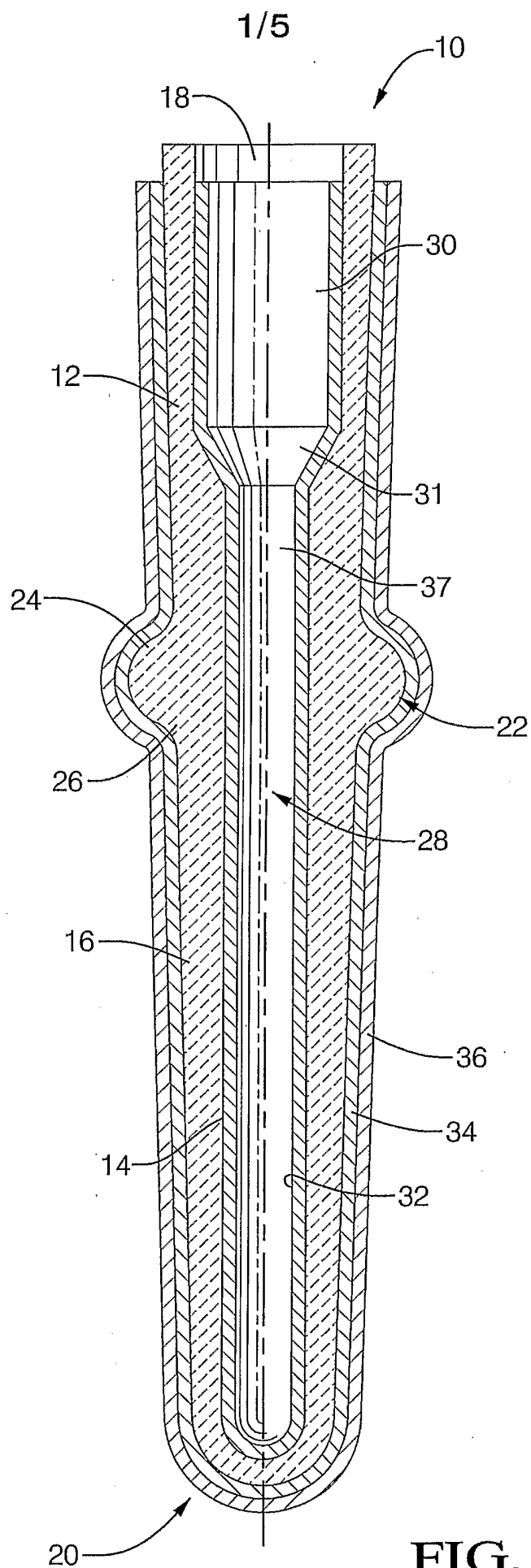


FIG. 1

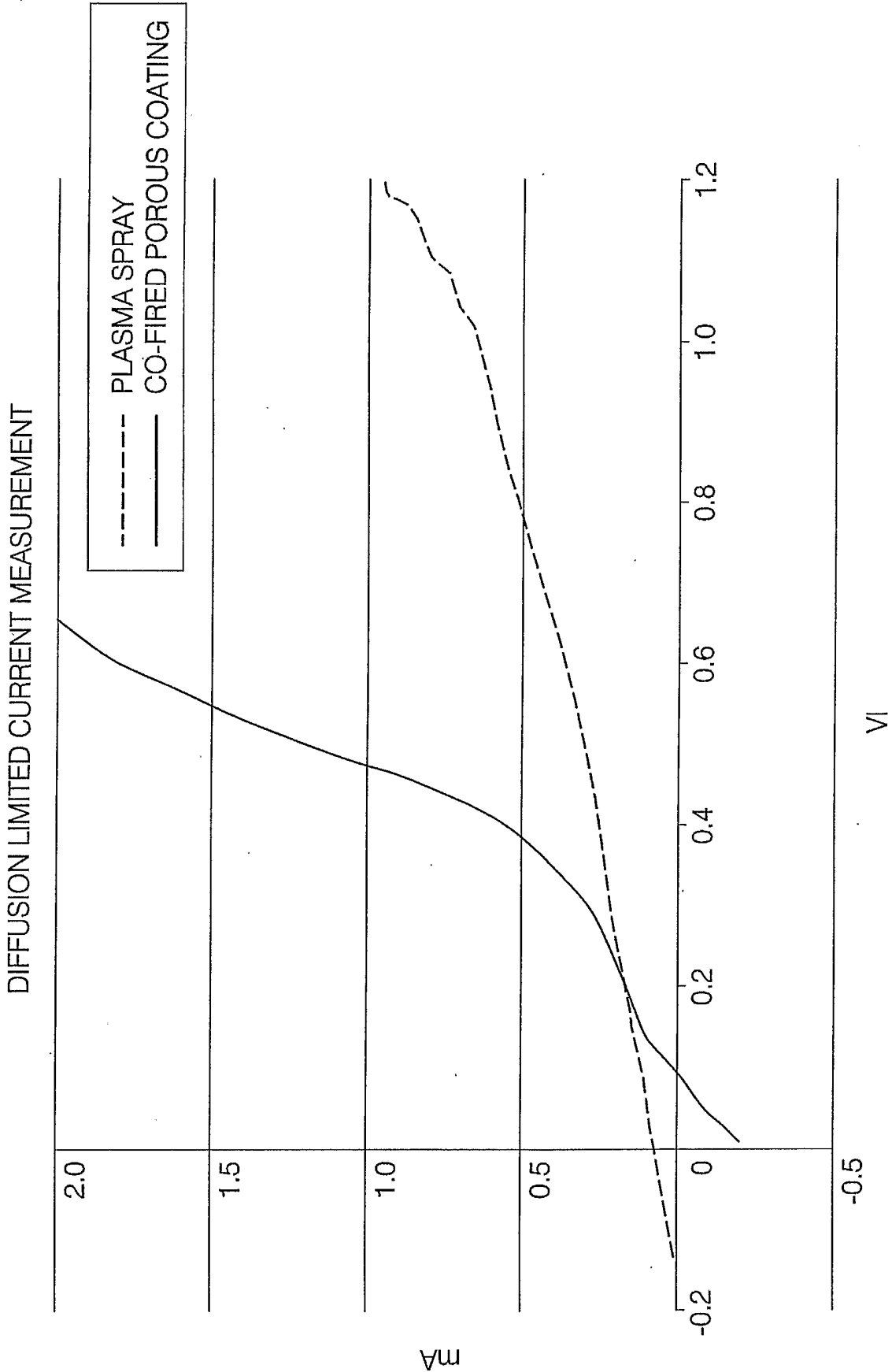


FIG. 2

3/5

Co-Fired Sensors with Porous Coating:
400C Unheated Sensor S-Curves, Both Directions.

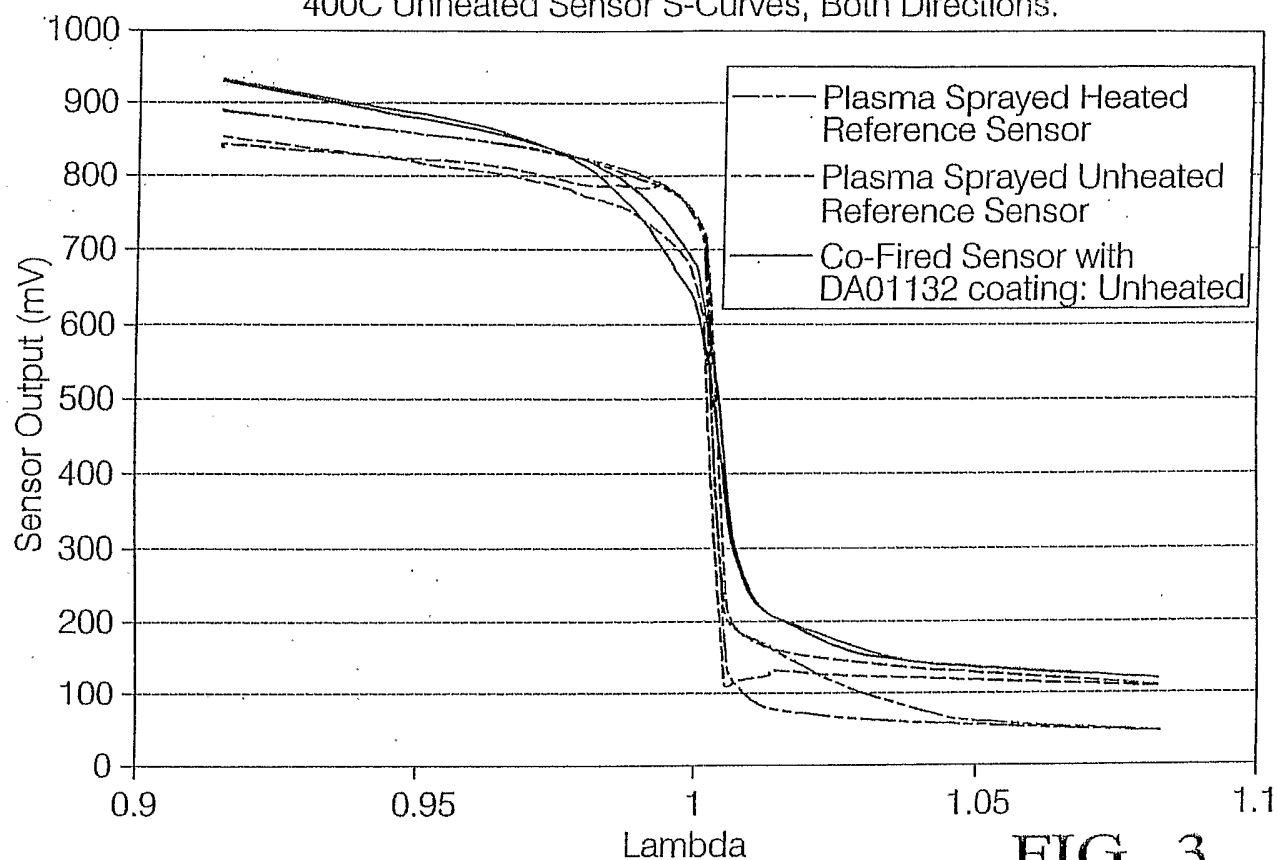


FIG. 3

Co-Fired Sensors with DA01132 Porous Coating:
450C Heated Sensor S-Curves, Both Directions.

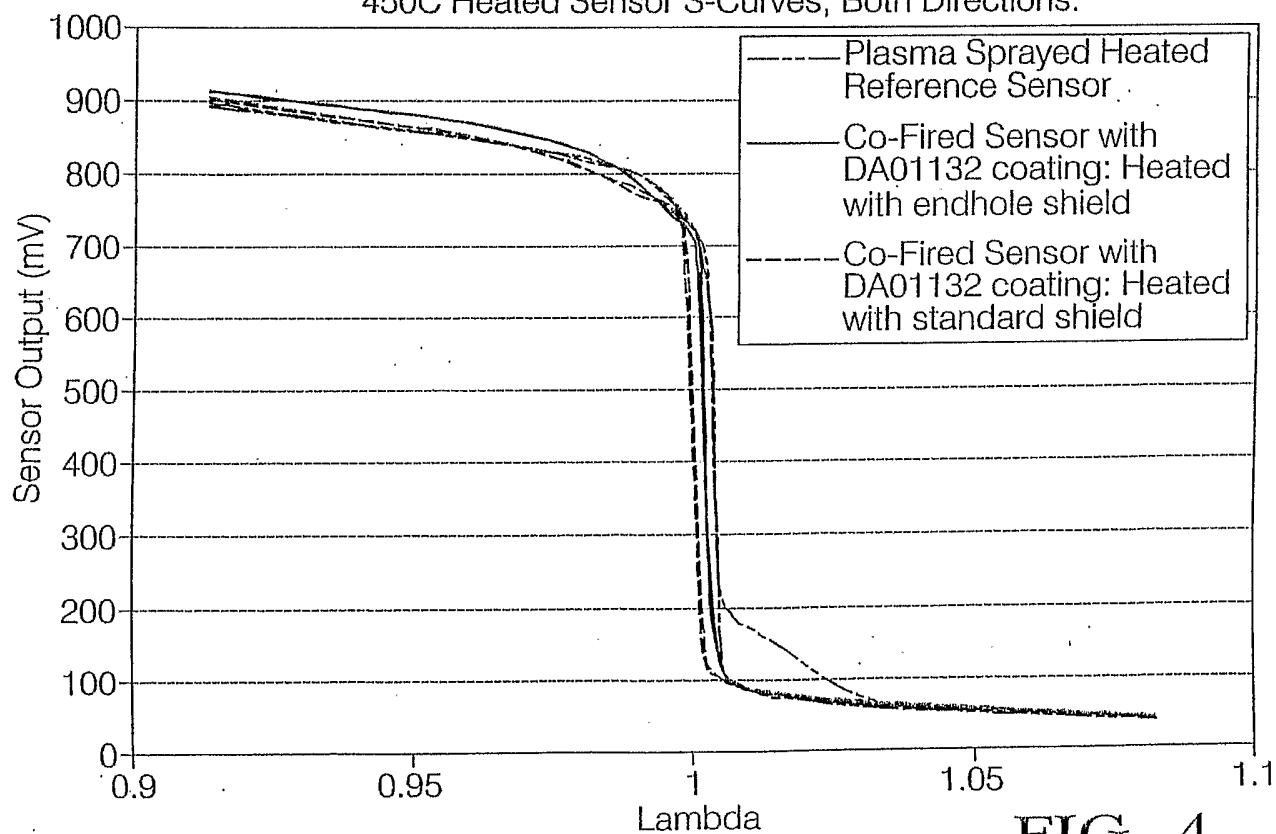


FIG. 4

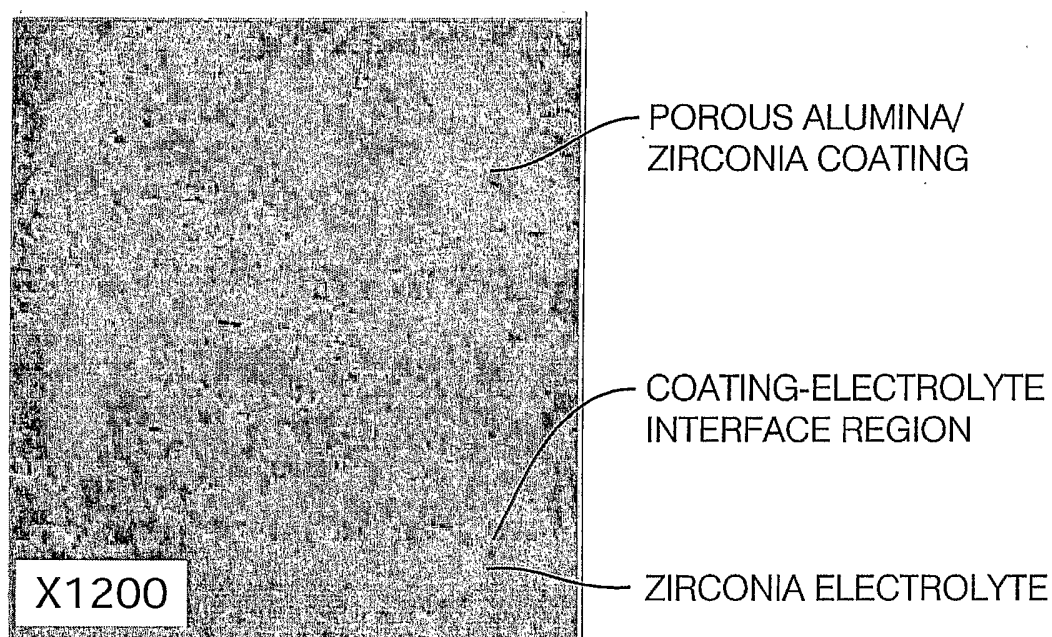


FIG. 5

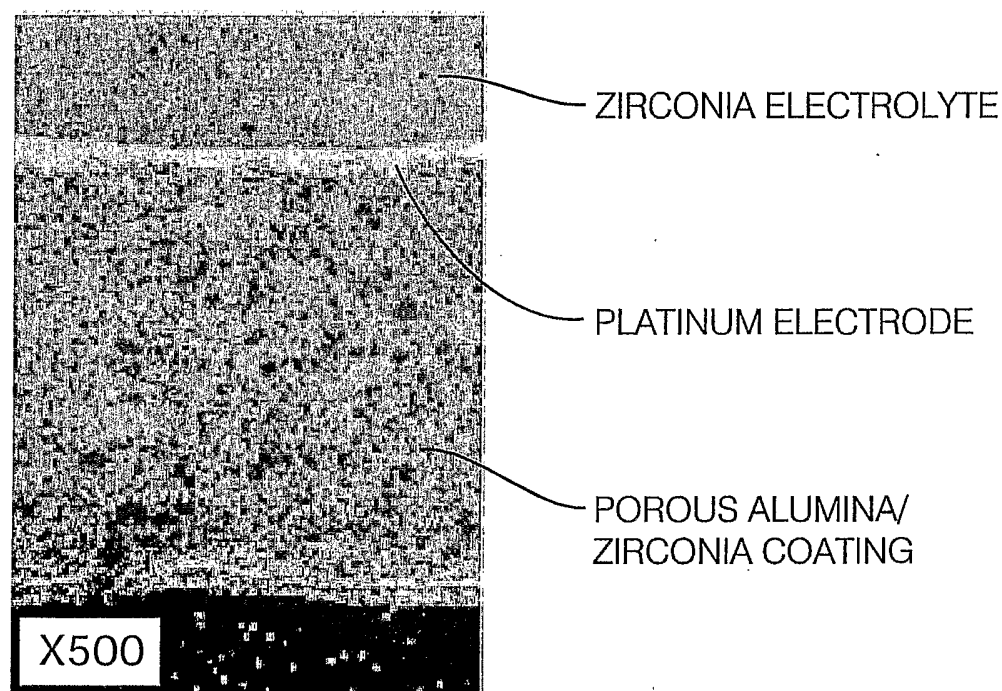
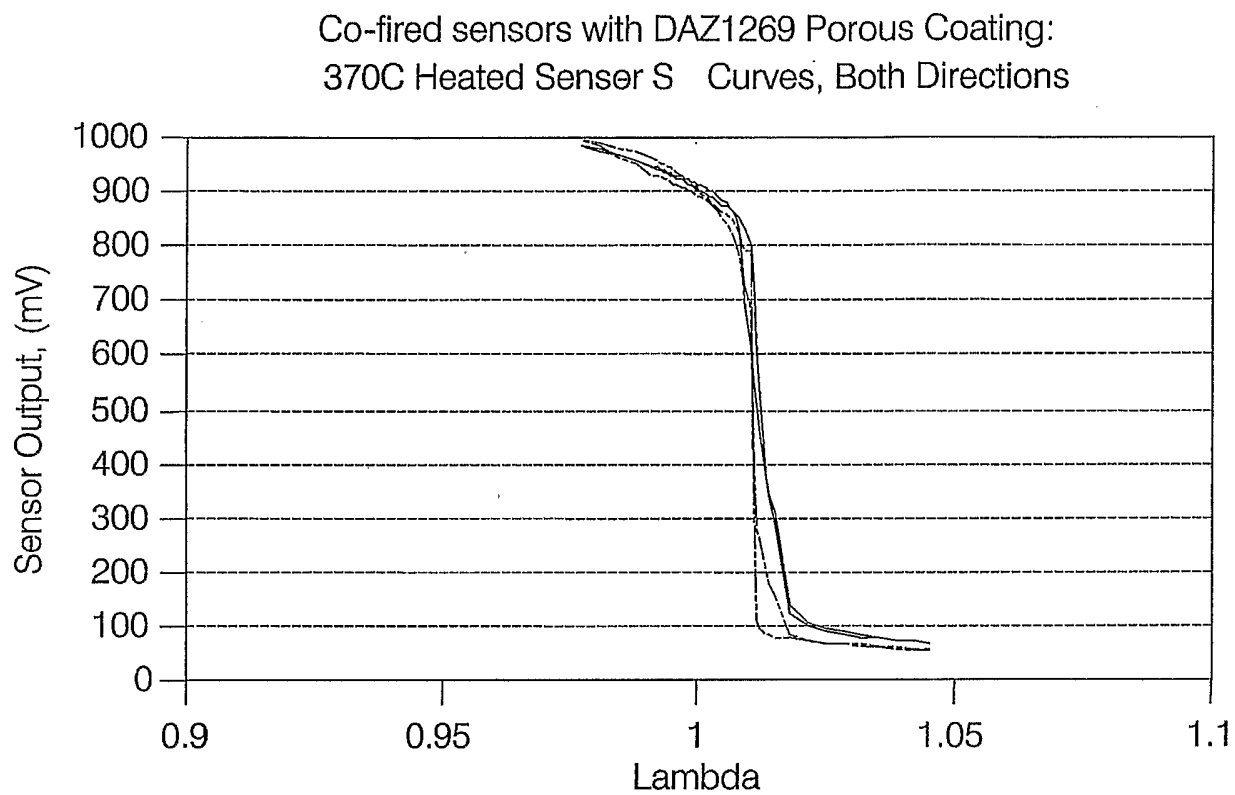


FIG. 6

**FIG. 7**

INTERNATIONAL SEARCH REPORT

PCT/US 03/10864

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 F02D41/14 G01N27/407

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 F02D G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2002/108853 A1 (DONELON MATTHEW J ET AL) 15 August 2002 (2002-08-15)	1-24
X	page 2, paragraph 34 -page 3, paragraph 40; figures 2,3	25,26
Y	EP 0 832 865 A (GEN MOTORS CORP) 1 April 1998 (1998-04-01) column 2, line 2-42 column 3, line 36 -column 5, line 2	1-24
A	US 5 628 848 A (FRIESE KARL-HERMANN ET AL) 13 May 1997 (1997-05-13) column 2, line 52 -column 4, line 38	1-24



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

9 December 2003

Date of mailing of the international search report

17/12/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Joffreau, P-0

INTERNATIONAL SEARCH REPORT

PCT/US 03/10864

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