PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 4 : G01N 27/46	A1	(11) International Publication Number: WO 87/ 02461
		(43) International Publication Date: 23 April 1987 (23.04.87)

(21) International Application Number: PCT/US86/02085

(22) International Filing Date: 3 October 1986 (03.10.86)

(31) Priority Application Number: 786,606

(32) Priority Date: 11 October 1985 (11.10.85)

(33) Priority Country: US

(71) Applicant: BECKMAN INDUSTRIAL CORPORATION PROCESS INSTRUMENTS DIVISION [US/US]; 600 Harbor South, La Habra, CA 90631 (US).

(72) Inventors: NETI, Radhakrishna, M. ; 945 East Red Budd Street, Brea, CA 92621 (US). FREUND, David, H. ; 2548 Deodar Street, Pomona, CA 91767 (US).

(74) Agent: VANDERBURGH, John, E.; Plante, Strauss & Vanderburgh, 1020 Broadway, 400 North Suite, Santa Ana, CA 92701 (US).

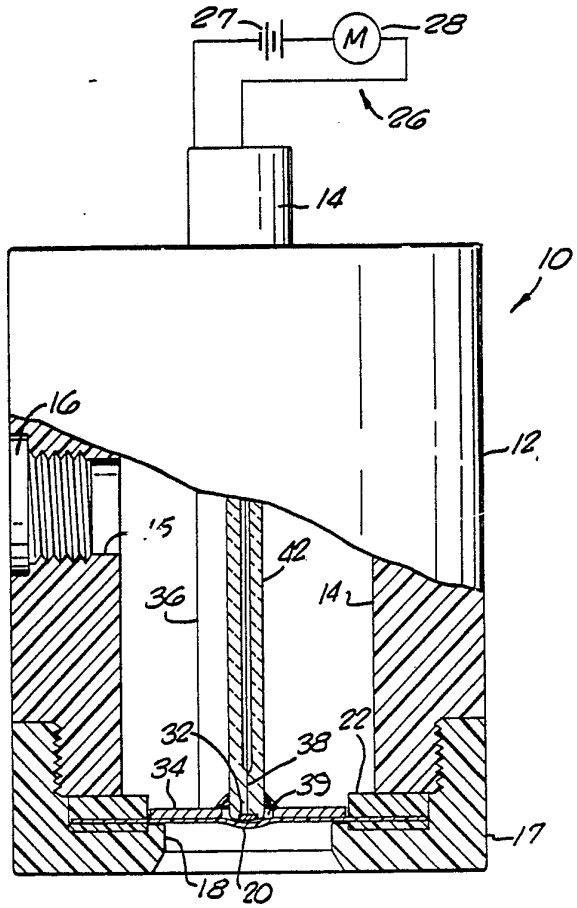
(81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent).

Published
With international search report.
With amended claims.

(54) Title: A METHOD OF FABRICATING RHODIUM FOIL-GLASS ELECTRODES

(57) Abstract

A sensor (10) for the detection of a gas in a fluid having an improved electrode assembly in which the assembly comprises a thin, disc-shaped noble metal electrode (32) fused in one end of a glass sheath (42) with a surface of the electrode exposed. A conductor (38) is electrically connected to the electrode surface opposite the exposed surface and extends axially through the sheath to the exterior thereof. A method for manufacturing the improved electrode assembly is also disclosed.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	**FR**	France	**ML**	Mali
AU	Australia	**GA**	Gabon	**MR**	Mauritania
BB	Barbados	**GB**	United Kingdom	**MW**	Malawi
BE	Belgium	**HU**	Hungary	**NL**	Netherlands
BG	Bulgaria	**IT**	Italy	**NO**	Norway
BJ	Benin	**JP**	Japan	**RO**	Romania
BR	Brazil	**KP**	Democratic People's Republic of Korea	**SD**	Sudan
CF	Central African Republic			**SE**	Sweden
CG	Congo	**KR**	Republic of Korea	**SN**	Senegal
CH	Switzerland	**LI**	Liechtenstein	**SU**	Soviet Union
CM	Cameroon	**LK**	Sri Lanka	**TD**	Chad
DE	Germany, Federal Republic of	**LU**	Luxembourg	**TG**	Togo
DK	Denmark	**MC**	Monaco	**US**	United States of America
FI	Finland	**MG**	Madagascar		

A METHOD OF FABRICATING RHODIUM FOIL-GLASS ELECTRODES

Background of the Invention

The present invention relates to sensors capable of detecting a gas in a fluid and more particularly to sensors for detecting the presence and the amount of oxygen (O_2).

A number of electrode assemblies are commercially available which may be used to detect the presence of oxygen in a gaseous or liquid medium. For example, U.S. Patent No. 3,449,231 (Adams et al.), U.S. Patent No. 3,577,332 (Porter et al.), U.S. Patent No. 4,078,981 (Neti et al.) and U.S. Patent no. 4,268,370 (Neti) relate to various designs and modifications of such sensors. Essentially, these sensors comprise assemblies for the determination of the partial pressure of oxygen, or other constituents, in the dissolved or gaseous state in a fluid medium utilizing a thin membrane, such as polyethylene, which is permeable to the constituent being analyzed in the fluid medium. The assemblies comprise a cathode and an anode, both of which are normally formed from a noble metal such as platinum, gold, silver, rhodium or the like, connected by an electrical circuit which includes a source of power and a suitable measuring instrument, such as an ammeter. The electrical circuit between the cathode and the anode is completed by a suitable electrolyte which is normally disposed as a thin layer between the membrane and at least the cathode. The body of the sensor defines a reservoir for the electrolyte which communicates with the thin layer so as, depending on the location of the anode, to complete the circuit between the cathode and the anode. In the case of oxygen sensors, oxygen passing through the membrane is

reduced at the cathode when a suitable polarizing voltage is imposed across the electrodes and this reaction causes a current to flow between the electrodes that is proportional to the partial pressure of oxygen in the medium being analyzed.

In co-pending application Serial No. 06/571,328 filed January 16, 1984, a number of problems encountered with the above-described sensors are set forth, not the least of which is the depletion of oxygen from the electrolyte immediately adjacent the cathode. The application sets forth an improved sensor which, although generally constructed as described above, is not dependent on the continuous diffusion of oxygen through the membrane but instead reduces oxygen in the electrolyte at the cathode and generates oxygen at the anode depending on the rate of oxygen consumption at the cathode. In this manner a steady state is created and depletion of oxygen in the electrolyte is minimized. Any change in the partial pressure of the oxygen in the medium being analyzed will cause oxygen to pass through the membrane in the direction of lower pressure to re-establish the equilibrium condition on each side of the membrane.

Such passage of oxygen through the membrane causes a change of the steady state of oxygen reduction and oxygen generation at the electrodes, thus producing a measurable change in the current flow between the electrodes until a steady state is again established. The change in current flow is directly related to the concentration of oxygen in the medium being analyzed.

Sensors of the types described above are often subjected to severe operating conditions, such as where the medium being analyzed is maintained at elevated temperature or where it is desired to subject the sensor to steam sterilization and it is highly desirable to protect the electrodes, normally by fusing

the electrode in a protective glass sheath, except for a defined area which is exposed to electrolyte contact. Under such operating conditions it is essential that the sheath remain free of cracks and leaks to prevent any reactions at the electrode, except at the exposed area, which will produce excess current and result in erroneous readings. For this reason care must be taken in the selection of the noble metal and the type of glass in which the electrode is to be sealed to ensure that the coefficient of expansion of the metal and glass are as close to being the same as is possible to avoid cracks in the glass due to uneven expansion and contraction of the materials as they are heated and cooled.

As is discussed in greater detail in U.S. Patent No. 3,449,231, certain noble metals are not preferred for such application. Thus, for example, platinum, which is ductile, can be fused in glass readily but is subject to interference by CO_2, while gold is not suited for fusion in glass. However, small diameter rhodium wire (less than .01 inch), which is resistant to CO_2 encountered in certain high temperature applications, can be fused with some degree of success in lead glass in the construction of cathode assemblies for oxygen sensors which may be exposed to high temperature operations.

It has been found, however, that rhodium wire electrodes in excess of .10 inches in diameter cannot be successfully fused in lead glass. It has also been found that in the process of fusing lead glass, lead may come out of solution in the glass which produces unacceptably high residual currents in the sensor and an unacceptable blackening of the glass tube. Also, it has been found that even with the use of lead glass, rhodium cathodes quickly develop cracks, even at room temperature, resulting in an unacceptably short useful

life for the cathode.

Plastic sealed electrodes have also been used and have been found to be subject to many of the same problems encountered with the glass sealed electrodes due to failure of the sealing materials when exposed to caustic electrolytes at elevated temperatures.

Summary of the Invention

In accordance with the present invention, there is provided an improved glass sealed electrode assembly and method of manufacture in which the electrode is resistant to thermal shock and has an increased useful life even under severe operating conditions.

According to the principal aspect of the invention, an electrode assembly is provided which comprises a thin, disc-shaped noble metal electrode onto one surface of which is spot welded a conductive wire. The electrode and conductive wire are fused in a tubular glass sheath and the surface of the metal electrode opposite the surface to which the conductive wire is connected is exposed for contact with the electrolyte.

The electrode is preferably formed from a noble metal foil such as gold, platinum, rhodium and alloys thereof. The conductive wire need not be of the same composition as the metal electrode and need not be formed from a noble metal, although it is preferred that the conductor also comprise a noble metal that will make a good seal with the glass. The choice of glass used to form the sheath of the electrode assembly of this invention is not critical and may comprise any of the glass compositions conventionally used for fused glass electrodes, such as lead glass, soda lime or the like.

In a preferred embodiment, the electrode assembly consists of a rhodium cathode and a platinum conducting

wire, both of which are disposed in a soda lime glass body. A second electrode consisting of an annular platinum body is fused to the glass body and is concentrically disposed with respect to and in close proximity to the rhodium electrode and serves as the anode in any oxygen sensor.

In manufacturing the fused glass electrode assembly in accordance with the present invention, the electrode is formed as a disc or button cut or stamped from a noble metal foil and the conducting wire is spot welded to one surface of the button. The free end of the wire is drawn into the bore of a glass tube, preferably a capillary tube, with the metal button abutting the end of the glass tube which has been blown into a cone shape to keep the button centered and perpendicular to the glass tube. The glass tube is flame worked to permit the glass to flow around the button and the wire. Following fusion, the assembly is annealed for sufficient time to relieve stress in the glass. The assembly is then subjected to a grinding operation to expose a contact surface and to obtain the desired radius of curvature for the finished electrode.

Other aspects and advantages of the invention will become apparent from the following detailed description taken in conjunction with the drawings.

Description of the Drawings

Fig. 1 is a side view, partially broken away and partially in section, of an oxygen sensor including a fused glass cathode constructed in accordance with the present invention

Fig. 2 is an exploded side view of the components of the cathode of Fig. 1 prior to fusion; and

Fig. 3 is a side view of the cathode of Fig. 1.

Description of the Preferred Embodiment

Referring to Fig. 1, there is illustrated an oxygen sensor, generally designated as 10, comprising a cylindrical plastic body 12 having a cylindrical recess 14 extending substantially through the body and opening at one end thereof. A second opening 15 is provided in the wall of the body 12 and is closed by a plug 16 which is screw-threaded into the second opening. The recess 14 is closed by means of a membrane 20 which is stretched across the opening of the recess 14 and held there by a holder 22 which is clamped between the end of the body 12 and a cap 17 which is threadably engaged with the end of the body. As is shown in the art, the membrane is selected from a material that is permeable to the component being analyzed, in this case oxygen, and that is substantially impermeable to the electrolyte. For oxygen sensors suitable materials include polyethylene or Teflon. The cap 17 is provided with a central opening 18 for contact between the membrane 20 and a fluid being analyzed. A connecting terminal 24 is disposed on the body 12 and is connected in a circuit, shown generally as 26 to a source of current 27 and a current measuring instrument 28. The connecting terminal 24 also serves as the mounting means for a glass sheath 42 carrying a cathode 32 and an anode 34. The cathode 32 and the anode 34 are connected through the terminal 24 of the circuit 26 by anode conductor 36 and a cathode conducting wire 38. When properly positioned in the sensor, the cathode 32 is located adjacent the opening 18 of the cap 17 so that the membrane 20 is stretched over the cathode to provide therebetween a thin electrolyte film space which is in communication with the cylindrical recess 14 of the body 12. In the embodiment shown, the anode 34 is an annular shaped member disposed concentrically with an immediately adjacent to the cathode 32 to

define therebetween an annular space 39, preferably between about .002 and .010 inches.

When the sensor 10 is used for the measurement of oxygen a preferred electrolyte is a 2% aqueous solution of potassium hydroxide. The anode is platinum and the cathode is rhodium.

In operation the electrolyte is introduced into the cylindrical recess 14 which serves as a reservoir for the electrolyte and sufficient voltage (on the order of 0.75 volts) is imposed between the anode 34 and the cathode 32 to cause reduction of oxygen at the cathode and generation of oxygen at the anode without causing the decomposition of the electrolyte. In the absence of any substantial amount of oxygen in the electrolyte there will be little or no current flow between the anode and the cathode. However, should the membrane 20 contact a fluid containing dissolved or gaseous oxygen, equilibrium on either side of the membrane 20 will be disturbed and in accordance with well known principles, oxygen will begin to diffuse through the membrane from the side of highest concentration, in this example the test fluid side, to the side of least concentration, the electrolyte side. As oxygen penetrates the membrane 20 it is reduced at the cathode 32, causing current to flow between the cathode and the anode 34. The anode 34 generates oxygen to replace the oxygen reduced at cathode 32 to restore steady state conditions within the body of the sensor 10. The amount of current flow is measured by the instrument 28 and is directly related to the oxygen level in the test fluid.

In accordance with the present invention, the cathode 32 is sealed in a glass sheath in the manner taught herein to provide an improved fused glass electrode assembly that is resistant to the development of cracks in the glass sheath due to exposure to high

temperature and caustic electrolyte, even though the coefficient of expansion of the cathode and the glass sheath may be dissimilar.

Referring to Fig. 1 and Fig. 3, there is illustrated a glass sheathed cathode assembly constructed in accordance with the invention consisting of the cathode 32 and the cathode conducting wire 38 which are fused in a glass sheath 42. The surface of the cathode 32 opposite the surface to which the conductor 38 is affixed is exposed to contact with the electrolyte and is smoothly configured to provide a uniform thin electrolyte space between it and the membrane 20.

The cathode, which may be composed of any of the noble metals that can withstand the flame working temperatures comprises a thin disc-shaped member formed from a foil of the desired noble metal. The foil thickness is not critical and normally is available in a range of between .01 and .025 inches in thickness. As already mentioned, the cathode 32 may comprise any of the noble metals such as gold, platinum, rhodium or alloys and combinations thereof, as they are relatively chemically inert with respect to the electrolyte and most fluids and gases ton which the sensor may be exposed and they have desirable electrical characteristics. However, as already mentioned, in oxygen analyzers, rhodium, or rhodium-plated material is preferred for use because of the resistance of rhodium to CO_2 interference.

It is well known in the art that the diameter of the electrode member to be fused in a glass body must be controlled, regardless of the coefficient of expansion of the glass, in order to obtain an electrode that is reasonably resistant to stress in the glass that eventually can cause glass cracks and the resultant failure of the electrode. Accordingly, the

electrode member of a fused glass electrode assembly made in accordance with the teachings of the prior art is limited in diameter to about .005 to about 0.010 inches. In accordance with the present invention, the diameter of the electrode member does not produce the stress effect on the glass as does a conventional electrode member and as a consequence the diameter of the electrode member is not so limited. Accordingly, if desired, the electrode diameter may be increased beyond the size conventionally employed in prior art devices to increase the output of the electrode.

As already discussed, with prior art fused glass electrodes it has been necessary to match as closely as possible the coefficient of expansion of the electrode member to the glass to ensure a good, stress free fusion between the electrode member and the glass sheath. For this reason lead glass is normally the glass of choice in rhodium fused glass electrode assemblies. However, during the fusion operation it has been found that lead may come out of solid solution and form a suspension in the glass. The suspended lead will be available for reaction with the electrolyte. The suspended lead and the reaction products thereof adversely affect the electrical characteristics of the electrode and render it unserviceable.

In accordance with the present invention, a close match of the coefficients of expansion of the electrode member and the glass is not critical, thus avoiding the necessity for using lead glass. Thus, it is preferred to utilize a more stable glass for the glass sheath, such as, for example, soda lime glass to avoid the manufacturing problems encountered with lead glass. However, if desired, lead glass may be used as the composition of the glass sheath.

Assembly of the glass sheathed electrode in accordance with the present invention is described

herein in connection with the rhodium cathode 32 shown in Fig. 1. However, the manufacturing technique will be the same regardless of the composition of the electrode in Fig. 3.

Referring to Fig. 2, a .10 inch diameter button 40 is stamped from a sheet of rhodium foil having a thickness of 0.010 inches. A .005 inch diameter platinum wire 38 is spot welded to one surface of the disc 40 using molybdenum-copper and copper electrodes. The free end of the wire 38 is drawn into the bore of a glass tube 44 until the button 40 abuts the end of the tube. While maintaining the button 40 in abutment against the end of the tube 44, the tube is heated to a temperature above the softening point of the glass to cause the glass to flow around the button 40 and the wire 38 and the assembly is allowed to cool to room temperature. It is necessary to heat only that portion of the tube 44 adjacent the button 40 to achieve the desired fusion.

Following the fusion operation, the assembly is annealed at a temperature of 960°C for 12 to 14 hours to relieve any stress in the glass and then slowly cooled to room temperature. At this point the button 40 is substantially encased in the glass. Accordingly, the end of the tube 44 is ground to expose the outer surface of the button 40 and to produce the desired radius of curvature and smoothness of the completed electrode 32 as illustrated in Fig. 3.

Best results are achieved utilizing capillary tubes in the manufacture of the fused glass electrode assemblies of this invention, that is, glass tubes having an O.D. of up to about 9 mm. and an I.D. of up to about 2 mm. Good results are achieved using capillary tubes having an O.D. of 6 mm. and an I.D. of about 1 mm.

Fused glass rhodium electrode assemblies

manufactured as described above were subjected to accelerated life tests by immersion in a 10% aqueous solution of potassium hydroxide and maintained therein at a temperature of between 70°C. and 90°C. for a period of two weeks. Following the two-week period, the test assemblies were examined for cracks under a microscope and returned to the heated caustic solution for an additional two weeks. Of the assemblies manufactured in accordance with this invention about 90% showed no sign of glass cracks or other adverse effects of the caustic solution. On the other hand, no fused glass rhodium electrode assemblies comprising .05 inch diameter rhodium wire fused in lead glass sheath in accordance with the prior art survived the test without exhibiting stress in the sheath and evidence of penetration of the caustic solution within the electrode assembly.

While the foregoing detailed description is directed toward an equilibrium type oxygen sensor and cathode assembly therefor, it will be understood that the present invention may be utilized in any type of polarization cell for the detection of a constituent in a fluid medium, particularly where the cell is exposed to high temperature, caustic fluids, etc.

Thus, while various embodiments and modifications of the invention have been described in the foregoing description and illustrated in the drawings, it well be understood that minor changes may be made in the details of construction as well as in the combination and arrangement of parts without departing from the spirit and scope of the invention as claimed.

What is claimed is:

1. A sensor (10) for the electrochemical analysis of a constituent in a fluid sample comprising a body (12) having an electrolyte reservoir (14) therein, an opening communicating between said reservoir and the exterior of said body, a thin polymeric membrane (20) permeable to said constituent and impermeable to electrolyte disposed across said opening, terminal means (24) in electrical connection with a source of electrical potential and current measuring means, a pair of electrode means defining an anode (34) and a cathode (32) disposed in said body, at least one of said electrode means being disposed adjacent said membrane to define an electrolyte space therebetween, said electrolyte space communicating with said reservoir, and means electrically connecting said electrode means through said terminal means to said source of electrical potential and said current measuring means, the improvement comprising:

at least one of said electrode means being an assembly consisting of a disc-shaped noble metal electrode fused in a glass sheath (42) and having one surface thereof exposed and a conductor (38) electrically connected to the opposite surface and extending through said glass sheath to the exterior thereof.

2. The sensor of claim 1 wherein the electrode of said electrode assembly comprises rhodium and serves as the cathode (32) of said sensor.

3. The sensor of claim 2 wherein said anode (34) comprises an annular platinum disc carried by said glass sheath (42) of said cathode assembly and is concentrically disposed adjacent to the exposed surface of said cathode.

4. The sensor of claim 1 wherein said electrode (32) or (34) of said electrode assembly has a diameter of up to about 0.3 inches.

5. An improved electrode assembly consisting of a thin, disc-shaped noble metal electrode (32) or(34) fused in one end of a cylindrical glass sheath (42) and having one surface thereof exposed and a wire conductor (38) affixed to the opposite surface of said electrode and extending axially through said sheath to the exterior thereof.

6. The electrode assembly of claim 5 wherein said electrode (32) or (34) comprises rhodium.

7. The electrode assembly of claim 6 wherein said glass sheath (42) is soda lime glass.

8. A method for the production of an electrode assembly comprising the steps of:

a) forming a disc-shaped electrode (32) or (34) from a noble metal foil;

b) affixing one end of a wire conductor (38) to a surface of said electrode;

c) drawing said wire conductor through the bore of a glass tube (44) until said electrode (32) or (34) abuts the end of the tube;

d) heating at least the end portion of said glass tube (44) adjacent said electrode (32) or (34) above the softening point of the glass to cause the glass to flow around and seal said electrode and a portion of said conductor (38) adjacent thereto;

e) annealing said electrode assembly at the annealing temperature of the glass; and

f) grinding said glass tube (44) to expose a surface of said electrode (32) or (34) at one end of said glass tube.

9. The method of claim 8 wherein said electrode (32) or (34) is formed by stamping from rhodium foil.

AMENDED CLAIMS
[received by the International Bureau on 5 March 1987 (05.03.87)
original claims 2,3 and 6 deleted; claims 1-4 amended; original claims
8 and 9 unchanged but renumbered as claims 5 and 6 (2 pages)]

1. A sensor (10) for the electrochemical analysis of a constituent in a fluid sample comprising a body (12) having an electrolyte reservoir (14) therein, an opening communicating between said reservoir and the exterior of said body, a thin polymeric membrane (20) disposed across said opening, said membrane being permeable to said constituent and impermeable to electrolyte disposed in said reservoir, terminal means (24) in electrical connection with a source of electrical potential and with current measuring means, a pair of electrodes disposed in said body, said electrodes defining an anode (34) and a cathode (32), said cathode being disposed adjacent said membrane to define therebetween an electrolyte film space in communication with said reservoir, and means electrically connecting said electrodes through said terminal means to said source of electrical potential and said current measuring means, the improvement comprising:

said cathode (32) comprising an assembly consisting of a rhodium disk fused in a glass sheath (42) and having one surface thereof exposed and a conductor (38) electrically connected to the opposite surface extending through said glass sheath to the exterior thereof.

2. The sensor of claim 1 wherein said rhodium cathode (32) of said electrode assembly has a diameter in excess of 0.01 inches.

3. An improved electrical assembly consisting of a thin rhodium disk (32) fused in one end of a cylindrical glass sheath (42) having one surface thereof exposed, a wire conductor (38) affixed to the opposite surface of said rhodium disk extending axially through said glass sheath to the exterior thereof.

4. The electrode assembly of claim 1 wherein said glass sheath (42) comprises soda lime glass.

5. A method for the production of an electrode assembly comprising the steps of:

(a) forming a disc-shaped electrode (32) from a noble metal foil;

(b) affixing one end of a wire conductor (38) to a surface of said electrode;

(c) drawing said wire conductor through the bore of a glass tube (44) until said electrode (32) abuts the end of the tube;

(d) heating at least the end portion of said glass tube (44) adjacent said electrode (32) above the softening point of the glass to cause the glass to flow around and seal said electrode and a portion of said conductor (38) adjacent thereto;

(e) annealing said electrode assembly at the annealing temperature of the glass; and

(f) grinding said glass tube (44) to expose a surface of said electrode (32) at one end of said glass tube.

6. The method of claim 5 wherein said electrode (32) is formed by stamping from rhodium foil.

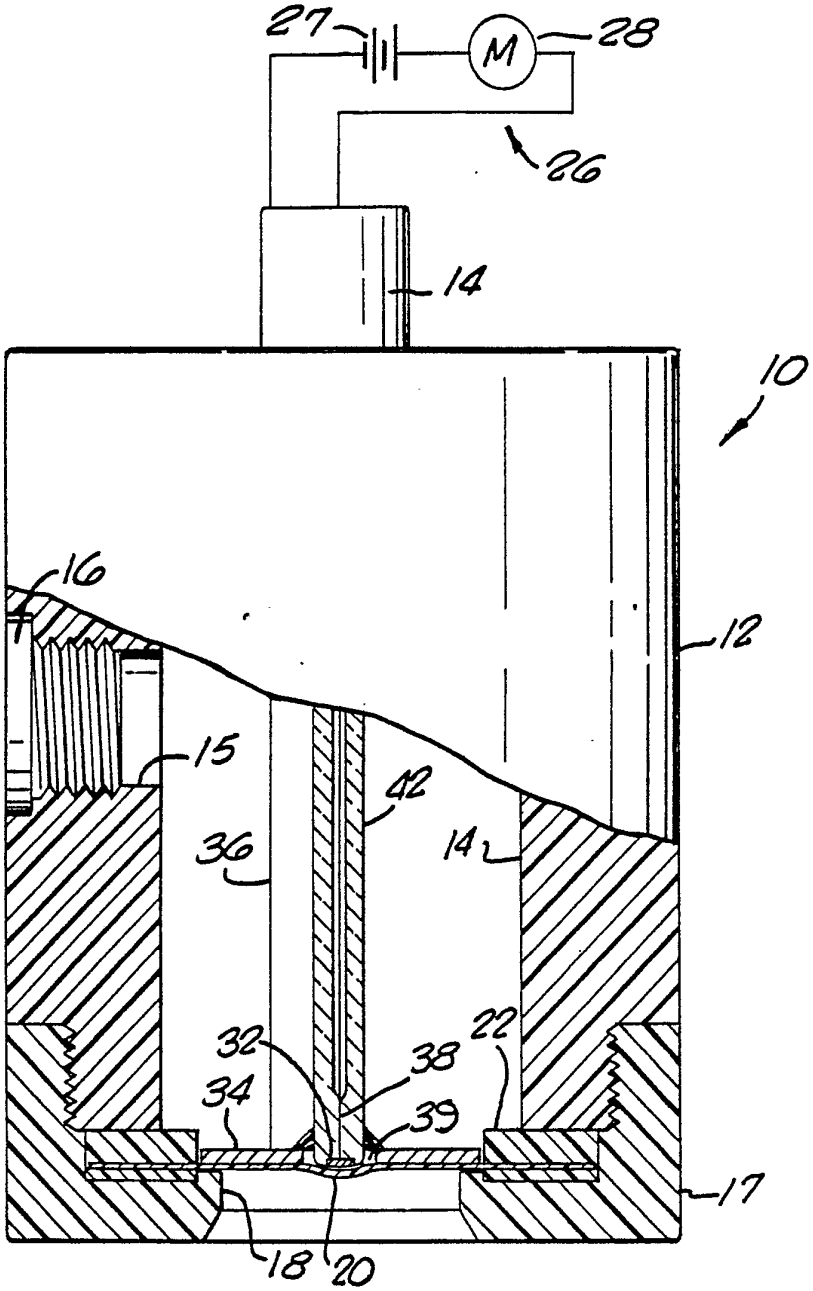


FIG. 1.

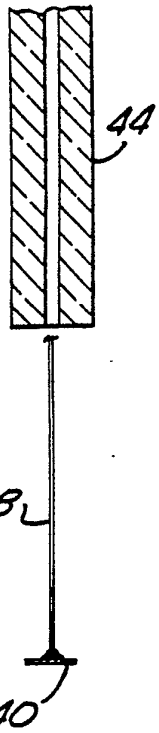


FIG. 2.

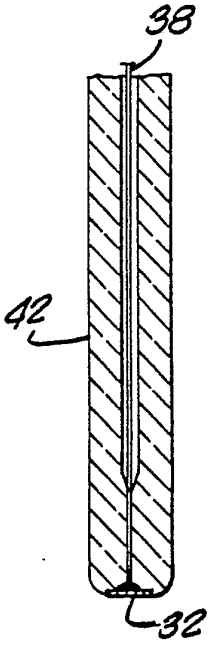


FIG. 3.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US86/02085

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

INT. CL. [4] G01N 27/46

U.S. CL. 204/415

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
U.S.	65/59.1, 59.2, 59.23, 59.24, 59.25, 59.26, 59.27, 59.28 204/415

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
A	US, A, 1,489,099, (Reynolds), 01 April 1924, See Figures 1-12	8
A	US, A, 2,511,164, (Koch), 13 June 1950, See Figures 1-3	8
Y	US, A, 2,913,386, (Clark), 17 November 1959, See Figure 1	1-7
Y	US, A, 3,070,539, (Arthur et al), 25 December 1962, See Figure 2	1-7
A	US, A, 3,221,386, (Demarest), 07 December 1965, See Figures 1-4	8
A	US, A, 3,260,656, (Ross), 12 July 1966, See Figure 2	1-7
Y	US, A, 3,328,277, (Solomons et al), 27 June 1967, See Figure 1	3
Y	US, A, 3,334,039, (Vlasak), 01 August 1967, See Figure 2	3

* Special categories of cited documents: [15]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
December 16, 1986	05 JAN 1987
International Searching Authority [1]	**Signature of Authorized Officer [20]**
ISA/US	T. Tung

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No [18]
Y	US, A, 3,449,231, (Adams et al), 10 June 1969, See col. 2, line 63	2,3,6,7
Y	US, A, 3,503,861, (Volpe), 31 March 1970, See Figure 2	1-7
Y	US, A, 3,526,577, (Molloy), 01 September 1970, See columns 3 and 4	1-7
Y	US, A, 3,530,046, (Mochizuki et al), 22 September 1970, See col. 4, line 36	7
A	US, A, 3,577,332, (Porter et al), 04 May 1971, See Figure 1	1-7
Y	US, A, 3,785,948, (Hitchman et al), 15 January 1974, See Figure 1	3
Y	US, A, 3,948,745, (Guilbault et al), 06 April 1976, See the Figure	1-7
A	US, A, 4,078,981, (Neti et al), 14 March 1978, See Figure 4	1-7
A	US, A, 4,163,656, (Monneraye et al), 07 August 1979, See Figure 1a	8
Y	US, A, 4,207,160, (Frankenberger et al), 10 June 1980, See element 4	3
A	US, A, 4,268,370, (Neti), 19 May 1981, See Figure 5	1-7
A	US, A, 4,377,404, (Hoshikawa et al), 22 March 1983, See Figure 1	8