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Section 29

AUSTRALIA
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PATENT REQUEST : STANDARD PATENT

I/We, being the person(s) identified below as the Applicant(s), request the grant of a Standard Patent to the person(s) identified below as the Nominated Person(s), for an invention described in the accompanying complete specification.

**Applicant(s) and
Nominated Person(s):** PILKINGTON PLC
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Invention Title: OXYGEN MEASURING PROBE

**Name(s) of Actual
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BASIC CONVENTION APPLICATION DETAILS

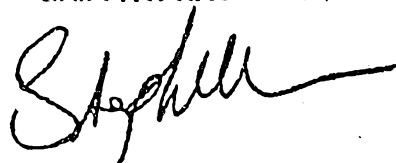
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DATED: 9 March 1993

PILKINGTON PLC

GRIFFITH HACK & CO



Patent Attorney for and
on behalf of the Applicant

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AUSTRALIA
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NOTICE OF ENTITLEMENT

I/We PILKINGTON PLC
A.R.B.N. 007 509 846

of PRESCOT ROAD
ST. HELENS
MERSEYSIDE WA10 3TT
ENGLAND

being the applicant(s) in respect of an application for a patent for an invention entitled
OXYGEN MEASURING PROBE, state the following:

1. The nominated person(s) has/have, for the following reasons, gained entitlement
from the actual inventor(s):

THE NOMINATED PERSON WOULD BE ENTITLED TO
HAVE ASSIGNED TO IT A PATENT GRANTED TO ANY
OF THE INVENTORS IN RESPECT OF THE SAID
INVENTION.

2. The nominated person(s) has/have, for the following reasons, gained entitlement
from the basic applicant(s) listed on the patent request:

THE APPLICANT AND NOMINATED PERSON IS THE
BASIC APPLICANT.

3. The basic application(s) listed on the request form is/are the first application(s)
made in a Convention country in respect of the invention.

DATE: 9 March 1993

PILKINGTON PLC

CARE FITH HACK & CO



Patent Attorney for and
on behalf of the applicant(s)



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- (74) Attorney or Agent
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- (56) Prior Art Documents
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US 4944861
US 3619381
- (57) Claim

1. An oxygen measuring probe for use with molten metal baths for the manufacture of glass, which probe comprises: a tubular probe body comprising an elongate tubular member closed by a separate tip part which is connected thereto, which tip part is formed of stabilised zirconia which constitutes a solid electrolyte through which oxygen ions can pass, said tubular member being formed of a heat resistant material different from said zirconia; and an emf measuring device for measuring the emf generated in use between inner and outer surfaces of the zirconia tip part, wherein a thermocouple disposed in contact with an inner surface of the zirconia tip part is provided for measuring the temperature of the zirconia tip part, wherein the zirconia tip part comprises a generally annular portion received within an end of the tubular member, at which the tip part is sealed to the elongate tubular member, and a hollow relatively short portion depending therefrom of substantially conical shape which has an apex at the end of the zirconia tip part remote from the tubular part, the thermocouple being arranged to contact the inner surface of the zirconia tip part at the apex thereof.

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COMPLETE SPECIFICATION
STANDARD PATENT

Applicant(s):

PILKINGTON PLC

A.R.B.N. 007 509 846

Invention Title:

OXYGEN MEASURING PROBE

The following statement is a full description of this invention, including the best method of performing it known to me/us:

OXYGEN MEASURING PROBE

The present invention relates to an oxygen measuring probe for use with molten metal baths for the manufacture of glass, and to a method of use of such a probe.

In the float glass process in which a bath of molten tin or tin alloy is used to support an advancing ribbon of glass, oxygen is a major contaminant. Oxygen is believed to be responsible directly or indirectly for reducing glass quality in several ways, giving rise to poor bloom grades, CO bubble, tin speck faults and for tin pick-up faults.

In the float glass process the bath atmosphere is controlled, generally by maintaining an atmosphere of nitrogen and hydrogen. In practical terms it is impossible to exclude oxygen completely from the bath; oxygen can enter the bath by various pathways, such as through the exit seal, through leaks in windows and side seals, as a contaminant of the atmosphere supply, or with the glass itself as dissolved oxides (e.g. SO_2 and H_2O). A series of interactions then take place with hydrogen in the atmosphere, with the tin, and with the glass itself. It is not economic to attempt to reduce the contamination below a particular level. Ingress can, however, be reduced to a level at which its deleterious effects are of little or no consequence.

It is clearly important to know the amount of oxygen present so that if this rises, appropriate steps can be taken to prevent further contamination, whilst the glass subject to contamination and the level of contamination can be readily identified.

The oxygen content of the tin can be measured by conventional analytical techniques; by removing a sample, reacting with

carbon under vacuum and measuring the carbon monoxide released. This is however a lengthy procedure which demands great skill and care if the required degree of precision is to be achieved; as a result, this measurement is rarely performed.

The chemical state of the bath with respect to oxygen contamination can also be monitored on a regular basis using indirect means such as an atmosphere extractive technique, measurement of the tin count, or measurement of the bloom grade. The extractive technique indicates the level of contamination of the atmosphere but does not necessarily say anything about the level of contamination in the tin. Further, being an extractive technique, the sample lines are prone to blockage. The tin count and bloom grade are measurements made on the glass, and are indicative of the amount of tin present in the surface, which is directly related to the level of oxygen contamination. Since these tests are carried out on the product there is necessarily a time delay and the results give little indication of the distribution of contamination within the bath.

A known technique for measuring the oxygen content of the molten tin on an in situ basis uses a measuring probe located in the bath so as to extend into the molten tin. This probe is the subject of US Patent No 3625026. The probe comprises a tubular body of zirconia which has been doped to induce conductivity to oxygen ions and which thereby constitutes a solid electrolyte. Electrical connection is made to the inside of the tube, and directly to the molten tin which as a conductor constitutes an electrical connection to the outside of the tube. A galvanic cell is thereby effectively set up, resulting from the oxygen concentration internally of the tube which tin by the solid zirconia electrolyte. The is separated from the oxygen concentration in the molten cell

emf is indicative of the oxygen concentration at the outside of the probe. By supplying a gas of constant oxygen concentration to the inside of the tube an absolute value for the oxygen concentration externally of the tube can be determined.

Various problems exist with this probe. The probe body of zirconia is particularly fragile, and is sensitive to thermal shock arising on insertion of the probe into the molten tin, which may typically be at 700°C. Zirconia has a high thermal coefficient of expansion, such that on this initial insertion, considerable stresses are set up within the zirconia body, rendering the probe liable to fracture. There is a further thermal effect which arises on more prolonged usage which can cause the probe to fracture. The stabilisation of the zirconia by the addition of dopants causes the zirconia to take a particular crystalline form (specifically, a cubic tetragonal form). Although this form is stable at the temperature of the molten tin, at lower temperatures, below about 400°C, the stable form of zirconia is a different crystalline form (specifically, a cubic monoclinic form), and on prolonged usage a transition to this form will occur. A substantial temperature gradient exists along the length of the probe when in use, such that the temperature conditions in which the second crystalline form is the stable form are generally found at a region of the probe remote from the molten tin. This change of crystalline structure involves a volume change, such that a junction region between the two forms of zirconia will constitute a particular site of stress at which the zirconia body is liable to fracture.

The present invention seeks to provide an oxygen measuring probe which overcomes these problems.

In order to derive an accurate measurement of the oxygen concentration, in addition to obtaining a value for the cell emf, one requires a value for the cell temperature. Such a value can be obtained from separately measuring the molten metal temperature with a thermocouple extending part way within the probe. neither of these means ensure accurate temperature measurement of the cell.

Accordingly to one aspect of the invention there is provided an oxygen measuring probe for use with molten metal baths for the manufacture of glass, which probe comprises: a tubular probe body comprising an elongate tubular member closed by a separate tip part which is connected thereto, which tip part is formed of stabilised zirconia which constitutes a solid electrolyte through which oxygen ions can pass, said tubular member being formed of a heat resistant material different from said zirconia; and an emf measuring device for measuring the emf generated in use between inner and outer surfaces of the zirconia tip part, wherein a thermocouple disposed in contact with an inner surface of the zirconia tip part is provided for measuring the temperature of the zirconia tip part, wherein the zirconia tip part comprises a generally annular portion received within an end of the tubular member, at which the tip part is sealed to the elongate tubular member, and a hollow relatively short portion depending therefrom of substantially conical shape which has an apex at the end of the zirconia tip part remote from the tubular part, the thermocouple being arranged to contact the inner surface of the zirconia tip part at the apex thereof.

The shortness and internal shape of the zirconia tip part facilitates appropriate location of the platinum paste and electrode on assembly of the probe.

By providing a thermocouple which is in contact with the zirconia tip part one obtains a direct measurement of the actual cell temperature. By providing only a tip

- 4a -

part of zirconia this will rapidly reach in its entirety the high temperature in or above the bath of molten metals, and so the risk of failure due to thermal shock is reduced.

- 5 Furthermore, when the probe is inserted in the molten metal with the entire tip part immersed, the entire tip part will be held at a temperature above that at which a change of crystalline form could occur.



A further advantage arising from the probe structure of the invention is that prior to assembly, the inside surface of the zirconia tip part can be easily accessed. The unitary zirconia body of the known probe is very long and thin such that access to the inside of the tip is very difficult, and it is therefore very difficult to form a good electrical connection of the electrode to the inner surface of the tip.

A further difficulty which arises is that it is problematic to secure the electrode to the inner surface of the zirconia tip part, and where a thermocouple is additionally provided this problem also applies to the thermocouple wires.

Preferably, the emf measuring device, and the thermocouple include a common electrode in the form of a metallic wire connected to an inner surface of the zirconia tip part, the thermocouple further comprising an additional thermocouple wire of different composition connected to the first electrode at the tip part to form a thermocouple junction therewith.

Preferably, with the present probe the first electrode wire and the additional thermocouple wire are connected to the inner surface of the zirconia tip part by means of a cement of platinum applied as a paste. This gives a particularly secure and effective electrical and thermal contact with the zirconia tip part. The common electrode may be formed of platinum, and the additional thermocouple wire formed of a platinum alloy.

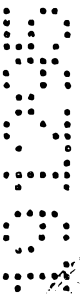
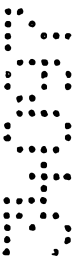
In an embodiment adapted specifically for measuring the oxygen concentration in the atmosphere above the tin bath, the emf measuring device comprises a first electrode connected to an inner surface of the zirconia tip part, a second electrode connected to the outer surface of the tip part, and a voltmeter connected between the first and second

electrodes. In this case both first and second electrodes are secured to the tip part by means of a cement of platinum applied as a paste.

A further problem encountered with the known probe arises from the fact an electrical connection must be made directly into the molten tin. Connection has previously been made by a platinum wire having a length of rhenium wire welded to the end of this platinum wire, with only the rhenium extending into the molten tin. Rhenium is used because, unlike platinum, it is not attacked by the molten tin, and is relatively stable towards oxygen at the concentrations which generally exist in float glass baths. However, if a severe oxygen contamination occurs, the rhenium can become oxidised, whereby the electrical connection is disrupted.

Preferably the oxygen measuring probe comprises

_____ earthing means connected to earth out of contact with the molten metal, and the emf measuring device is connected to the first electrode and to said earthing means, whereby in use the molten metal acts as an earth such that the voltage indicated by said emf measuring device represents the voltage generated across the solid electrolyte.



With this arrangement there is no reliance on direct electrical connection to the molten metal. The arrangement uses the observation that the molten metal is effectively an earth, so that measurement of the emf between the probe electrode and a direct connection to earth is effectively equivalent to measurement between the probe electrode and

molten metal which is in contact with an outer side of the zirconia, subject to correction of any emf's arising from junctions in the electrical connections earth. This modification also simplifies construction and reduces the cost of the probe.

Preferably, the elongate tubular member is formed of alumina, and the zirconia tip part is sealed to the alumina tube by a glass ceramic material having a thermal expansion coefficient intermediate between that of alumina and zirconia. The use of a glass ceramic material of matched thermal expansion provides an effective non-porous seal, which is able to absorb to some extent the thermal expansion of the zirconia tip on initial insertion into or location adjacent to the molten metal.

The probe preferably also includes means for direction of an oxygen-containing reference gas onto the inner surface of the zirconia tip part. Maintaining a known concentration of oxygen within the probe tip is essential where an absolute value for oxygen concentration on the outside of the probe tip is required.



The invention in a further aspect also resides in a method of measuring the oxygen concentration in molten metal with a probe as defined hereinabove, wherein the probe is inserted into the molten metal and said earthing means are connected to earth out of contact with the molten metal.

Embodiments of the present invention are described, by way of example only, with reference to the following drawings in which:

Figure 1 is a schematic view of a first embodiment of a measuring probe in accordance with the invention, adapted for measuring the oxygen concentration in molten tin; and

Figure 2 is a schematic view of a second embodiment of a measuring probe in accordance with the invention, adapted for measuring the oxygen concentration in the atmosphere above a bath of molten tin.

Turning to Figure 1 of the drawings, a first embodiment of an oxygen measuring probe 2 is shown, the probe comprising a tubular probe body 4 closed at one end which constitutes a measuring end, which in use is immersed in a bath of molten tin of a float glass bath. The probe body 4 comprises a cylindrical tubular member 6 formed of a heat-resistant refractory material, such as alumina, which is closed at its lower end by a tip part 8 formed of zirconia (zirconium oxide). The zirconia is stabilised by the addition of one or more of CaO , MgO and Y_2O_3 as is known in the art, whereby

the zirconia constitutes a solid electrolyte which allows conduction of oxygen ions therethrough. The zirconia tip part 8 comprises an annular portion 10 at which the tip part 8 is attached to the tubular part 6, and a hollow generally conical portion 12 depending therefrom.

The tip part 8 is connected to the tubular member 6 by means of a glass ceramic material 14 which forms a non-porous seal therebetween. The glass ceramic material is arranged to have a coefficient of thermal expansion intermediate between that of zirconia and alumina. This matched expansion glass ceramic seal is formed according to the method of Rogers, Butler and Steele as disclosed in J. Sci. Inst. (J. Physics E) 1969 Ser. 2 volume 2 page 102, although in the present case the seal is formed between alumina and zirconia, instead of between a alumina and metal as in the reference.

A reference electrode 16 comprises a wire, formed preferably of platinum, extending within the probe body 4 along the length thereof, which is electrically and thermally connected to the inner surface of the tip part 8 at the inner apex thereof.

A particularly effective connection can be obtained by cementing the electrode to the zirconia tip by means of a platinum paste, indicated at 17. The paste comprises a suspension of platinum in a viscous organic medium which is applied to the inside of the tip part with the electrode embedded therein, and then fired to volatilise the organic medium, leaving the electrode cemented to the tip part.

It is intended that on assembly of the probe, the connection of the platinum wire electrode 16 is made to the tip part 8 prior to the connection of the tip part 8 to the tubular member 6, since easy access is then possible.

An internal annular tube 20 of refractory material, preferably alumina, surrounds the electrode wire 16. This internal tube 20 forms a passageway for the supply of a reference gas containing a known amount of oxygen, typically air, to the inner surface of the tip part 8. Maintenance of a known oxygen concentration at the inner surface of the tip is necessary where it is required to calculate an absolute value for oxygen concentration in the molten tin, as is apparent from the calculations shown below. It is also highly desirable to maintain a constant oxygen concentration internally where only relative changes of emf are used to indicate relative change of oxygen concentration in the bath. The tube 20 also serves to protect the platinum electrode 16 from the effects of heat.

A further wire 22 extends within the probe body 4 and is connected to the electrode wire 16 where this is cemented to the tip part 8, to form a thermocouple junction with the electrode wire 16. Thus, the electrode wire 16 forms a common electrode wire for both the voltage measurement and temperature measurement. This simplifies the design and assembly. The wire 22 is preferably formed of a platinum alloy, for example a 13% Rh/Pt alloy. A millivoltmeter 23 provided externally of the probe body 4 is connected between the wire 16 and wire 22; measurement of the thermoelectric emf developed between the electrode wire 16 and wire 22 enables a value for the temperature at the tip to be obtained, which temperature value is necessary for a calculation of an absolute value for oxygen concentration in the molten tin. Tube 20, electrode 16 and thermocouple wire 22 are supported in fixed positions at an upper end of the probe housing 4 within a sleeve member (not shown).

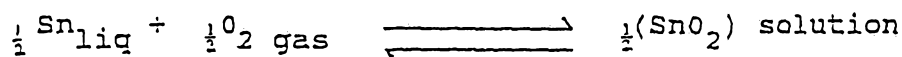
Also externally of the probe body 4, the reference electrode 16 is connected to a millivoltmeter 24 which is in turn

connected to a measuring electrode 26. This measuring electrode 26 is in turn connected to earth. Typically, a metal portion of the bath casing or unpainted water pipe provides the earth. The electrode 26 may, but need not, be of platinum. In practice the platinum of electrode 16 may terminate at the probe head and have a lead to the meters of a different material, the electrode 26 also being of that different material. Use of the same electrode material for the electrodes on both sides of the millivoltmeter obviates the need for correction of the measurement of emf resulting from the electrode/millivoltmeter junction; however, a correction to the measured emf is required as a result of an emf generated by the junction of the measuring electrode 26 and earth return. The millivoltmeter is a high impedance millivoltmeter, for example of input impedance 10^{13} ohms, whereby polarisation of the cell is avoided.

In use, the probe is positioned with the tip part 8 entirely immersed in the molten tin. The tin level is indicated in Figure 1 by reference numeral 27. The entire tip part 8 therefore remains at a temperature above that at which a change of crystalline form could occur. The region where the temperature conditions exist which would cause the change of crystalline form in zirconia are found at the part of the probe formed of alumina, in which no such change occurs and so presents no thermal stress problem. Furthermore, the surface of the molten tin, which also constitutes a site of thermal stress, lies in the region of the alumina tubular member 6, which material is considerably less susceptible to thermal stress-induced fracture than zirconia. Air is directed at the inner surface of the tip part 8 via the tube 20, and measurements taken of the emf shown by the voltmeter 24, which emf is indicative of the oxygen concentration in the molten tin.

The relationship between the measured emf and oxygen concentration in the molten tin is derivable as follows:

Oxygen reacts with tin according to the equation:



By Mass Action Law:

$$K = \frac{a_{(0)\text{Sn}}}{a_{\text{Sn}}^{\frac{1}{2}} \cdot P_{\text{O}_2}^{\frac{1}{2}}}$$

thus

$$P_{\text{O}_2}^{\frac{1}{2}} = \frac{a_{(0)\text{Sn}}}{K \cdot a_{\text{Sn}}^{\frac{1}{2}}}$$

where

K = Equilibrium constant
a_{Sn} = Activity of tin, taken as 1
a_{(0)Sn} = Activity of Oxygen in tin

from thermodynamic tables:

$$K = \frac{15317}{T} - 5.63$$

where

T = absolute temperature

The activity of oxygen in tin is defined as follows:

$$a_{(0)\text{Sn}} = \frac{\text{Concentration of Oxygen in tin} = C}{\text{Saturated Concentration of Oxygen } C_s \text{ in Tin}}$$

The saturated concentration of oxygen in tin is given in the reference "Thermodynamics and Solubility of oxygen in liquid metals Part 2 - Tin, T.N. Belford and C.B. Alcock TFS 61,443 (1965)" as:

$$C_S \text{ (ppm)} = 1.345 \times 10^{\left(\frac{-5730 + 4.19}{T} \right)}$$

Thus we can relate the oxygen partial pressure over a solution of oxygen in tin to the oxygen concentration as follows:-

$$\log P_{O_2} = 2 \log C_S - 3.378 - \frac{19174}{T}$$

The Nernst equation relates this partial pressure to the Emf as follows:-

$$E = \frac{RT \ln (P_{O_2} \text{ reference})}{4F P_{O_2}}$$

If

E = Emf developed in millivolts
R = Universal gas constant
F = Faraday constant
Reference Gas = Air
P_{O₂} reference = 0.21 atmospheres

then

Oxygen concentration (C_S) =

$$10^{\left(\frac{0.9512 + 1.339 \times 10^{-4} \times T - E \times 10^{-3}}{9.922 \times 10^{-5} \times T} \right)} \quad \text{Equation 1}$$

The above relation ignores any error which exists as a result of an emf generated by the platinum wire 26/earth return couple. Where only changes in oxygen concentration in the tin are required to be measured, it is not necessary to correct for this thermoelectric emf. However, this may be done readily by modifying the constant appropriately:

The thermoelectric emf generated by the platinum wire/earth return couple (E') may be represented by the equation:

$$E' = 0.01025 \times T - 6.45$$

then, the emf E in equation 1 above is replaced by (E + E').

A modification of the measuring probe of Figure 1 allows the measurement of oxygen concentration in the atmosphere above the tin bath. This modified probe is shown in Figure 2, in which like numerals are used to indicate like parts. In this case, since the zirconia tip part 8 which constitutes the solid electrolyte is not immersed in the molten tin, electrical connection to the outer surface of the tip must be provided; the measurement of the emf generated by the cell requires direct measurement of the potential at the inner and outer surfaces of the zirconia tip part 8. This connection is preferably in the form of a platinum wire 30 which is connected to the millivoltmeter 24 and to a length of rhenium wire 32 at a welded joint 34. The rhenium wire 32 is cemented by platinum paste at 36 to the outer surface the zirconia tip part 8, opposite the internal connection of the electrode 16, in the manner as described above in relation to the connection of the electrode 16. A further alumina tube 38 is used to enclose the platinum wire 30 and upper portion of the rhenium wire 32 to protect these from the atmosphere.

In this case, the Nernst equation can be used to relate the emf developed to the oxygen concentration in the atmosphere as follows:

$$E = \frac{RT}{nF} \ln \frac{(P_{O_2} \text{ reference})}{P_{O_2}}$$

If E = Emf developed by probe in millivolts
 R = Universal gas constant
 F = Faraday constant
 T = Absolute temperature
 Reference gas = Air
 P_{O_2} reference = 0.21 atmospheres

$$\text{then } P_{O_2} \text{ (atm)} = 0.21 \times 10^{\frac{(-E \times 20.16)}{T}}$$

Here, since the bath atmosphere contains hydrogen, the platinum cement on the outer surface of the probe tip catalyses a reaction between hydrogen and oxygen, and the voltage generated by the measuring probe will relate not to free oxygen, but to that which would be present at equilibrium.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. An oxygen measuring probe for use with molten metal baths for the manufacture of glass, which probe comprises: a tubular probe body comprising an elongate tubular member closed by a separate tip part which is connected thereto, which tip part is formed of stabilised zirconia which constitutes a solid electrolyte through which oxygen ions can pass, said tubular member being formed of a heat resistant material different from said zirconia; and an emf measuring device for measuring the emf generated in use between inner and outer surfaces of the zirconia tip part, wherein a thermocouple disposed in contact with an inner surface of the zirconia tip part is provided for measuring the temperature of the zirconia tip part, wherein the zirconia tip part comprises a generally annular portion received within an end of the tubular member, at which the tip part is sealed to the elongate tubular member, and a hollow relatively short portion depending therefrom of substantially conical shape which has an apex at the end of the zirconia tip part remote from the tubular part, the thermocouple being arranged to contact the inner surface of the zirconia tip part at the apex thereof.

2. An oxygen measuring probe according to claim 1 wherein the emf measuring device, and the thermocouple include a common first electrode in the form of a metallic wire connected to an inner surface of the zirconia tip part at the apex thereof, and wherein the thermocouple further comprises an additional thermocouple wire of different composition connected to the first electrode at the tip part to form a thermocouple junction therewith.

3. An oxygen measuring probe according to claim 2 wherein the first electrode wire and the additional thermocouple wire are secured to the tip part by means of a cement of platinum applied to the tip part as a paste.



4. An oxygen measuring probe according to claim 2 or 3 wherein the first electrode comprises a platinum wire, and wherein the additional thermocouple wire comprises a platinum alloy wire.

5. An oxygen measuring probe according to any one of claims 2 to 4 wherein the emf measuring device further comprises a second electrode connected to earth out of contact with the molten metal, and a voltmeter connected between the first and second electrodes.

6. An oxygen measuring probe according to any one of claims 2 to 4 wherein the emf measuring device further comprises, a second electrode connected to the outer surface of the tip part, and a voltmeter connected between the first and second electrodes.

7. An oxygen measuring probe according to claim 6 wherein the second electrode is secured to the zirconia tip part by means of a cement of platinum applied as a paste.

8. An oxygen measuring probe according to any preceding claim wherein the elongate tubular member is formed of alumina, and wherein the zirconia tip part is sealed to the alumina tube by a glass ceramic material having a thermal expansion coefficient intermediate between that of alumina and zirconia.

9. An oxygen measuring probe according to any preceding claim wherein gas supply means are provided for direction of an oxygen containing reference gas onto the inner surface of the zirconia tip part.



10. An oxygen measuring probe as claimed in claim 2 or any claim appended thereto, comprising earthing means connected to earth out of contact with the molten metal, and wherein the emf measuring device is connected to the first electrode and to said earthing means, whereby in use the molten metal acts as an earth such that the voltage indicated by said emf measuring device represents the voltage generated across the solid electrolyte.

11. An oxygen measuring probe according to claim 10 wherein electrical connections to the voltage measuring means from the first electrode and from the earthing means are of the same material.

12. An oxygen measuring probe according to claim 10 or 11 wherein a wire of platinum alloy extends within the tubular member and is connected to the first electrode at the apex of the zirconia tip part to form a thermocouple junction therewith.

13. A method of measuring the oxygen concentration in a molten metal employed in the manufacture of glass with a probe according to any one of claims 10 to 12 comprising the steps of inserting the probe into the molten metal, connecting the earthing means to earth out of contact with the molten metal and measuring the voltage generated between the first electrode and the earthing means as oxygen ions pass through the solid zirconia electrolyte.

14. A method of measuring the oxygen concentration in a molten metal employed in a bath for the manufacture of glass with a probe according to any one of claims 1 to 9 comprising the steps of inserting the probe into the molten metal until the zirconia tip part is fully immersed therein, measuring the



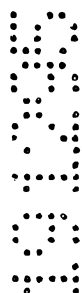
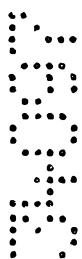
temperature of the zirconia tip part with said thermocouple, and measuring the voltage between the inner and outer surfaces of the zirconia tip part as oxygen ions pass through the solid zirconia electrolyte.

15. An oxygen measuring probe substantially as hereinbefore described with reference to Figures 1 or 2 of the accompanying drawings.

16. A method of measuring oxygen concentration in a molten metal substantially as hereinbefore described with reference to Figures 1 or 2 of the accompanying drawings.

DATED THIS 19th DAY OF December 1995 :
PILKINGTON PLC
By its Patent Attorneys:
GRIFFITH HACK & co

Fellows Institute of Patent Attorneys of Australia



ABSTRACT

OXYGEN MEASURING PROBE

An oxygen measuring probe for use with molten metal baths for the manufacture of glass which probe comprises a probe body (4) comprising an elongate tubular member (6) closed at one end by a separate tip part (8) formed of stabilised zirconia which constitutes a solid electrolyte through which oxygen ions can pass, said tubular member (6) being formed of a heat-resistant material different from said zirconia, a first electrode (16) connected to the inner surface of the zirconia tip part (8), earthing means adapted for connection to earth out of contact with the molten metal and voltage measuring means (24) connected between the first electrode (16) and said earthing means (26).

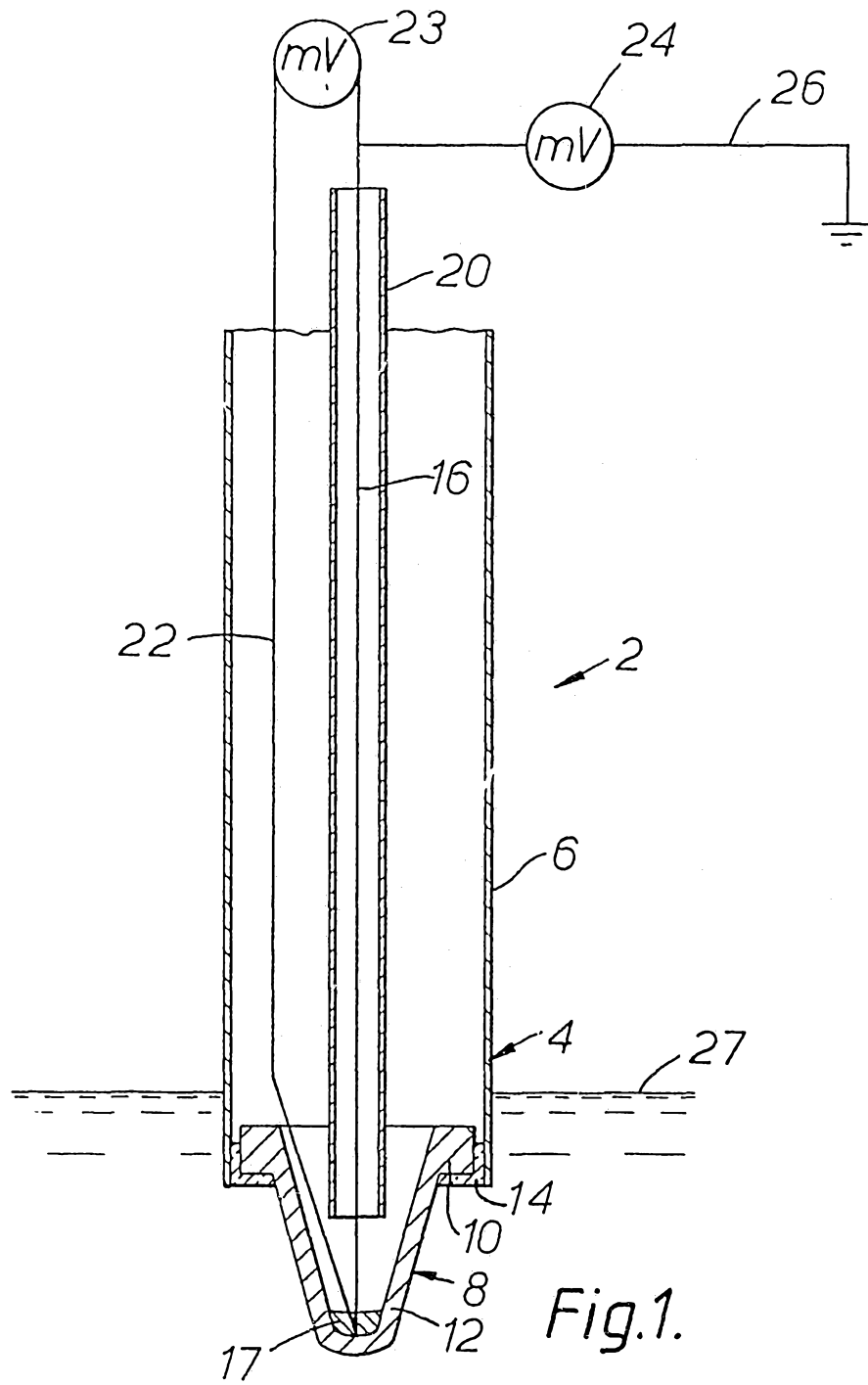


Fig.1.

