GOVERNMENT OF INDIA: THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Provisional Specification No. 114169, Application No. 114169 dated 24th January, 1968. Complete Specification left on 20th November, 1963. (Application accepted 28th October, 1969.)

Index at Acceptance-14D2 [LVIII(i)].

PROVISIONAL SPECIFICATION

IMPROVEMENTS IN OR RELATING TO AIRDEPOLARISED CELLS

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, (Rafi Marg, New Delhi 1, India, An Indian, Registered Body incorporated Under the Registration of Societies Act (Act XXI of 1860)

The following specification describes the nature of this invention:—

This is an invention by ABDUL KHADER ABDUL WAHEED, Scientist, Central Electrochemical Research Institute, Karaikudi-3, CHINNASAMY CHAKKARAVARTHY, Senior Scientific Assistant, Central Electrochemical Research Institute, Karaikudi-3 and Prof. KADARUNDALIGE SITARAMA GURU-RAJA DOSS, Retired Director, No. 1/1 Venkatarama Iyer Street, T. Nagar Madras-17, all Indian citizens.

This invention relates to primary cells of the Air Depolarised type and refers more particularly to an improved construction of such cells.

The primary cell of the air depolarised type is based on the principle of utilisation of oxygen (of the air) as the cathode component and consists of a porous carbon element as the cathode, zinc as the anode and sodium hydroxide as the electrolyte.

Such an air depolarised Cell has an open circuit voltage of 1.40—1.45 volts, operates at 1.10—1.20 volts and has a constant voltage discharge curve for the entire running period at normal discharge rates; it is designed to be assembled in the field.

Dependability under variable weather conditions and a relatively long life are the special attributes of the Air Depolarised cells. These cells do not require frequent servicing and operate properly and predictably.

Air Depolarised Cells have proved to be useful in connection with the operation of railway signal lights, signal motors, block instrument and in the track circuits wherein they find their special use on a large scale. In addition, the air depolarised cell has several other civil and military applications.

The conventional carbon electrodes for use in air depolarised cells are made from selected charcoal or graphite, employing carbonizable compounds as binders and they are made by a process which involves four steps, viz. blending, pressing, baking and water-proofing.

Two recently developed processes reported in Indian specification No. 90957 (sealed) and No. 107347 (pending) described in particular a porous carbon electrode of certain improved features and made by a very much simplified process. The electrode of the inventions is of the block type. However, the porous carbon electrode made according to these recent specifications is capable of giving a current density of 5 mA/cm^2 continuously and 25 mA/cm^2 intermittently for short durations of the order of a few seconds only.

It is the principal object of the present invention to provide an air depolarised cell capable of withstanding a high drain of current continuously for extended periods of time.

The present invention achieves these objectives by making use of a new design of the porous carbon electrode element. The present invention also provides with an improved composition.

The porous carbon electrode resulting from this invention is capable of giving a continuous high discharge of the order of 25 mA/cm^2 as against about 5 mA/cm^2 obtained from commercially available electrodes in general.

According to the main aspect of the present invention, namely, its improved design, the electrode consists of a hollow cylindrical shape, which imparts to it greater breather surface and reduced thickness of the carbon electrode through which air can diffuse. Such a design of the porous carbon electrode when used in the special railway type air depolarised cell is capable of giving surprisingly high current drains of the order of 5 amperes (25 mA/cm^2) continuously around one volt.

According to another aspect of the present invention the porous carbon electrode consists of an active carbon such as calcined petroleum coke or activated vegetable charcoal to which a relatively small quantity of highly conducting carbon black (10—30% preferably 20%) or acetylene black (5—15% preferably 10%) has been added, as also a suitable binder such as polymethyl methacrylate (1.5—3% preferably 3%).

In practising the present invention an active carbon such as calcined petroleum coke or activated coconut shell charcoal in a powdered form between −100 and +140 mesh may be employed.

The porous carbon electrode of the present invention consists essentially of a cup like hollow cylindrical shape of 1.5 cm. thickness, 6 cm. inside diameter and 9.5 cm. height. The outside wall of the electrode is mild steel expanded metal (nickel plated) upto 6 cm. height which becomes a continuous mild steel plate (16G thickness, nickel plated) of 3.5 cm. height at the top where it extends as a sleeve of 1.5 cm. width. (The sleeve is provided with a hole for making electrical connections). While very good results have been obtained with the arrangement of the design described, which permits contact to a maximum degree between air and the cathode, it is possible to vary the dimensions of the electrode, obtaining good results with less than this breather surface. These variations should however be viewed in the context of current capacity, mechanical strength.

In order that the present invention, which effects the aforesaid improvements, may be clearly understood and practised, the following procedure for making porous carbon electrode element for the special railway type air depolarised cell of capacity 500 watt hours (the special railway type air depolarised cell is more fully described in B.S. 1335: 1946) is described in detail in the following example.

EXAMPLE I

This method of making the porous carbon electrode element makes use of the following composition:

400 gms. of calcined petroleum coke (80%)

100 gms. of highly conducting carbon black (20%)

15 gms. of polymethyl methacrylate (perspex) binder (3%)

The carbons (400 gms. of calcined petroleum coke and 100 gms. of conducting carbon black) are first dry mixed in a mixing machine (Kneading machine). The polymethyl methacrylate (perspex) binder (15 gms.) is dissolved in about 250 cc. of a suitable solvent such as benzene or trichlorethylene and added to the mix and the mixing continued for about ten minutes. The mix is then pressed in the form of hollow cylindrical shape electrode in the nickel plated expanded metal cup by using suitable moulds at a pressure of about ½ ton per sq. inch. In pressing the carbon in the expanded metal cup, first the bottom layer is pressed to the required thickness (about 1.5 cm.) using a suitable plunger. A solid metal rod is now placed centrally and the carbon mix poured around the rod and pressed to form the walls of the carbon electrode using a hollow cylinder of suitable dimensions. After pressing, the electrodes could either be dried in an oven at 70°C or could be weather dried. The dried hollow cylindrical porous carbon electrode element could then be assembled into an Air Depolarised cell.

As another example the following composition could be used instead of the composition of Example I.

EXAMPLE II

315 gms. of activated coconut shell charcoal (90%)

35 gms. of highly conducting carbon black (10%)

10.5 gms. of polymethyl methacrylate (perspex) binder (3%).

The quantities of the activated carbon (which form the bulk constituent) and the highly conducting carbon black used in Example I and II result in an electrode of the above design having a surface area of about 200 sq. cm. The different quantities of both active carbon (bulk constituent) and the highly conducting carbon black are necessitated by the difference in the density of a particular variety in each of these two materials. For instance the apparent densities of calcined petroleum code and activated coconut shell charcoal are 0.88 gm./cc. and 0.77 gm./cc the densities of the highly conducting carbon black and acetylene black are 0.18 gm/cc and 0.08 gm/cc. Performance characteristics of the special railway type air depolarised cell of capacity 500 ampere-hours assembled with the hollow cylindrical porous carbon electrode element described above are shown in the following Table I.

Advantages: The present invention is attended with the following advantages due to the new design and use of newer compositions.

Composition of the porous carbon electrode element (hollow cylindrical type)	Open circuit voltage	Short circuit current	Closed circuit voltage on continuous discharge at		
			1 amp. (5 mA/cm^2)	2 amp. (10mA/cm^2)	5 amp. (25mA/cm^2)
80% calcined petroleum coke					
20% highly conducting carbon black	1.35—	18—	1.15— 1.20	1.10— 1.15	0.95— 1.00
3% polymethyl methacrylate (perspex) Binder	1.40 (volts)	20 (Amp)	(volts)	(volts)	(volts)
Example I					
90% activated coconut shell charcoal					
10% acetylene black	1.35—	18—	1.15	1.10—	0.95
3% polymethyl methacrylate (perspex) Binder	1.40 (volts)	20 (Amps.)	1·20 (volts)	1.15 (volts)	1.00 (volts)
Example II					

(i) As a result of the new design of the hollow cylindrical shape alone, it has been possible to make a porous carbon electrode of the air depolarised cell which gives a current of 5 amps. continuously over extended periods of time at a terminal voltage of around 1 volt as against the block type electrode which could give this current at the same terminal voltage intermittently for short durations only of the order of a few seconds. In view of the fact that in one of the applications of the air depolarised cell, namely in the signal motor, a current of 5 amperes at one volt is required for several seconds, this newly worked out design of the electrode is of great significance.

(ii) In addition, due to the new design, the electrode uses much less quantities of the raw materials of the order of 35—50%, thus resulting in great economy. (The weight of the electrode of the new design ranges from 350—500 gms, depending on the particular composition as against the block type electrode which weighs approx 1000 gms.).

(iii) The new composition of the present invention which makes use of calcined petroleum coke for the active carbon part (the main constituent) of the porous carbon electrode is more economical.

Dated this 18th day of January, 1968.

PATENTS OFFICER,
Council of Scientific & Industrial Research.

COMPLETE SPECIFICATION

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed:

This invention relates to primary cells of the air depolarised type and refers more particularly to an improved construction of such cells.

The primary cell of the air depolarised type is based on the principle of utilisation of oxygen (of the air) as the cathode component and consists of a porous carbon element as the cathode, zinc as the anode and sodium hydroxide as the electrolyte.

Such an air depolarised cell has an open circuit voltage of 1.40—1.45 volts, operates at 1.10—1.20 volts and has a constant voltage discharge curve for the entire running period at normal discharge rates; it is designed to be assembled in the field.

The cell reactions are as follows:

Overall anodic reaction :

$$Zn + 4OH^- \longrightarrow ZnO_2^- + 2H_2O + 2e^-$$

Overall cathodic reaction :

$$2e^- + o + H_2O \longrightarrow 2\,OH^-$$

Overall cell reaction :

$$Zn + 2\,OH^- + O \longrightarrow ZnO_2^- + H_2O$$

An essential requirement for the satisfactory performance of an air depolarised cell is a high degree of depolarising activity for the oxygen electrode or cathode. It is therefore important that the electrode shall have maximum access to air. The electrode should have sufficient electrical conductivity. It should also be non-wettable.

Two recently developed processes reported in Indian Specification No. 90957 (sealed) and No. 107347 (pending) describe in particular a porous carbon electrode of certain impoved feature and made by a very much simplified process. The electrode of the inventions is of the block type. The composition of the above electrode consisted of activated carbon, acetylene black or highly conducting carbon black and a high polymer water-proofing agent such as polymethyl methacrylate (perspex) as its binder. However, the porous carbon electrode made according to these recent specifications is capable of giving a current density of 5 mA/cm^2 continuously and 25 mA/cm^2 intermittently for short durtion of the order of a few seconds only.

It is the principal object of the present invention to provide an air depolarised cell capable of withstanding a high drain of current continuously for extended periods of time. Another object of the present invention is to make the production of such cells more economical.

The present invention achieves these objectives by making use of a new design of the porous carbon electrode element as well as an improved composition.

The porous carbon electrode resulting from this invention is capable of giving a continuous high discharge of the order of 25mA/cm^2 as against about 5 mA/cm^2 obtainable from commercially available electrodes in general.

According to the present invention, the porous carbon electrode element consists essentially of a cup-like hollow cylindrical shape, which by virtue of its enhanced breather surface allows of contact to a maximum degree between air and the cathode and provides reduced thickness of carbon electrode through which air can diffuse. The reduced thickness results in a more efficient utilization of oxygen of the air. The outside wall of the carbon electrode element of cup-like hollow cylindrical shape makes use of an expanded metal with a sleeve at the top.

The porous carbon electrode element may consist of calcined petroleum coke, highly conducting carbon black or acetylene black and a binder such as polymethyl methacrylate (perspex). It may consist of the bulk of calcined petroleum coke having a particle size between −100 and +140 mesh, highly conducting carbon black (10—30% by weight) or acetylene black (3—15% by weight) and polymethyl methacrylate (perspex) (1.5—3% by weight).

Thus, the porous carbon electrode element of a cup-like hollow cylindrical shape may consist of calcined petroleum coke, highly conducting carbon black or acetylene black and polymethyl methacrylate (perspex) binder.

The invention includes within its scope the method of making the porous carbon electrode element of a cup-like hollow cylindrical shape by pressure moulding the carbon mix on to an expanded metal container, more specifically according to the method described in the examples, given hereinbelow, and an air depolarised cell incorporating the porous carbon electrode element made according to the said method.

Applicants are aware that it has been proposed to construct an electrode assembly for a primary cell comprising an electrode of magnesium, a second electrode and a layer of fibrous material of open texture lying between and in contact with these electrodes and adopted to carry electrolyte; the second electrode being in the form of carbon of an open structure, that the carbon electrode could be formed of powder pressed into the meshes of a woven fabric made wholly or in part of wire, space for the passage of air being provided between the particles of carbon, that the magnesium electrode and the fibrous layer could be placed within a metal container and the intervening space filled with granular of powdered carbon and that the carbon electrode could be expansible, for instance, being formed as a split tube.

It may be pointed out that there is hardly anything common between the hitherto proposed construction just referred to above and the present invention. The idea of the so-called porous carbon electrode in the shape of a split tube is unusable in the case of a wet type air depolarised cell. The entire breather surface inside the hollow cylindrical shape which is not in contact with the electrolyte would be completely lost in the split tube design.

Thus, the invented electrode consists of a cup-like hollow cylindrical shape, which imparts to it greater breather surface and reduced thickness of the carbon electrode through which air can diffuse. Such a design of the porous carbon electrode when used in the special railway type air depolarised cell is capable of giving very high current drains of the order of 5 amperes (25 mA/cm^2) continuously at around one volts. The new design, at the same time, results in very great economy of the materials.

According to another aspect of the present invention, its new composition, the porous carbon electrode consists of an active carbon such as calcined petroleum coke to which a relatively small quantity of highly conducting carbon black (10—30% preferably 20%) or acetylene black (5—15% preferably 10%) has been added, as also a suitable binder such as polymethyl methacrylate (1.5—3% preferably 3%). Activated vegetable charcoal such as activated coconut shell charcoal could also be used instead of calcined petroleum coke in making the porous carbon electrode of the newly developed design of cup-like hollow cylindrical shape.

In practising the present invention, an active carbon such as calcined petroleum coke or activated coconut shell charcoal in a powdered form between −100 and +140 mesh may be employed.

This invention will now be more particularly described with reference to Figures 1 to 3 of the accompanying drawings wherein figures 1 to 3 show the elevation, sectional end elevation and plan respectively of a porous carbon electrode (Scale: full size).

The porous carbon electrode 1 illustrated in Figures 1 to 3 of the drawing consists essentially of a cup-like hollow cylindrical shape of 1.5 cm. thickness, 6 cm. inside diameter and 11 cm. height. The outside wall 2 of the electrode, obtaining good results with less than this breather 8 cm. height which becomes of continuous mild steel plate 4 (16 G thickness, nickel plated) of 3 cm. height at the top where it extends as a sleeve 5 of 1.5 cm. width. (The sleeve is provided with a hole 6 for making electrical connections). While very good results have been obtained with the arrangement of the design described, which permits contact to a maximum degree between air and the cathode, it is possible to vary the dimensions of the electrode, obtaining good results with less than this breather surface. The variation may also include the use of smaller thickness. These variations should however be viewed in the context of current capacity and mechanical strength.

In order that the present invention, which effects the aforesaid improvements, may be clearly understood and practised, the following procedure for making porous carbon electrode element 1 for the special railway type air depolarised cell of capacity 500 watt hours (the special railway type air depolarised cell is more fully described in BS 1335:1946) is described in detail in the following examples:

EXAMPLE I

This method of making the porous carbon electrode element 1 makes use of the following composition:

346.5 gms. of calcined petroleum coke (77%)

90.0 gms. of highly conducting carbon black (20%)

13.5 gms. of polymethyl methacrylate (perspex) binder (3%)

The carbon (346.5 gms.) of calcined petroleum coke and 90 gms. of highly conducting carbon black are first dry mixed in a mixing machine (kneading machine). The polymethyl methacrylate (perspex) binder (13.5 gms.) is dissolved in about 250 c.c. of a suitable solvent such as benzene or trichloroethylene and added to the mix and the mixing continued for about ten minutes. The mix is then pressed in the form of a cup-like hollow cylindrical shape electrode 1 in the nickel plated expanded metal cup 3 by using suitable moulds at a pressure of about ½ ton per sq. inch. In pressing the carbon in the expanded metal cup 3, first the bottom layer 7 is pressed to the required thickness (about 1.5 cm.) using a suitable plunger (not shown). A solid metal rod (not shown) is now placed centrally and the carbon mix 8 poured around the rod and pressed to form the walls of the carbon electrode using a hollow cylinder of suitable dimensions. After pressing, the electrodes could either be dried in an oven at 70°C or could be weather dried. The dried hollow cylindrical porous carbon electrode element 1 could then be assembled into an air depolarised cell as shown in Figures 4, 5 and 6 wherein figures 4 to 6 show the elevation, plan and sectional end elevation respectively of the air depolarised cell incorporating the cup-like hollow cylindrical porous carbon electrode element 1 (scale: half full size). Figure 4 shows the assembled air depolarised cell wherein the cup-like hollow cylindrical porous carbon electrode element 1 of the present invention is fixed to the lid 9 through the hole 10 by means of a bolt and nut. The zinc electrode 11 is fixed to the lid 9 through the holes 12 by suitable bolts and nuts. The electrode assembly is then placed on the container 13 containing the required amount of caustic soda solution 14 which serves as the electrolyte.

As other examples, the following composition could be used instead of the composition of Example I.

EXAMPLE II

391.5 gms. of calcined petroleum coke (87%)

45.0 gms. of acetylene black (10%)

13.5 gms. of polymethyl methacrylate (perspex) binder (3%)

EXAMPLE III

308 gms. of activated coconut shell charcoal (77%)

80 gms. of highly conducting carbon black (20%)

12 gms. of polymethyl methacrylate (perspex) binder (3%)

EXAMPLE IV

348 gms. of activated coconut shell charcoal (87%)

40 gms. of acetylene black (10%)

12 gms. of polymethyl methacrylate (perspex) binder (3%)

The quantities of the activated carbon (which form the bulk constituent) and the highly conducting carbon black or acetylene black used in Examples I—IV result in an electrode of the above design having a surface area of about 200 sq. cm. The different quantities of both active carbon (bulk constituent) and the highly conducting carbon black are necessitated by the difference in the density of a particular variety in each of these two materials. For instance, the apparent densities of calcined petroleum coke and activated coconut shell charcoal are 0.88 gm./cc. and 0.77/cc; the desities of the highly conducting carbon black and acetylene black are 0.18 gm./cc. and 0.08 gm./cc.

Performance charcteristics of the special railway type air depolarised cell of capacity 500 ampere-hours assembled with the cup-like hollow cylindrical porous carbon electrode element described above are shown in the following Table I.

TABLE I

No.	Composition of the porous carbon electrode element (hollow cylindrical type)	Open circuit voltage	Short circuit current	Closed circuit voltage on continuous discharge at		
				1 amp. ($5 mA/cm^2$)	2 amps. ($10 mA/cm^2$)	5 amps ($25 mA/cm^2$)
1.	77% calcined petroleum coke					
	20% highly conducting carbon black	1.35—	18—	1.15—	1.10—	0.95—
	3% polymethyl methacrylate (perspex) binder-Example I	1.40 (volts)	20 (volts)	1.20 (volts)	1.15 (volts)	1.00 (volts)
2.	87% calcined petroleum coke					
	10% acetylene black					
	3% polymethyl methacrylate (perspex)	1.35—	18—	1.15—	1.10	0.95—
	binder-Example II	1.40 (volts)	20 (amps.)	1.20 (volts)	1.15 (volts)	1.00 (volts)
3.	77% activated coconut shell charcoal					
	20% highly conducting carbon black	1·35—	18—	1.15—	1.10—	0.95—
	3% polymethyl methacrylate (perspex) binder—Example III	1.40 (volts)	20 (amps.)	1.20 (volts)	1.15 (volts)	1.00 (volts)
4.	87% activated coconut shell charcoal					
	10% acetylene black	1.35—	18—	1.15—	1.10—	0.95—
	3% polymethyl methacrylate (perspex birder—Example IV	1.40 (volts)	20 (amps.)	1·20 (volts)	1.15 (volts)	1.00 (volts)

ADVANTAGES: The present invention is attended with the following advantages due to the new design and use of newer compositions:

1. As a result of the new design of the cup-like hollow cylindrical shape alone, it has been possible to make a porous carbon electrode of the air depolarised cell which gives a current of 5 amperes continuously over extended periods of time at a terminal voltage of around 1 volt as against the block type electrode which chould give this current at the same terminal voltage intermittantly for short durations only of the order of a few seconds. In view of the fact that in one of the applications of the air depolarised cell, viz. in the signal motor, a current of 5 amperes at one volt is required for several seconds, this newly worked out design of the electrode is of great significance.

2. In addition, due to the new design, the electrode uses much less quantities of the raw materials of the order of 40—48%, thus resulting in great economy.

(The weight of the electrode of the new design ranges from 400—450 gms. depending on the particular composition as against the block type electrode which weighs approximately 1000 gms.)

3. The new composition of the present invention which makes use of calcined petroleum coke for the active carbon part (the main constituent) of the porous carbon electrode is more economical.

WE CLAIM:

1. A porous carbon electrode element essentially of a cup-like hollow cylindrical shape, which by virtue of its enhanced breather surface allows of contact to a maximum degree between air and the cathode and provides reduced thickness of carbon electrode through which air can diffuse.

2. A porous carbon electrode element of a cup-like hollow cylindrical shape as described in Claim 1 wherein the outside wall of which electrode makes use of an expanded metal with a sleeve at the top.

3. A porous carbon electrode element as claimed in Claim 1 or 2 consisting of calcined petroleum coke, highly conducting carbon black or acetylene black and a binder such as polymethyl methacrylate (perspex).

4. A porous carbon electrode element as claimed in Claim 3 consisting of the bulk of calcined petroleum coke having a particle size between −100 and +140 mesh, highly conducting carbon black (10—30% by weight) or acetylene black (3—15% by weight) and polymethyl methacrylate (perspex) (1.5—3% by weight).

5. A porous carbon electrode element of a cup-like hollow cylindrical shape as described in Claim 1 consisting of calcined petroleum coke, highly conducting carbon black or acetylene black and polymethyl methacrylate (perspex) binder.

6. A porous carbon electrode element substantially as described in the examples.

7. A method of making the porous carbon electrode element of a cup-like hollow cylindrical shape as claimed in any of the preceding claims by pressure moulding the carbon mix on to an expanded metal container, more specifically according to the method described in the examples.

8. An air depolarised cell incorporating a porous carbon electrode element made according to the method as claimed in Claim 7.

Dated this 15th day of November, 1968.

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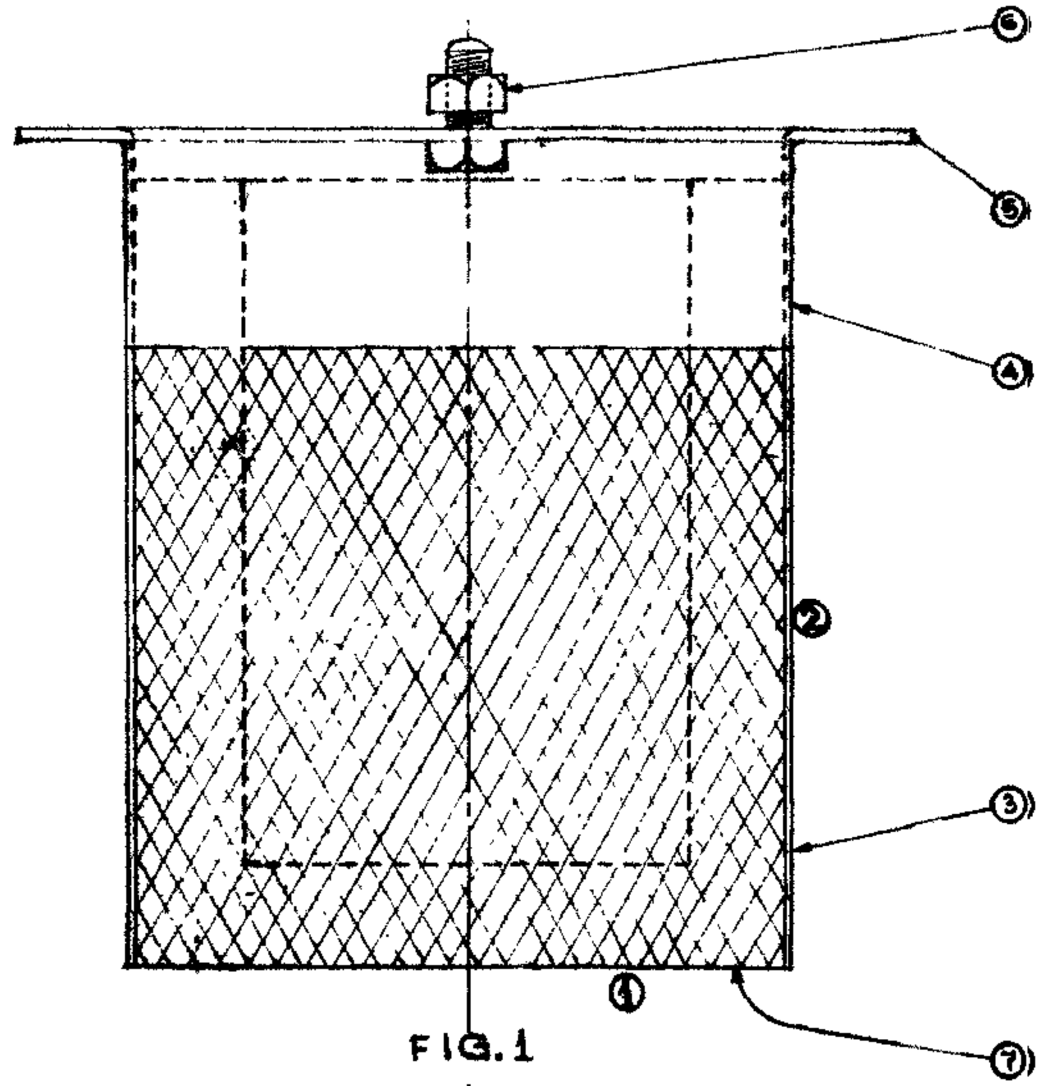

FIG. 1

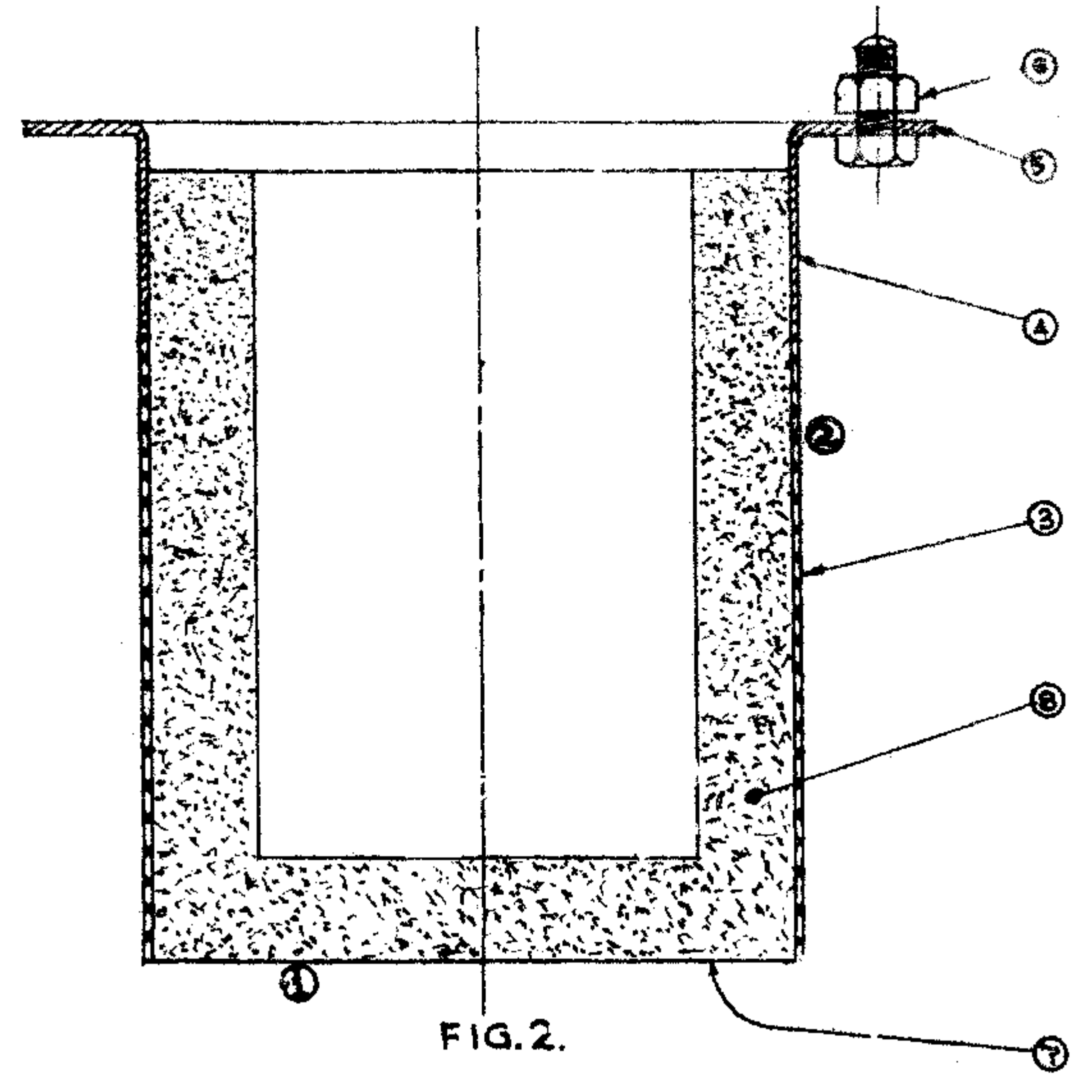

FIG. 2.

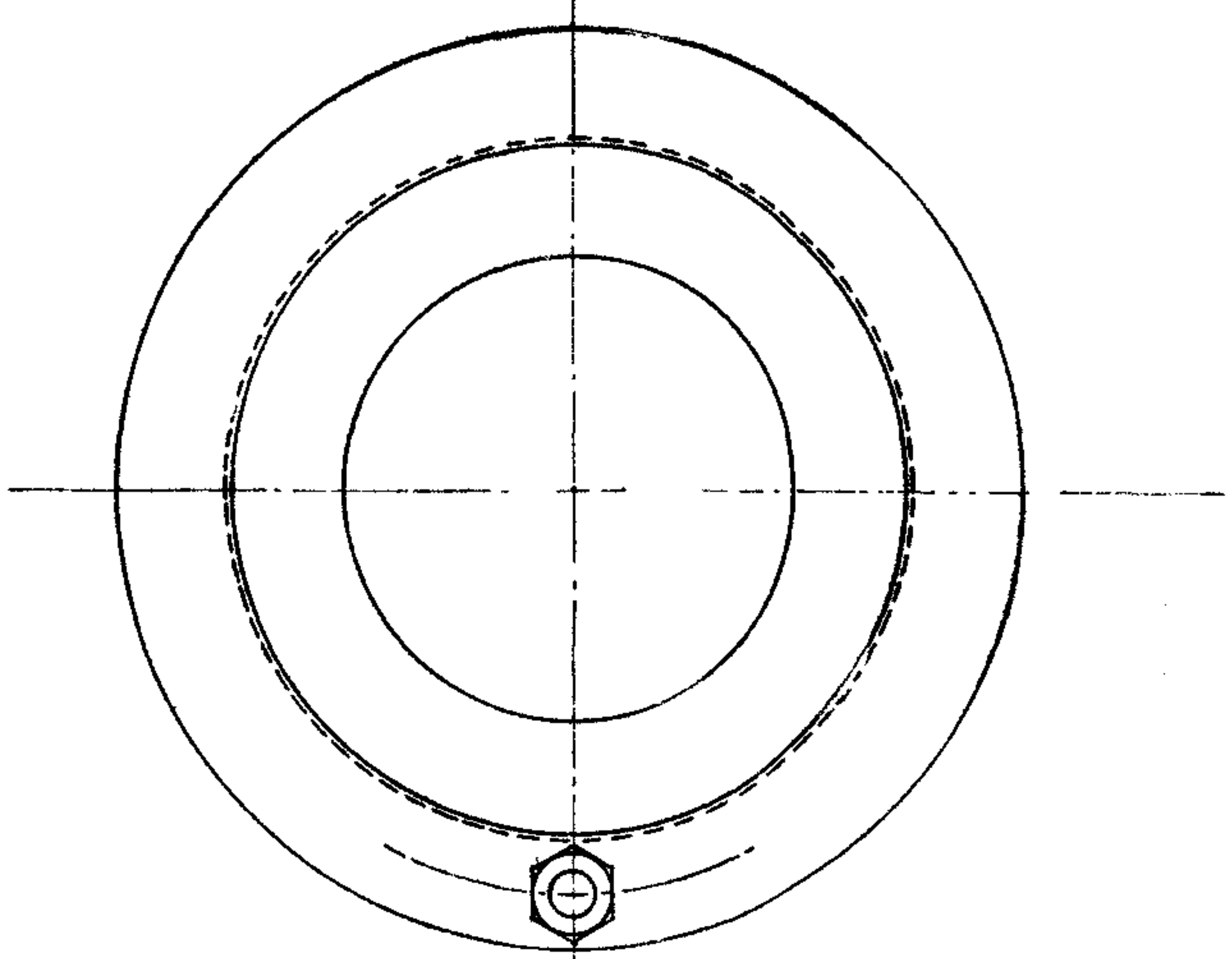

FIG. 3.

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COMPLETE SPECIFICATION

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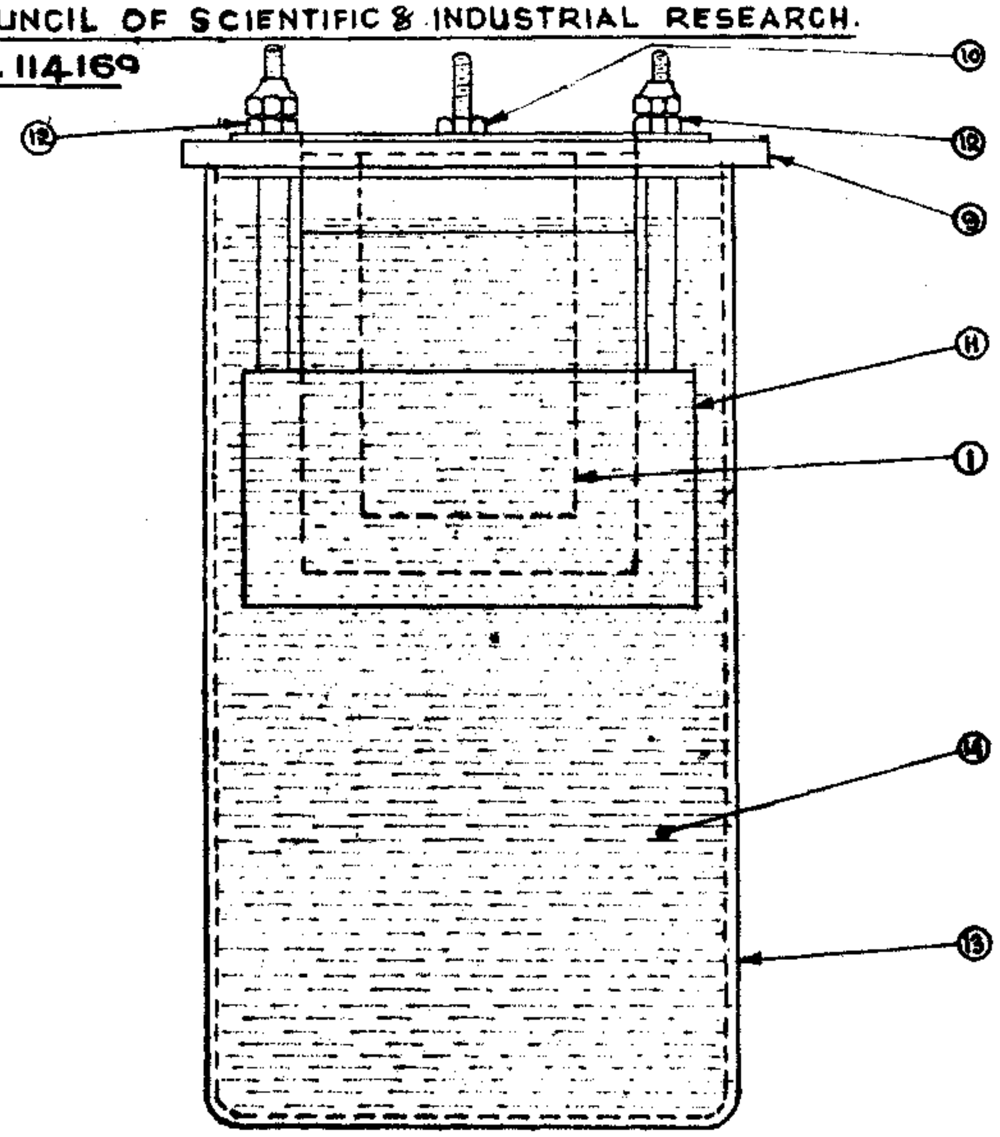

FIG-4.

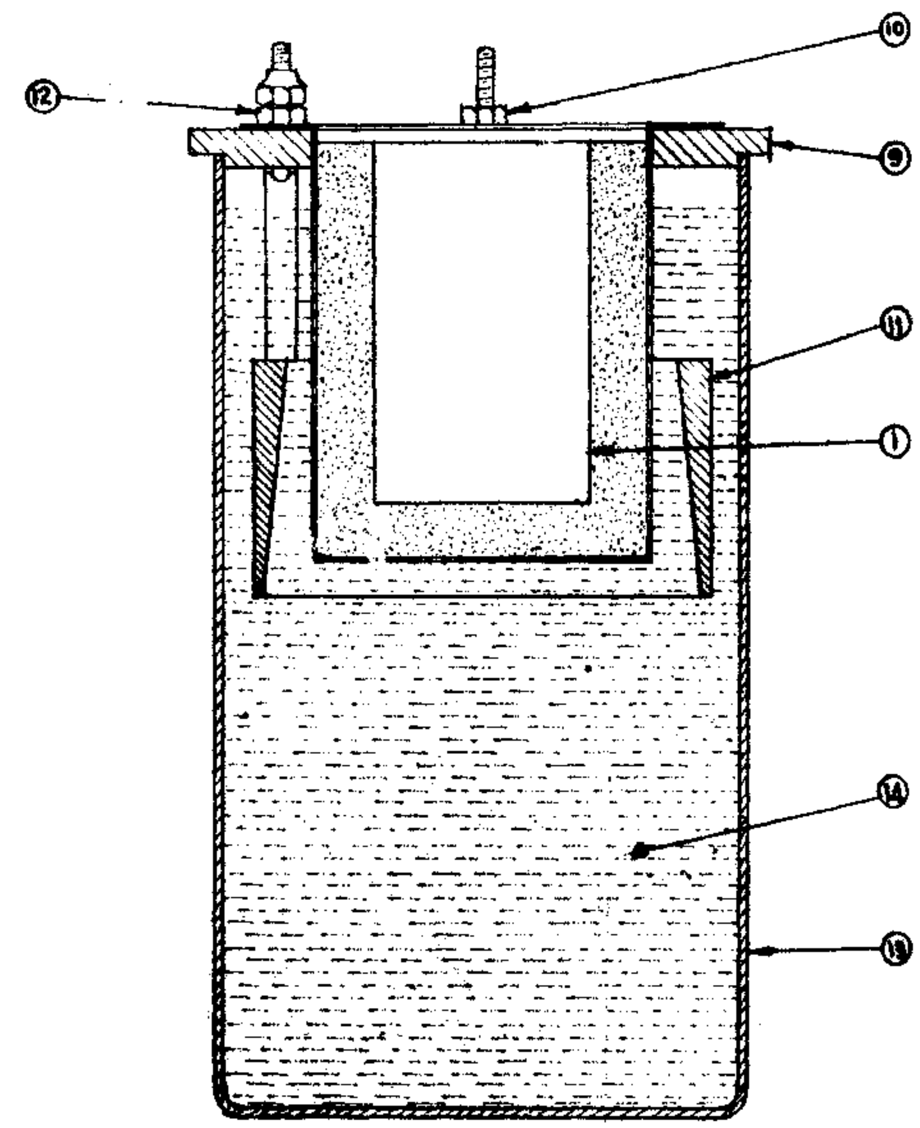

FIG-6

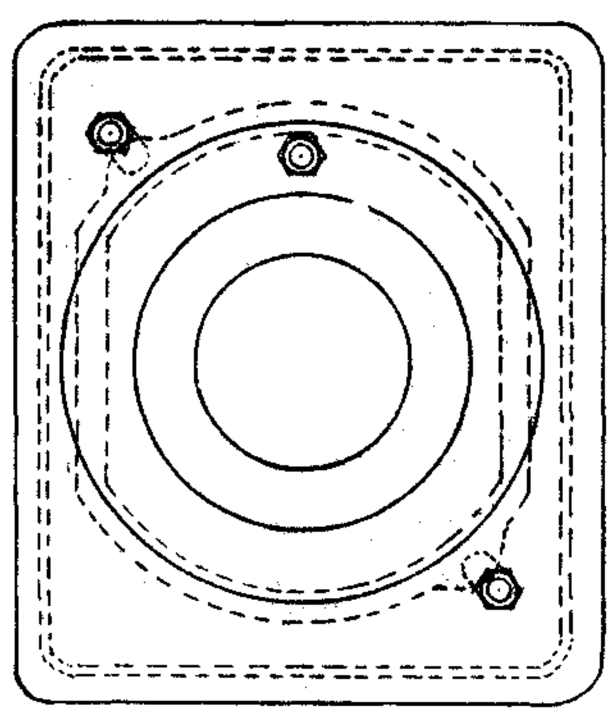

FIG-5

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