GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, ACHARYA JAGDISH BOSE ROAD, CALCUTTA-17.

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Index at acceptance—14B+D2[LVIII(1)]

"IMPROVEMENTS IN OR RELATING TO AIR DEPOLARISED BATTERIES"

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH, RAFI MARG, NEW DELHI-1, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1860)

This is an invention by:

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PROVISIONAL

The following Specification describes the nature of this invention.

This invention relates to improvements in or relating to primary cells of the Air Depolarised type and refers more particularly to the design of a new type of water-activated Air Depolarised Batteary.

The present invention is a further development of the work reported earlier in Indian Patent No 90957 (1963)

The Air Depolarised cell of this invention is based on the principle of utilisation of oxygen of the air as the cathode component and consists of a tubular porous carbon element as the cathode, cast zinc plate (amalgamated) as the anode and sodium hydroxide as the electrolyte, incorporated in the cell in the solid form The carbon electrode of this cell by virtue of its tubular structure accords larger breather surface to the electrode and thus makes it possible to draw comparatively higher currents at fairly constant voltage for the full duration of its life

A cell of this type has an open circuit voltage of 1 40 volts and operates at a fairly constant voltage of 1 25 volts for the entire length of discharge at a drain of about 200 mA (2 mA/cm^2) constant current,

The complete pre-assembled cell can be water-activated before actual use

The cell reactions are as follows .

Overall anodic reaction : $Zn + 4OH^- \rightarrow ZnO_2^- + 2e + 2H_2O$

Overall cathodc reaction $2e + O + H_2O \rightarrow 2OH^-$

Ovarall cell reaction : $Zn + 2OH^- + O \rightarrow ZnO_2^- + H_2O$

The Air Depolarised Battery of this invention, then consists of any required number of these newly designed cells connected in series to give a desired voltage

The Air Depolarised Battery could be used for both low continuous and high intermittent current discharge purposes (upto one ampere) Once installed the battery delivers power smoothly at a fairly constant terminal voltage and requires no maintenance work The tubular porous carbon cathodes could be used for several cycles of zinc anodes and caustic soda electrolyte i e , the battery could be renewed at the end of its useful life by simply changing the exhausted zinc electrodes with fresh zinc anodes and changing the electrolyte This brings down the cost of replacement considerably

The 8 4 volt, 30 ampere hour Air Depolarised Battery comprising of six individual cells connected in series, has been developed especially for the Community Radio Receiver Sets which require about 200 mA for their operation (the cut off voltage being 6 0 volts).

However, these batteries would also be useful in many a scientific appararus, in Defence, Railways and P & T Departments and several other applications.

The Air Depolarised Battery of this invention could be used for both mobile and stationary devices but is ideally suited for stationary use. The Air Depolarised Battery of the above type to the best knowledge of the authors, has not been so far reported in either technical or patent literature.

Hitherto it has been the practice to use dry batteries of the Leclanche type consisting of manganese dioxide-zinc cells in such appliances as the Community Radio Receiver Sets, various scientific apparatus But they suffer mainly from the disadvantage that the voltage of these commercially available batteries does not remain constant at the required current drain The other disadvantages of the dry battery are comparatively poor shelf, life low output per unit weight and volume and higher costs, originally and in replacements.

The water-activated Air Depolarised Battery resulting from this invention is such as to be free from the said disadvantages

To these ends, the invention broadly consists in the development of a water-activated Air Depolarised Battery as described in the following example which also illustrates the invention.

Each individual cell of this invention consists of a tubala porous cathode, made according to the method described below under the "Preparation of the tubular porous carbon cathode element", of 40 mm diameter and 115 mm height with a central hole of 15 mm diameter extending to a depth of more than half the height of the carbon cathode and with a lug (12 5 mm x 12 5 mm) bent at right angles for connections, the cathode weighing about 165 gms, cast amalgamated zinc plate anode of size 45 mm x 85 mm thicker at the top (6 mm) and thinner at the bottom (3 mm) with a lug (10 mm x 25 mm) suitably bent for giving the necessary series connections, the anode weighing approximately 130 gms and about 120 gms of solid caustic soda as electrolyte

Price : TWO RUPEES.

(Rayon Grade). The porous carbon cathode and the amalgamated zinc anode are fitted to the lid (plastic). The solid caustic soda electrolyte is kept at the bottom of the container (plastic). The breather holes and the holes for adding water on the lid and all other seams are suitably sealed to avoid damage to the caustic soda electrolyte and the cathode and anode elements. At the time of actual use, the Breather holes and the water holes are punctured and the battery is activated with ordinary drinking water added through the water holes. About 400 cc of water is required for each compartment of the battery. During activation a lot of heat is generated due to dissolution of caustic soda but it has no detrimental effect on the components of the battery. Once activated with water the battery becomes available for use immediately.

Example :

The Air Depolarised Battery of 8.4 volts open circuit voltage and 50 ampere hour capacity consists of six individual Air Depolarised Cells connected in series as shown in Figures 1 to 3 of the accompanying drawings, wherein Figure 1 represents sectional elevation on section 'AA' of Figure 3, Figure 2 represents sectional end elevation on section 'BB' of Figure 3, and Figure 3 represents the plan of the Air Depolarised Battery with lid removed.

The performance characteristic of the 8.4 volt, 50 ampere hour battery is shown in the graph illustrated in Figure 4 of the drawings.

Preparation of the tubular porous carbon cathode elements :

The porous carbon electrode is the most important component of the Air Depolarised Battery from the point of view of its manufacture and it is made as follows :

A 3 mm expanded metal tube of diameter 40 mm and height 115 mm is welded on the top with a strip of mild steel, 12.5 mm wide with a lug (12.5 mm x 12.5 mm size) bent at right angles, the entire tube being nickel plated.

A blend of carbon consisting of 128.0 gms of activated coconut shell charcoal (90%), in the size range of -100, +140 mesh and 14.00 gms of finely divided acetylene black (10%) is first prepared by mixing in a kneading machine. To this blend 4.25 gms of polymethyl methacrylate (Perspex) binder to the extent of 3% of the mass of the carbon blend, dissolved in 145 cc of benzene or trichloroethylene is added and the mixing is continued for some more time to get uniform dispersion of the binder.

Alternatively a suitable quantity of a blend consisting of 80% calcined petroleum coke and 20% highly conducting carbon black obtained as a byproduct in the fertiliser industry, could also be used along with the same percentage of binder in the manner described above, in the making of the porous carbon electrodes.

The tubular porous carbon electrode is then prepared by pressing the carbon blend along with the binder on to the nickel plated expanded metal tube using a suitable die in a hydraulic press at a total thrust of 1-2 tons.

After pressing the carbon electrodes are either weather dried or dried in an oven under controlled conditions.

After drying, the carbon electrode would be ready for assembly into a cell.

The binder used in this process also acts as a waterproofing agent which property is very essential for the successful functioning of the porous carbon electrode as an Air Depolarised electrode.

The porosity obtained by selecting the particular size range, the breather surface and the thickness of the walls of the carbon electrode used herein, have been suitably adjusted so as to get maximum air depolarisation.

The design is such that the overall dimensions of the battery, the size and shape of both the carbon element and zinc element can be conveniently altered to suit any specific requirements of capacity and voltage for a particular use.

The following are among the main advantages of the invention :

1. The Air Depolarised Battery works at constant voltage throughout the length of discharge which ensures satisfactory performance in such appliances as the transistor radios.
2. The battery has a fairly high amperage hour capacity for a given weight and volume.
3. It requires least maintenance.
4. Once the Battery is exhausted, it could very easily be renewed by replacing the used up anode and electrolyte. The porous carbon cathode, the battery container, lids and other connections could be repeatedly used. The carbon electrode could be used for three or four cycles of the zinc electrodes.

Replacement of exhausted anode and electrolyte costs very little when compared to the cost of purchasing a new battery as would be required in case of using the dry batteries.

5. The Air Depolarised Battery would work out cheaper comparatively both initially and in replacement.
6. The design is quite easily adaptable for commercial production on any scale requiring use of very simple equipment.
7. Raw materials and equipments required are indigenously available.

COMPLETE

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 improvements in or relating to primary cells of the air depolarised type and refers more particularly to the design of a new type of water-activated air depolarised battery.

The present invention is a further development of the work reported earlier in Indian Patent No. 90957 (1963).

Hitherto it has been the practice to use dry battery of the Leclanche type consisting of Manganese dioxide-zinc cells in such appliances as the community radio receiver sets and various scientific apparatus. But they suffer mainly from the disadvantage that the voltage of these commercially available batteries does not remain constant at the normally required current drain even during the entire useful range of service The other disadvantages of the dry battery are comparatively poor shelf life, low output per unit weight and volume and higher costs, originally and in replacements

Also hitherto, while the air depolarised cells have been known for quite some time, the method of making the same suffers from all the disadvantages mentioned in some detail in the Indian Patent No 90957 (1963) To recount briefly, for instance, the method of making the porous carbon electrodes of such earlier cells was very cumbersome, involving baking at a high temperature, separate water-proofing etc The design of the electrode also tended to be very complicated whenever any effort was made to increase the degree of air depolarisation by enlarging the breather surface area Moreover, these were single cells of large capacity mostly for Railway signalling

The object of the present invention is to develop a water-activated air depolarised battery which will be free from the said disadvantages

According to the present invention, there is provided an air depolarised battery consisting of an array of individual cells connected in series so as to get any desired voltage in multiples of about 1 4 volts, each individual cells comprising a porous carbon cathode element, a zinc anode and a solid alkaline electrolyte which is activated by the the addition of water at the time of use, and all arranged in a container, characterised in that the said cathode element is in the form of a tube for at least part of its length.

An air depolarised battery is also provided wherein each individual cell comprises a metal reinforced tubular porous carbon cathode element and amalgamated zinc anode and sodium hydroxide electrolyte, such a cell giving an open circuit voltage of 1 4 volts

An air depolarised battery of 8 4 volts open circuit voltage and 50 ampere hour capacity is provided mainly for use in transistorised radio receiver sets, such a battery consisting of six individual air depolarised cells connected in series, each cell comprising a tubular porous carbon cathode element with metal reinforcement, zinc anode and a solid alkaline electrolyte which is activated by the addition of water at the time of use all arranged in a container.

Each individual cell comprises a tubular porous carbon cathode element made with either activated carbon such as activated cocoanut shell charcoal or calcined petroleum coke as the bulk constituent, with the addition of acetylene black or highly conducting carbon black and polymethyl methacrylate as binder.

The cells are in any suitable number, for a particular requirement, connected either in series or parallel, to give the desired voltage or current

The electrolyte is initially incorporated in the solid form, the battery being conveniently water-activated subsequently before actual use

It would be understood that the invention includes within its scope a single air depolarised cell with in its components namely a porous carbon cathode element, a zinc anode and a solid alkaline electrolyte, which is activated by the addition of water at the time of use, all arranged in a container, such a cell giving an open circuit voltage of 1 4 volts, characterised in that the said cathode element is in the form of a tube for at least part of its length.

The tubular porous carbon cathode element has a central hole extending to a depth of more than half the length of the carbon cathode, and a bent lug terminal, the said cathode being reinforced by an expanded metal tube which is nickel plated and wherein the anode is amalgamated zinc, thicker at the top and thinner at the bottom with a bent lug terminal, the two electrodes being fitted to the lid.

Thus, the tubular porous carbon cathode element may be formed by compressing a blend of 128 gms of activated cocoanut shell charcoal (90%) in the size range of -100, + 140 mesh size, 14 gms of acetylene black (10%) and 4 25 gms of polymenthyl methacrylate binder to the extent of 3% of the mass of the carbon blend

Or the tubular porous carbon cathode element may be formed by compressing a blend of carbon, consisting of calcined petroleum coke (80%) highly conducting carbon black (20%), and polymethyl methacrylate binder, to the extent of 3% of the mass of the carbon blend

The tubular porous carbon cathode element may be provided with metal reinforcement

The air depolarised cell of this invention is based on the principle of utilisation of oxygen of the air as the cathode component, which diffuses (at ordinary atmospheric pressure) through the tubular porous carbon cathode, and has cast zinc plate (amalgamated) as the anode and sodium hydroxide as the electrolyte, incorporated in the cell in the solid form The cell can be represented as follows $(O_2)/NaOH$ 6 ON/Zn, The complete preassembled cell can be water-activated before actual use

The carbon electrode of the cell, by virtue of its tubular structure, is accorded larger breather surface and thus could deliver comparatively higher currents at fairly constant voltage

A cell of this type, working at about 30°C, has an open circuit voltage of 1.4 volts and operates at a fairly constant voltage of 1 25 volts for the entire length of discharge at a drain of about 200 mA constant current This current drain corresponds to a current density of 2 mA/cm^2 on the porous carbon cathode

The cell reactions are as follows

Overall anodic reaction $Zn + 4OH^- \rightarrow ZnO_2^- + 2H_2O + 2e$

Overall cathodic reaction $2e + O + H\ O \rightarrow 2\ OH^-$

Overall cell reaction $Zn + 2OH^- + O \rightarrow ZnO_2 + H_2O$

The air-depolarised battery of this invention, then consists of any required number of these newly designed cells, connected either in series and/or parallel to give a desired voltage and capacity

The air-depolarised battery could be used for both low continuous (upto 250 mA) and high intermittent current discharge (upto one ampere) purposes Once installed, the battery delivers power smoothly at a fairly constant terminal voltage and requires no maintenance work The tubular porous carbon cathodes could be used for several cycles of zinc anodes and caustic soda electrolyte, i e the battery could be renewed at the end of its useful life by simply changing the exhausted zinc electrodes with fresh zinc anodes and changing the electrolyte. This brings down the cost of replacement considerably

The 8 4 volt, 50 ampere hour air depolarised battery, comprising six individual cells connected in series, has been developed especially for the community radio receiver sets which require about 200 mA for their operation (the cut off voltage being about 6 0 volts)

However, these batteries would also be useful in many a scientific apparatus, in Defence, Railways and P & T departments and several other applications, in view of their performance characteristics and compactness

The air-depolarised battery of this invention could be used for both mobile and stationary devices but is ideally suited for stationary use. The air-depolarised battery of the above type, to the best of the knowledge of the authors, has not been so far reported in either technical or patent literature To these ends, the invention broadly consists in the development of water-activated air-depolarised battery as described in the following with the help of drawings accompanying this specification, in which Figs 1 and 2 are sectional elevation on section EE of Fig 2 and plan of the air depolarised cell (1 4 volts 50 AH capacity) respectively Figs 3 and 4 are elevation and plan of the metal reinforced tubular porous carbon electrode element Figs 5 and 6 are elevation and end elevation of the zinc element Figs 7 and 8 are sectional elevation on section FF of Fig 8 and plan of the lid of the air depolarised cell.

Figs 9 to 11 represent sectional elevation on section 'AA' of Fig 11, sectional elevation on section 'BB' of Fig 11 and the plan respectively of the 8 4 volts, 50 AH capacity air depolarised battery, with lid removed

Figs 12 to 14 represent the plan of the lid, Sectional elevation on section CC of Fig 12 and Sectional elevation on section DD of Fig 12 respectively (of the air depolarised battery)

Method of making the cell

Each individual cell (Figures 1 and 2) of this invention consists of (i) a metal reinforced tubular porous carbon cathode (3), made according to the method described in the following under the heading "Method of making the tubular porous carbon cathode element", of 40 mm diameter and 115 mm height, with a central hole of 15 mm diameter, extending to a depth of more than half the height of the carbon cathode to enhance the breather surface area of the electrode and minimise its wall thickness for better diffusion of oxygen (air), and provided with a lug (3a) of size 12 5 mm x 12 5 mm, bent at right angles for connections as shown in Figures 3 and 4 the cathode weighing about 165 gms, (ii) cast amalgamated zinc plate anode (5) of size 45 mm x 85 mm thicker at the top (6 mm) and thinner at the bottom (3 mm) with a lug (5a) of size 10 mm x 25 mm, suitably bent for giving the necessary series connections as also shown in Figures 5 and 6 the anode weighing approximately 130 gms (amalgamation is desirable in order to prevent loss of zinc due to local cell action as also passivation and to ensure smooth dissolution of zinc in the electrolyte), the anode being arranged beside the said cathode, both being fixed to the lid by means of nuts (7) and (iii) about 120 gms of solid caustic soda (Rayon grade) as electrolyte (6) The porous carbon cathode (3) and the amalgamated zinc anode (5) are fitted to the plastic lid (1) of the cell container (2). The solid caustic soda electrolyte (6) is kept at the bottom of the container (2) The Breather holes (1a) and the holes for adding water (1b) on the lid (1) and all other seams are suitably sealed to avoid damage to the caustic soda electrolyte and the cathode and anode elements At the time of actual use, the breather holes (1a) and the water holes (1b) are punctured and the battery is activated with water added through the water holes (1b).

About 400 c c of water is required for each compartment of the battery container. Ordinary drinking water is sufficient for the purpose During activation a lot of heat is generated due to dissolution of caustic soda but it has no detrimental effect on the components of the battery Once activated with weter, the battery becomes available for use immediately without requiring any soaking time

Method of assembling the battery

The air depolarised battery of 8 4 volts open circuit voltage and 50 ampere hour capacity consists of six individual air depolarised cells, connected in series as shown in Figures 9 to 11 of the drawings

Method of making the tubular porous carbon cathode element

The porous carbon electrode is the most important component of the air depolarised battery from the point of view of its manufacture and is made as follows

A 3 mm expanded metal tube (3b) of diameter 40 mm and height 115 mm is welded on the top with a strip of mild steel (3c), 12 5 mm wide with a lug (3a) (12 5 mm n 12.5 mm size), bent at right angles, the entire tube being nickel plated (Figures 3 and 4)

A blend of carbon consisting of 128 0 gms of activated cocoanut shell charcoal (90%), in the size range of -100 + 140 mesh and 14 gms of finely divided acetylene black (10%), is first prepared by mixing in a kneading machine, To this blend, 4 25 gms of polymethyl methacrylate (Perspex) binder to the extent of 3% of the mass of the carbon blend, dissolved in 145 cc of benzene or trichloroethylene, is added and the mixing is continued for some more time to get uniform dispersion of the binder The quantity of binder at 3% was found to be optimum A higher ratio of binder has the effect of increasing the internal resistance of the cell, and also of requiring soaking time after activation, whereas a lesser quantity of the same does not give good non-wettability

Alternatively about 150 gms, of blend consisting of 80% calcined petroleum coke and 20% highly conducting carbon black obtained as a by product in the fertilizer industry, could also be used along with the same percentage of binder in the manner described above, in the making of the porous carbon electrodes

The tubular porous carbon electrode (3) is then prepared by pressing the carbon blend along with the binder (4) on the nickel plated expanded metal tube, using a suitable die in a hydraulic press at a total thrust of about 1-2 tons

After pressing the carbon electrodes are either weather dried or dried in an air oven under controlled temperature of the order of about 80°C so as to completly remove the solvent.

After drying, the carbon electrode would be ready for assembly into a cell

The binder used in this process also acts as a waterproofing agent, which property is very essential for the successful functioning of the porous carbon electrode as an air depolarised electrode

The porosity, the breather surface and the thickness of the walls of the carbon electrode used herein, have been suitably adjusted so as to get maximum air depolarisation for the particular size battary

The design is such that the overall dimensions of the battery, the size and shape of both the carbon element and zinc element can be conveniently altered to suit any specific requirements of capacity and voltage for a particular use.

The following are among the main advantages of the invention :

The air depolarised battery works at constant voltage throughout the length of discharge which ensures satisfactory performance in such appliances as the transistor radios

The battery has a fairly high ampere hour capacity for a given weight and volume

Once the battery is exhausted, it could very easily be renewed by replacing the used up zinc anode and electrolyte. The porous carbon cathode, the battery container, lid and other connections could be repeatedly used The carbon electrode could be used for three or four cycles of the zinc electrodes

Replacement of exhausted anode and electrolyte costs very little when compared to the cost of purchasing a new battery as would be required in case of using the dry batteries

The battery requires least maintenance The air depolarised battery would work out cheaper comparatively both initially and in replacement.

The design is quite easily adaptable for commercial production on any scale and requires use of very simple equipment.

Raw materials and equipment required, are indigenously available.

We claim :

1. An air depolarised battery consisting of an array of individual cells arranged in such a way as to get any desired voltage in multiples of about 1.4 volts, each of such individual cells comprising a porous carbon cathode element, a zinc anode and a solid alkaline electrolyte which is activated by the addition of water at the time of use, and all arranged in a container, characterised in that the said cathode element is in the form of a tube for at least part of its length.
2. An air depolarised battery as claimed in claim 1 wherein each individual cell comprises a metal reinforced tubular porous carbon cathode clement and amalgamated zinc anode and sodium hydroxide electrolyte, such a cell giving an open circuit voltage of 1.4 volts.
3. An air depolarised battery as clamed in claim 1 or 2 which has 8.4 volts open circuit voltage and 50 ampere hour capacity, mainly for use in transistorised radio receiver sets, such a battery consisting of six individual air depolarised cells connected in series.
4. An air depolarised battery as claimed in any of the preceding claims wherein said cathode element is formed by either activated carbon such as activated cocoanut shell charcoal or calcined petroleum coke as the bulk constituent with the addition of acetylene black or highly conducting carbon black and polymethyl methacrylate as binder.
5. An air depolarised battery as claimed in any of the preceding claims wherein the cells are in any suitable number, for a particular requirement, connected either in series or parallel, to give the desired voltage or current.
6. An air depolarised battery as claimed in any of the preceding claims wherein the electrolyte is initially incorporated in the solid form, the battery being conveniently water-activated subsequently before actual use.
7. An air depolarised battery as claimed in any of the preceding claims wherein the tubular porous carbon cathode element has a central hole extending to a depth of more than half the length of the carbon cathode, and a bent lug terminal, the said cathode being reinforced by an expanded metal tube which is nickel plated and wherein the anode is amalgmated zinc, thicker at the top and thinner at the bottom with a bent lug terminal, the two electrodes being fitted to the lid.
8. An air depolarised battery as claimed in any of the preceding claims wherein the said cathode element is formed by compressing a blend of carbon consisting of 128 gms of activated cocoanut shell charcoal (90%) in the size range of -100, + 140 mesh size, 14 gms of acetylene black (10%) and 4.25 gms of polymethyl methacrylate binder to the extent of 3% of the mass of the carbon blend.
9. An air depolarised battery as claimed in any of the preceding claims wherein the said cathode element is formed by compressing a blend of carbon, consisting of calcined petroleum coke (80%), highly conducting carbon blaek (20%), and polymethyl methacrylate binder, to the extent of 3% of the mass of the carbon blend.
10. An air depolarised battery consisting of an array of individual cells, each of such individual cells comprising a tubular porous carbon cathode element, a zinc anode and an alkaline electrolyte, substantially as described in this specification.

Dated this 17th day of June 1971

Sd.

of Couneil of Scientific & Industrial Research

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No. 129940.

PROVISI N SPECIFICATION

NO. OF SHEETS :- 2
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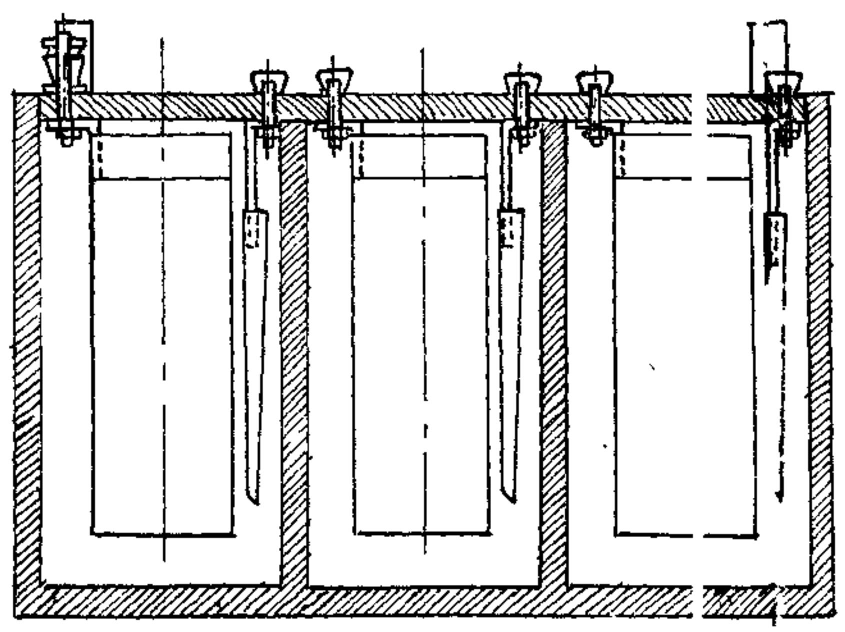

FIG. 1.

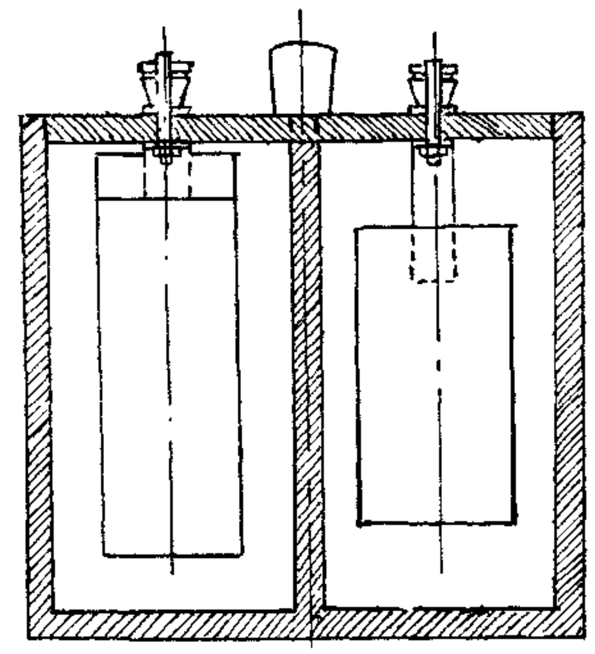

FIG. 2.

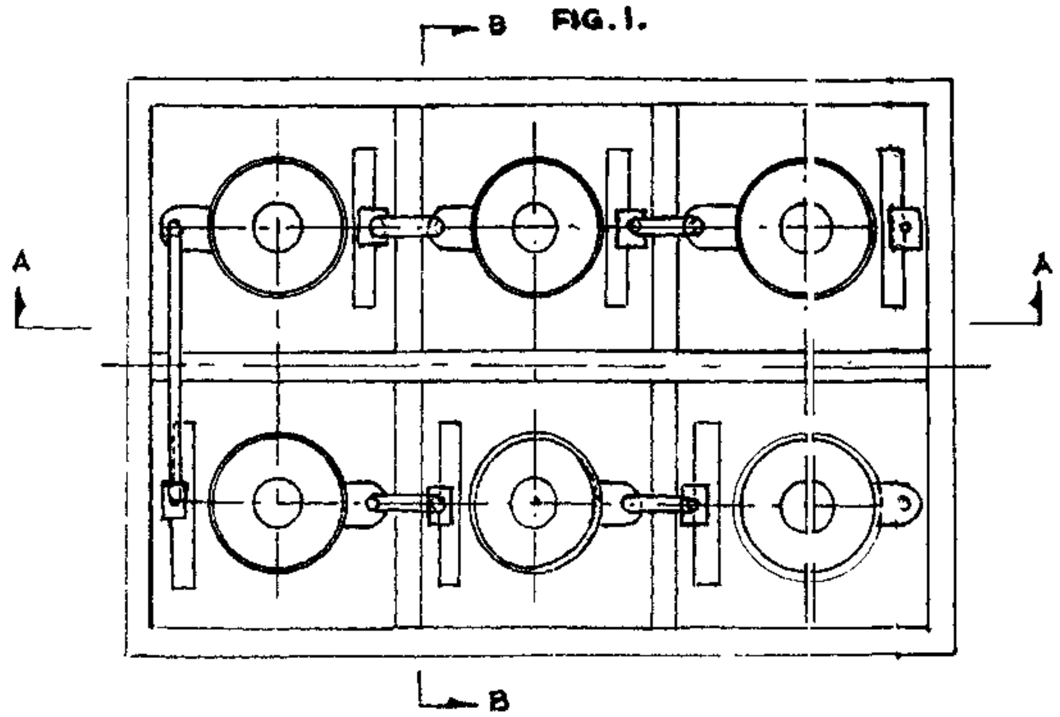

FIG. 3.

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No. 129940.

PROVISIONAL SPECIFICATION

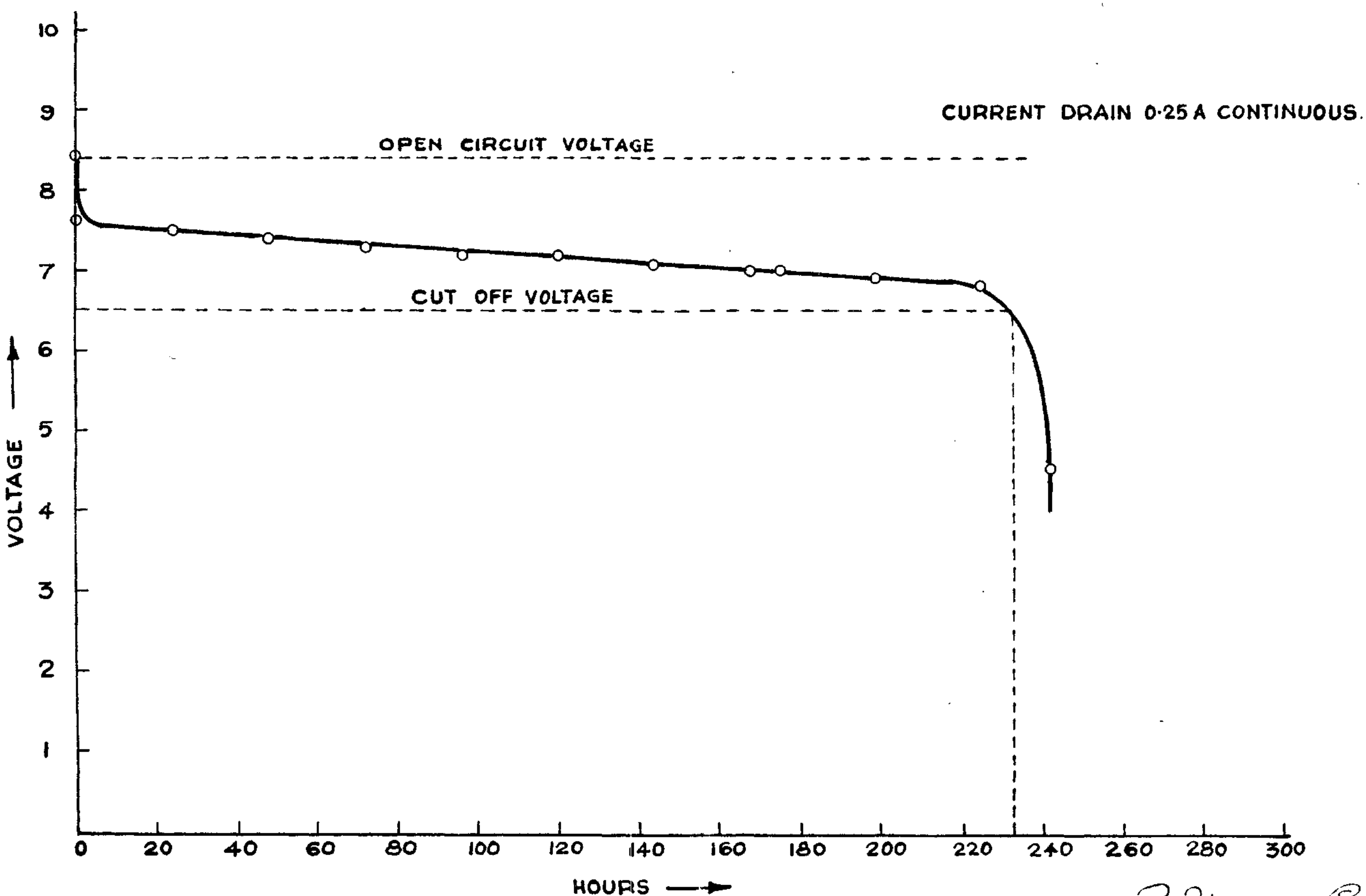

FIGURE-4.

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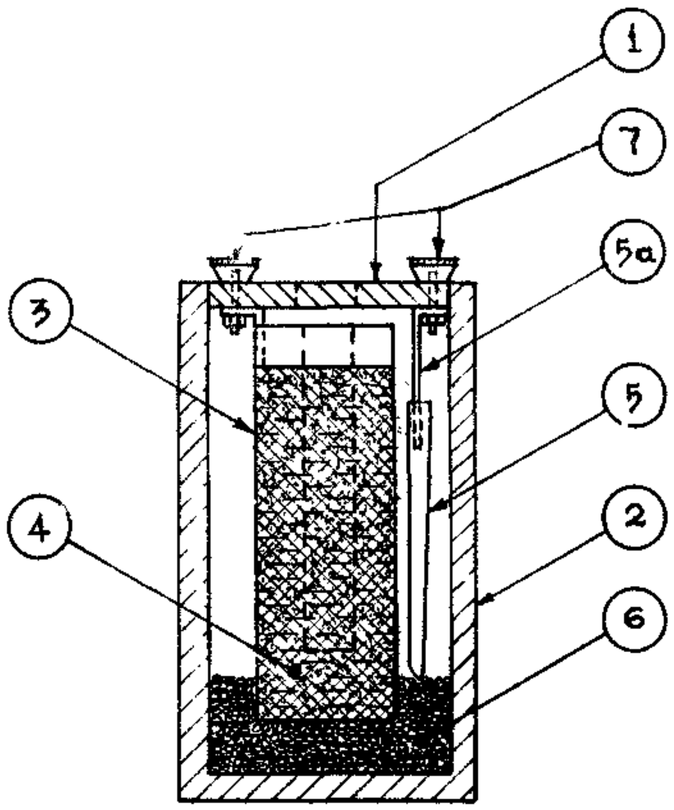

FIG - 1

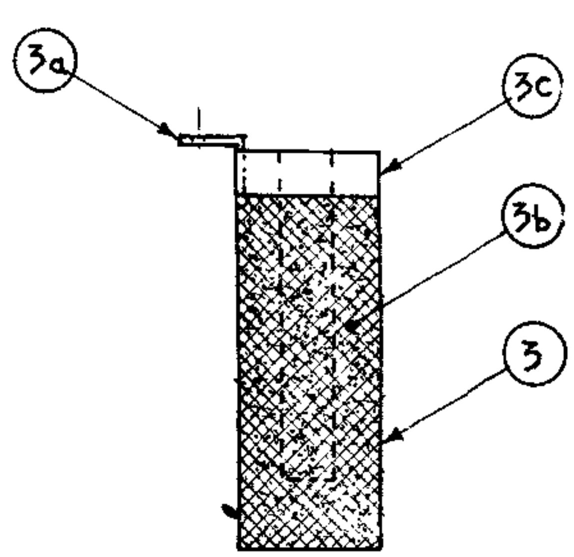

FIG - 3

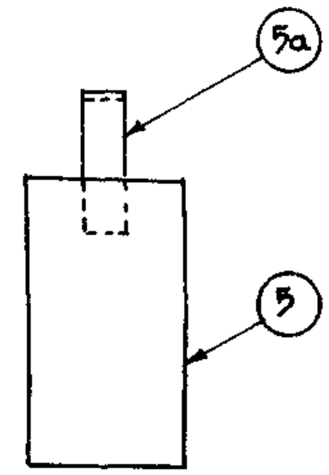

FIG - 5

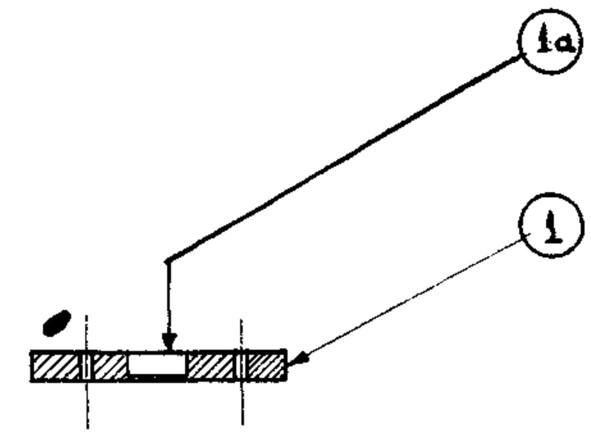

FIG - 7

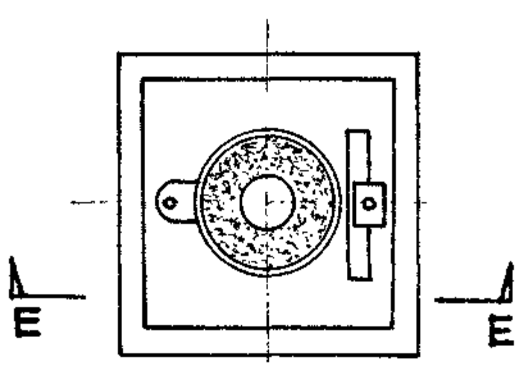

FIG - 2

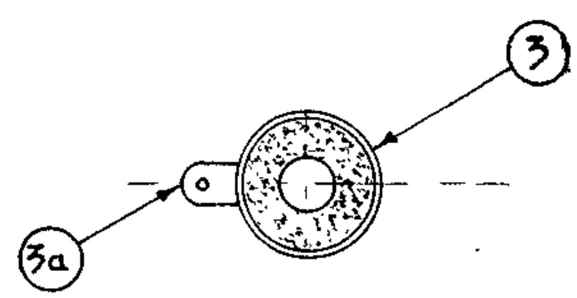

FIG - 4

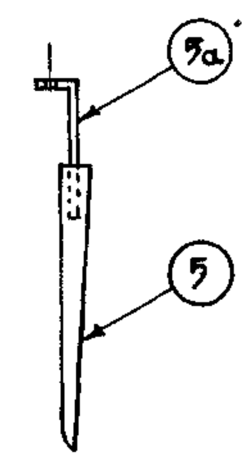

FIG - 6

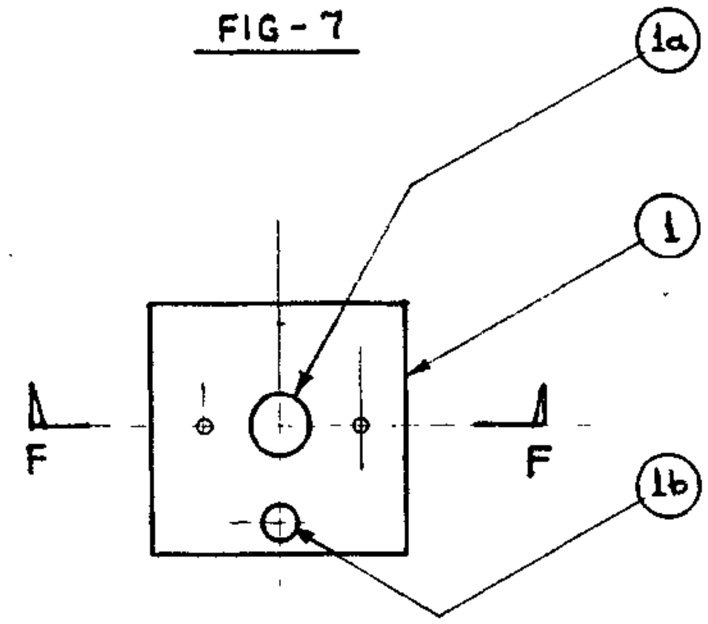

FIG - 8

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COMPLETE SPECIFICATION

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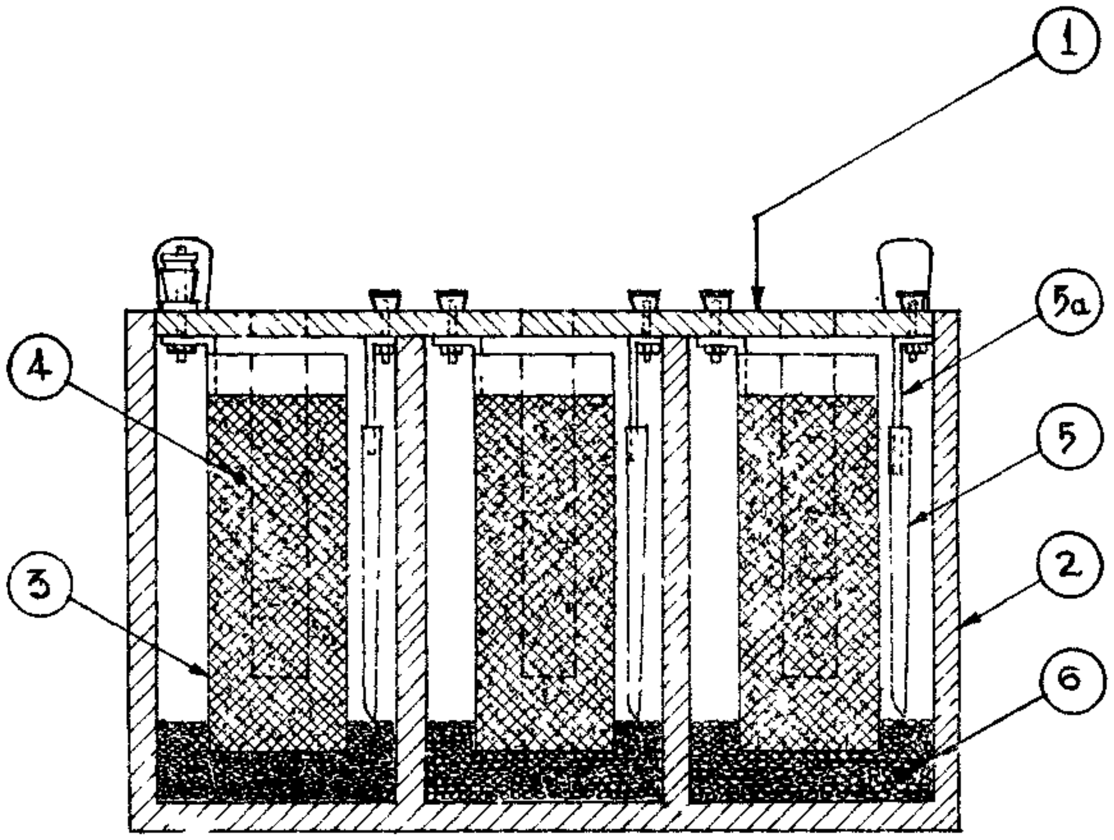

FIG - 9

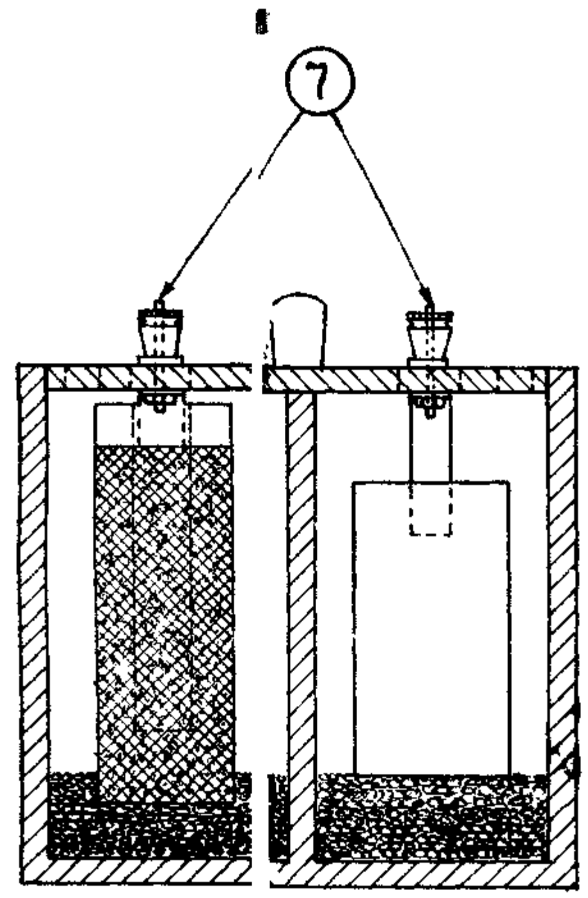

FIG - 10

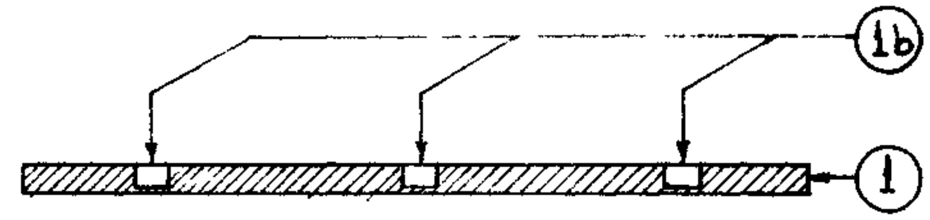

FIG - 14

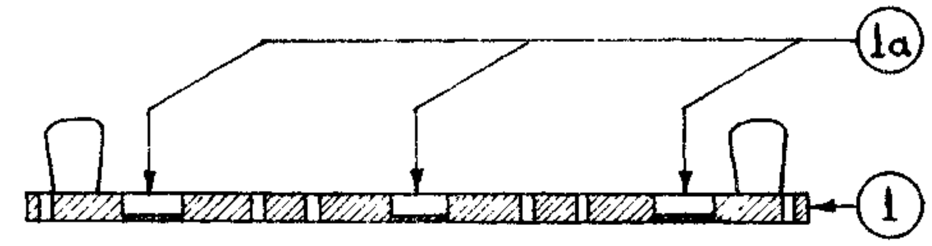

FIG - 13

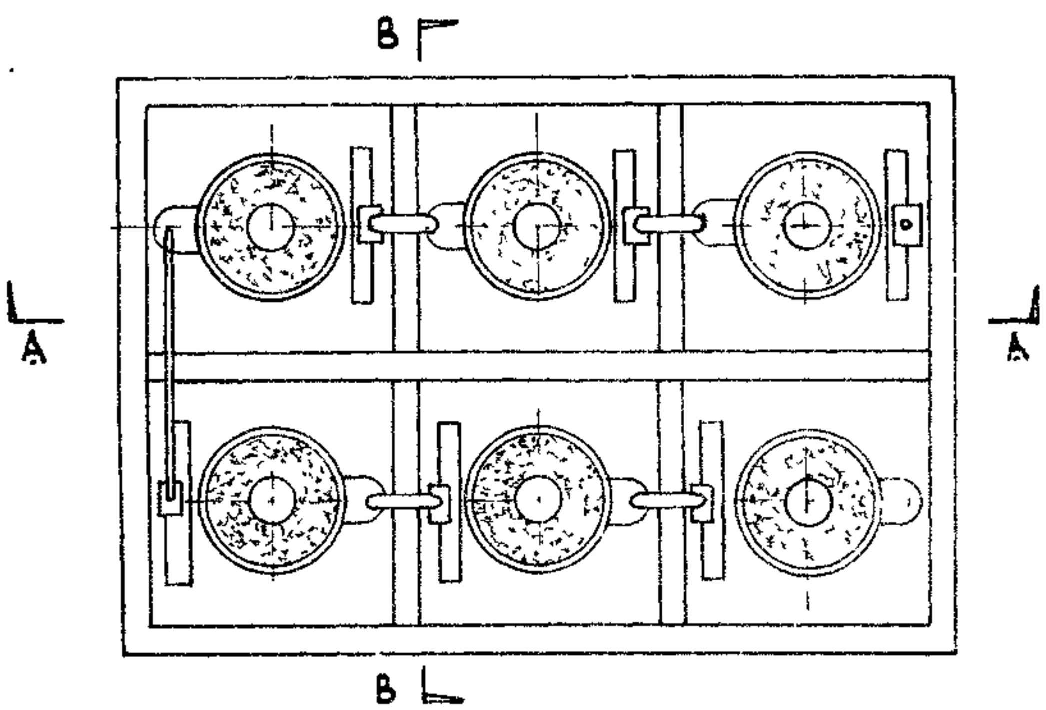

FIG - 11

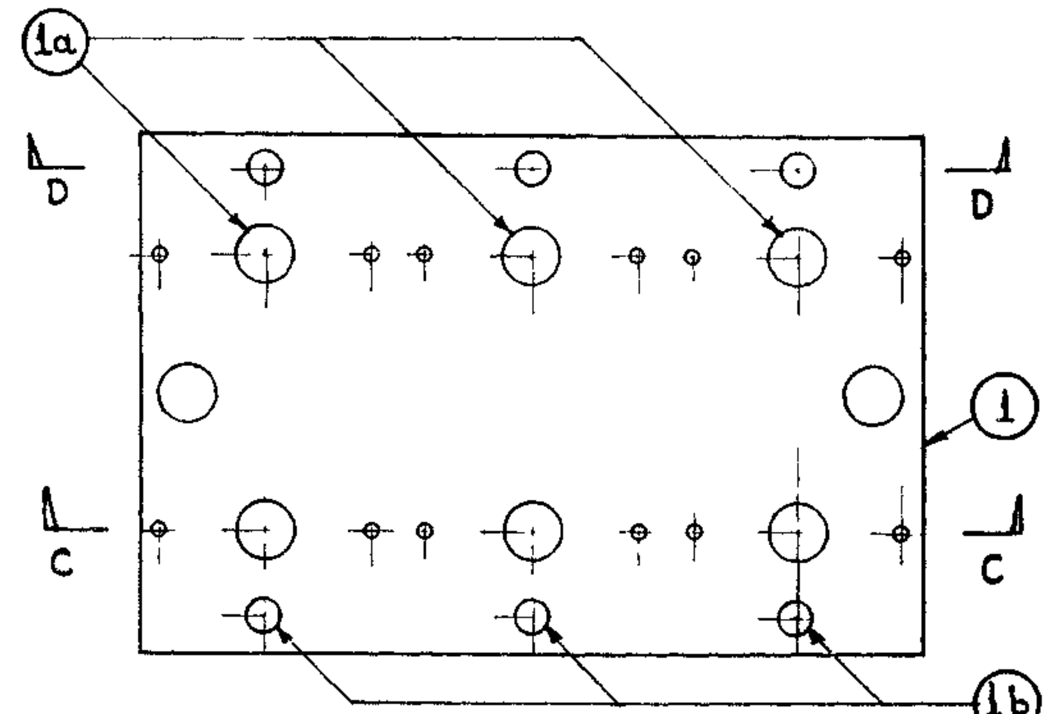

FIG - 12

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