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

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Index at acceptance—14A2 + D2[LVIII(1)]

"LEAD CHLORIDE WATER ACTIVATED CELL SYSTEM"

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).

This is an invention by Shri Kanakarajan Dakshinamurthi and Dr. Prem Behari Mathur, both of Central Electrochemical Research Institute, Karaikudi-3, S. Rly., India, both Indian Citizens.

## **PROVISIONAL**

The following Specification describes the nature of this invention.

This invention relates to the improvement in or relating to the development of cells/batteries which incorporate lead chloride cathode in conjunction with conventional metal anode like Magnesium, Zinc or Aluminium and which is activated by water or an electrolyte solution.

Hitherto it has been the practice to use silver chloride and cuprous chloride as the cathodic materials in salt water activated batteries.

As Silver chloride is a fairly stable compound, silver chloride cells have long shelf life in comparison to the cuprous chloride cells which deteriorate in the atmosphere. On the cost considerations, Silver chloride cells are very expensive and therefore cannot be profitably used in some of the commercial application. Since sparingly soluble halide compounds are highly reversible electrochemically, they are prone to fast activation in common salt water, sea water or tap water. Therefore they are more suitable for applications where the battery activation is easily possible with ordinary water or any of the above mentioned electrolytes. Incorporation of electrolyte within cell has the limitation of increasing cell volume thereby decreasing the energy density per unit volume of the system. Therefore, if a cell system made out of a stable but a cheap halide cathodic material which gets activated quickly and easily with sea water or common salt solution or tap water, it may find wide use in civilian as well as defence applications.

The object of this invention is to obviate the disadvantages of high cost and lack of stability met with in conventional halide batteries by substituting the cathode material by lead chloride in place of silver chloride or cuprous chloride.

To these ends, the invention broadly consists in the development of lead chloride-magnesium cell/battery capable of activation in water or saline water solutions. Magnesium lead chloride battery consists of lead chloride cathode prepared by the method of press compacting and using a suitable binder like carboxy methyl cellulose, polyvinyl alcohol, starch, cellulose acetate and polyvinyl acetate and treating at suitable temperature. Copper or silver wire or mesh is used as the grid. Pure magnesium or its alloy is used as anode material. Materials like filter paper, nylon cloth, cellophane, tissue paper, micro-porous plastics are used as separators. Electrodes are stacked very close to one another leaving just sufficient space for the flow of electrolyte solution.

High tension batteries are fabricated by using duplex electrode system in place of inter cell series connection systems. This helps in the reduction of the space acquired by the cells in series. Duplex electrode consists of copper foil cladded magnesium sheet. The magnesium face acts as anode whereas the lead chloride affixed on the copper face functions as the cathode element for the subsequent cell.

Thus such duplex electrodes alternately placed separated by porous separator material constitute a high tension series connection battery. Such batteries placed in suitable size frame work are activated with water or salt water or sea water to generate high tension electrical power.

The following typical examples are given to illustrate the invention:

# Example 1

To magnesium Electrode of area 25 sq. cm. is attached a copper lead by soldering technique described in an earlier The cathode of same size is made Indian Patent (113763). by pressing 10 g lead chloride containing 1 g lead powder and mixed with carboxy-methyl cellulose binder over a copper wire mesh. Alternatively graphite or acetylene black is used with lead chloride to make the cathode. The cathode is wrapped in a filter paper and is assembled as a cell with two magnesium anodes. The cell is activated with saline water. Following performance results are obtained. The open circuit voltage of the cell is 1.1 and it operates at 1 V to 0.8 V on load at current drains ranging from 10 to 20 mA/cm<sup>2</sup>. The cathodic material efficiency of the cell is as high as 90%. The cell system is capable of operating at sub-zero temperatures.

# Example 2

A battery with working voltage of 112 V-95 V is made in Magnesium Lead Chloride system. Duplex electrodes are made by attaching copper foil to Magnesium anode and attaching lead chloride to copper face which then acts as cathode. 108 such cells are placed in series and separated by cotton separator. The size of the magnesium electrode is  $3.5 \times 2$  cm and cathode size  $2.5 \times 1.5$  cm<sup>2</sup>. About 150 to 160 g of cathode material is used. The battery is activated with saline water. The following performance results are obtained

Batteray discharged for four hours continuously at 40-30 mA current drain at a load of 3100 ohm and cut off voltage 95 V. The discharge curve is graphically shown in the accompanying drawings.

Unlike the cuprous chloride battery which takes nearly half an hour to attain maximum voltage, this battery takes only 5-10 minutes to attain peak voltage after activation. The nature of discharge performance is depicted in the discharge curve.

The following are among the main advantages of the invention:

 The use of lead chloride in place of silver chloride as cathode material in salt water activated batteries has profoundly decreased the cost of activated batteries.

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The use of lead chloride as cathode material has given advantage over cuprous chloride in activated battery in respect of stability, better shelf life and cost.

- 3. The fabrication of lead chloride cathode for battery system is much simple from engineering point of view than that of cuprous chloride battery in high tension units. This will be an important factor of cost reduction in large scale production.
- Lead chloride is more commonly available in the country at low cost in comparison to silver or copper halides.
- As the cell system is capable of being discharged at high as well as low currents per unit area of the cell electrodes, it may find wide utility in a variety of applications.

#### 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 magnesium/lead chloride battery systems.

Activated battery systems using metal chlorides like cuprous chloride and silver chloride are well known.

Activated type of battery employing silver chloride as cathodic material is very expensive while battery incorporating cuprous chloride as cathodic material does not possess good stability and appreciable shelf life because of the unstable nature of cuprous chloride.

The object of the present invention is to overcome the handicaps referred to above. We have found that lead chloride can be used in place of silver or cuprous chloride in activated battery systems as lead chloride is highly stable and cheap.

- (i) Cell systems incorporating lead chloride cathodes are capable of being discharged at high rates.
- (ii) The cell system is capable of being activated very quickly.
- (iii) The cell system gives over 80% of its capacity at fairly constant potential level in contrast to the discharge characteristics of cuprous chloride system. Therefore the battery system is superior to cuprous chloride system especially in high tension applications.
- (iv) Lead chloride is as stable as silver chloride in marine as well as industrial atmospheres and hence highly dependable performance characteristics are obtainable from this battery system as expected from much more expensive silver chloride system. Hence this system may find wide applications in marine equipment and other civilian applications.
- (v) The technology of fabrication of lead chloride cathodes for batteries is much simpler than that of cuprous chloride batteries in high tension units. This is an important factor in reducing the cost of production on large scale. So far water activated lead chloride battery system has not been developed or commercialised nor has it appeared in the market.

According to the present invention, there is provided a magnesium/lead chloride battery system comprising active metal anode like magnesium or its alloys characterised in that the said anode is coupled with a lead chloride cathode element.

The invention includes within its scope a process of making the magnesium/lead chloride battery system which consists in making the lead chloride electrode from a mixture consisting of lead chloride, a conducting material like copper powder, lead powder, acetylene black, graphite powder and a binder material like polyvinyl alcohol, carboxymethyl cellulose, polyvinyl acetate, starch, agar-agar supported on a conducting metallic grid or a wire mesh, and the magnesium anode is made from pure magnesium metal or its alloy.

The lead chloride cathode is prepared by pressing the cathode mix over a conducting metallic grid or a wire mesh and subjecting it to heat-treatment.

So far water activated lead chloride battery system has not been developed, or commercialised and appeared in the market. Hence this battery system may appear in the market as a new one.

The voltage-time discharge curve of the battery is shown in the drawings accompanying the provisional specification.

#### Example 1

A typical size cell in magnesium-lead chloride system is fabricated as described below:

Magnesium alloy (AZ 31) plate of 25 sq. cm. area was cut out from 0.032" thick sheet. A copper lead is soldered at one corner of the cut out plate by a technique described in Indian Patent No. 113763. Two such electrodes after proper cleaning are used as anode element in the fabrication of magnesium-lead chloride cell described here. A same size lead chloride cathode was made by mixing lead chloride (10 g) with 5 to 15% of lead powder or graphite or acetylene black and an organic binder and pressing or pasting this mix over a copper grid. Cathode is wrapped in filter paper. The cell was assembled and activated with water.

Following performance results are obtained. The cell exhibited 1.1V open circuit voltage and 0.95V at 10 mA/cm<sup>2</sup> drain. The cathodic material efficiency of the cell was about 90%. The cell operates between 1V to 0.8V at different drains and can stand a discharge of 20 mA/cm<sup>2</sup>. The cell operates satisfactorily at sub zero temperature.

# Example 2

A battery with working voltage of 112 V - 95 V is made in Magnesium Lead Chloride systems. Duplex electrodes are made by attaching copper foil to Magnesium electrode and attaching lead chloride which then acts as cathode to copper face. 108 such cells are placed in series and separated by cotton separator. The size of the magnesium electrode is  $3.5 \times 2$  cm and cathode size  $2.5 \text{ cm} \times 1.5 \text{ cm}$ . About 150 to 160 g of cathode material is used. The battery is activated with saline water using 3% sodium chloride solution. The following performance results are obtained.

Battery discharged for four hours continuously at 40-30-mA current drain at a load of 3100 ohm to cut off voltage 95 V. The discharge curve is graphically shown.

This battery takes only 5-10 minutes to attain peak voltage after activation. The nature of discharge performance is depicted in the discharge curve.

Noble metal chloride cathodes have long been proved as good cathode elements in activated battery systems which meet specific applications where other conventional batteries like Leclanche cells or lead acid battery do not meet the requirement. So far only cuprous and silver chloride batteries have been commercialised and put for Navai, Meteorological applications, where a long shelf life and instantaneous activation are the main requirements. Because

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of the high cost of silver chloride and poor stability of cuprous chloride, the chloride bateries found limited area of application as activated system out of the multifarious similar applications. The new system which consists of lead chloride as cathodic material will over-come these drawbacks of water activated chloride systems and therefore it is expected to acquire large area of applications. Since this cathode material can successfully be coupled with such light metals as magnesium, the power density of such systems will remain appreciably high. It will be comparable to magnesium silver chloride system. Further the lead chloride compound can easily be manufactured indigenously from lead which is at present obtained in large bulk for lead acid battery and also the lead acid battery waste.

## We claim:

1. A process of making a magnesium lead chloride battery system which consists in making lead chloride cathode from a mixture consisting of lead chloride, a conducting material like copper powder, lead powder, acetylene black, graphite powder and a binder material like polyvinyl alcohol, carboxymethyl cellulose, polyvinyl acetate, starch, agar-agar pressing the mixture over a conducting metallic grid or a wire mesh and subjecting it to heat treatment.

A magnesium lead chloride battery prepared by the process as claimed in the above claim.

Dated this 24th day of September 1971.

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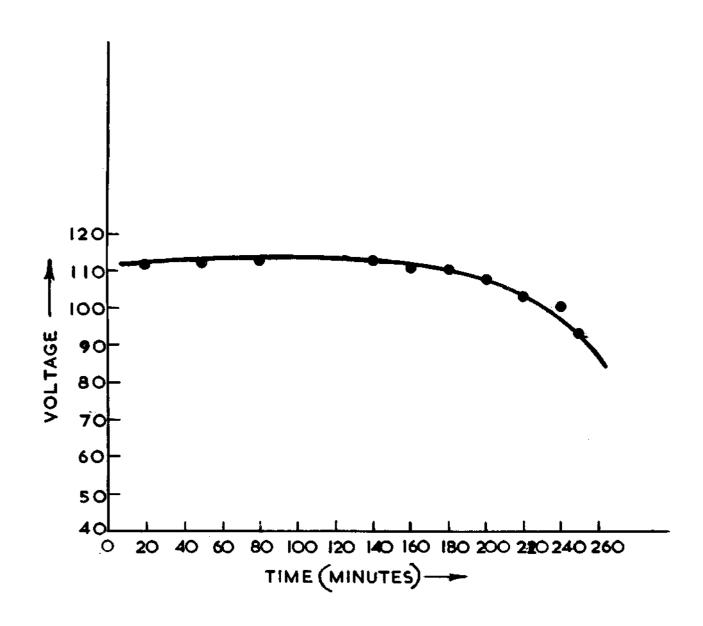
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# PROVISIONAL SPECIFICATION

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No. 130788

SHEET NO.- 1



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