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PRIMARY CELLS

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Fig. 1

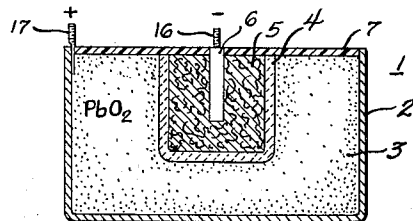
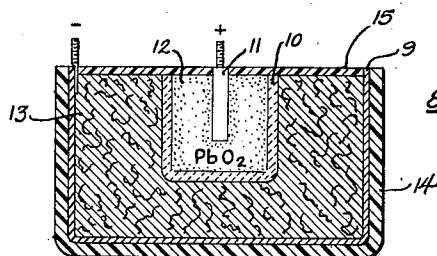


Fig. 2



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HIS AGENT

UNITED STATES PATENT OFFICE

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PRIMARY CELLS

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1 Claim. (Cl. 136—137)

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This invention relates to electrolytic apparatus, such as primary cells, apparatus including electrolytic baths and the like. It is a primary object of the present invention to provide improved apparatus of this type.

Presently known electrolytic methods for continually generating insoluble lead salts from a lead anode rely, in general, upon the presence in the electrolyte of critical concentrations of ions capable of forming soluble lead salts, and upon the maintenance of closely controlled current density. It is an important object of the present invention to provide improved electrolytic apparatus in which the current density and ion concentration are not limited by such necessity for critical control.

Presently available primary cells of the Leclanché type, incorporating zinc and carbon electrodes and an ammonium chloride electrolyte, suffer from several limitations. These limitations arise from the fact that polarization occurs at both carbon and zinc electrodes, such polarization resulting in decreased cell potential during operation. Furthermore, the watt hour capacity of such a cell is reduced when an increased rate of discharge is required. As an approximate numerical example, if a Leclanché cell is capable of delivering one watt hour of electricity when discharged at the rate of 5 milliamperes, it will yield in the order of only one-fifth of a watt hour if the rate of discharge is increased to 50 milliamperes. The voltage obtainable from such a cell is too low for some applications; of even more importance, the volume efficiency of such a cell is seriously limited when the theoretically possible maximum volume efficiency is borne in mind.

Therefore it is an object of the invention to provide an improved primary cell.

It is a further important object of this invention to provide a primary cell in which the cell potential is substantially independent of current drain.

Yet a further object of the invention is to provide an improved primary cell of this type which is characterized by a substantially higher terminal voltage than that of a conventional Leclanché cell.

Still a further object of the invention is to provide an improved primary cell which is capable of supplying large current output without an accompanying large reduction in volume efficiency.

Yet another object of the present invention is to provide an improved primary cell which is not subject to pronounced gassing effects.

Another object of the invention is to provide an improved primary cell in which the formation of an electrically resistive layer on one of the electrodes is prevented.

The features of the present invention which are

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believed to be novel are set forth with particularity in the appended claim. The invention, together with further objects and advantages thereof, may more readily be understood, however, by reference to the following description taken in connection with the accompanying drawing, in which:

Figure 1 is a cross sectional view of one embodiment of the present invention, and

Figure 2 is a cross sectional view of an alternative form of the embodiment shown in Figure 1.

Throughout the specification and claim, that electrode at which metal tends to pass into solution as ions is referred to as the anode; the other electrode is referred to as the cathode. The polarity of the electrodes is conventionally referred to in connection with the direction of current flow in the external circuit, the direction of current flow in the external circuit being from positive to negative. In a primary cell, therefore, the anode as defined above is referred to as the negative electrode, and the cathode as the positive electrode.

There is shown in Figure 1 as a preferred embodiment a primary cell 1 which includes a positive electrode or cathode comprising a case 2 of conductive material, such as lead; alternatively, case 2 may comprise lead or carbon deposited on the inner surface of a non-conductive material such as a plastic. Packed in close contact with the conductive inner surface of case 2 is a mixture or paste 3 of lead dioxide and electrolytic solution, an inner container 4 of porous chemically inert material may be provided to permit diffusion of electrolyte throughout the cell and to separate the mixture 3 from the inner electrode. As an example, the inner container 4 may be made of porous earthenware or woven glass. Chemically inert material 5, having large absorption capacity, may be packed into container 4 so as to provide means for retaining relatively large quantities of the electrolytic solution; such material may be, for example, glass wool.

The negative electrode or anode 6 is of lead, preferably amalgamated and supported in the inert material 5 so as to be in contact with the electrolytic solution. The cell 1 may be hermetically sealed by a layer 7 of wax or pitch, which layer may also aid in supporting the negative electrode 6.

The electrolytic solution includes sulphuric acid, and, in accordance with the present invention, a surface active agent composed of one or more non-polar long chain groups associated with a polar grouping consisting of one or more polar groups and substantially resistant to deterioration by sulphuric acid. In one preferred embodiment, the surface active agent may be dodecylbenzene sodium sulfonate.

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Other surface active agents which may be used are, for example, isopropyl naphthalene sodium sulfonate, sodium lauryl sulfate, sodium myristyl sulfate, and the alkyl phenoxy polyethoxyethanols, such as methyl phenoxy polyethoxyethanol.

In operation, when the external electrical circuit is conductively closed between negative terminal 16 connected to the anode 6 and positive terminal 17 connected to the conductive case 2, current flows and the lead dioxide 3 is gradually reduced. A layer of lead sulphate tends to form upon the anode 6 until such time as all of the sulphate ions are combined with the lead anode, or until the anode is disintegrated. The acid used in the electrolytic solution should be of approximately 50% concentration, this being considerably higher than that used normally in lead storage cells. The reason for using such a high concentration of acid is to increase the volume efficiency of the cell.

Furthermore the volume efficiency of the cell may be increased by the use of a saturated solution of a sulphate of an alkali metal or ammonium in the sulphuric acid electrolyte, together with an excess of solid sulphate to maintain saturation during cell discharge. As a further alternative, a saturated solution of a bisulphate of an alkali metal or ammonium, together with an excess of solid bisulphate for maintaining saturation, may be employed for this purpose.

As the cell discharges and a lead sulphate layer tends to form on the surface of the lead anode 6, the internal resistance of the cell tends to increase. To prevent the resistance of the battery from increasing substantially, the electrolytic solution, with which inert material 5 is saturated, includes a surface active agent, comprising one or more non-polar long chain groups associated with a polar grouping consisting of one or more polar groups and resistant to deterioration by the electrolyte forming the remainder of the electrolytic solution. It has been found that the addition of such surface active agent inhibits adhesion of the lead sulphate layer to the lead anode, so that if space is available within the cell, the lead sulphate falls off the lead anode and the internal resistance remains low. In the case of a cell construction like that of an ordinary flashlight dry cell where all the space within the cell is packed with functional material, the surface active agent prevents the sulphate from forming into a continuous layer; therefore, conductivity is maintained at a satisfactory level through contact of the electrolyte with the portions of the anode not effectively covered by the sulphate.

As has been previously mentioned, the anode is preferably amalgamated, the purpose of amalgamation being to aid in inhibiting the adhesion of an electrically resistive lead sulphate layer to the anode, and to minimize the susceptibility of the anode to attack by the electrolyte when the cell is not being discharged.

The use of the surface active agent in the electrolytic solution permits the utilization of a solid lead anode instead of requiring a spongy lead type of anode such as that used in the conventional lead storage cell. As a result, the deterioration of the anode is less rapid and the life of the battery is increased in comparison with lead storage cells of conventional construction.

In order to prevent the formation of a thin layer of lead sulphate on the inner surface of conductive case 2, which constitutes the cathode

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of the cell, that case may have the inner surface anodized with a layer of lead dioxide. Any appropriate anodizing process may be used. As an example, the case may be made the anode in an electrolytic process in which the electrolyte is lead nitrate; of course, caution must be exercised in maintaining the current density and the electrolyte concentration at appropriate values.

As the cell is discharged, the sulphuric acid is dissipated by the formation of lead sulphate. By the use of a cation exchange material such as sulfonated coal, it may be possible to bring about a partial regeneration of the sulphuric acid. The use of such a cation exchange material provides hydrogen ions to displace the lead ions in solution.

It is to be understood that the inner surface of case 2 may be of stainless steel or other conductive material not attacked by usual concentrations of sulphuric acid. Furthermore, the cathode mixture may comprise a mixture of lead dioxide with finely divided carbon particles such as acetylene black or graphite.

In Figure 2, the order of the cell elements is reversed from that shown in Figure 1. The primary cell 8 includes an anode 9 of lead formed into a case, an inner container 10 of chemically inert porous material such as a ceramic, a cathode conductor 11 of lead or carbon supported within the inner container 10 and having cathode active material 12 of lead dioxide, or a mixture of lead dioxide with finely divided carbon particles, packed tightly in contact therewith and moistened with electrolytic solution. Inner container 10 is surrounded by inert material 13 which is absorbent and which retains the electrolytic solution of the cell. Purely by way of example, spun glass may be employed for this purpose.

The electrolytic solution preferably contains a comparatively concentrated solution of sulphuric acid in addition to a surface active agent which is resistant to deterioration by the acid, such as an agent having one or more non-polar long chain groups associated with a polar grouping consisting of one or more polar groups. The anode 9 may be amalgamated as before. As in the case of the cell described in connection with Figure 1, the surface active agent in the electrolytic solution inhibits the formation of a continuous highly resistive layer of lead sulphate on the anode 9.

The cathode 11 is preferably anodized to prevent formation of a film of lead sulphate on its surface.

The anode 9 of Figure 2 may be placed within a plastic cover 14 to prevent leakage through the case. The cell 8 may be hermetically sealed by means of a heat fusible cap 15 constructed of tar, pitch, or the like.

While the invention has been shown and described in connection with a present preferred embodiment, it is apparent that numerous variations and modifications may be made, and it is therefore contemplated in the appended claim to cover all such variations and modifications as fall within the true spirit and scope of the invention.

I claim:

70 A primary cell comprising: a lead anode; a cathode supported in spaced relation to said anode; a body of depolarizing material adjacent said cathode and spaced from said anode and comprising predominantly lead dioxide; and an electrolytic solution dispersed between said de-

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polarizing body and said anode and including a sulphuric acid electrolyte and a surface active agent resistant to deterioration by said electrolyte, said surface active agent having a chemical composition comprising at least one non-polar long chain group associated with a polar group-
 ing consisting of at least one polar group.

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