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McClelland et al.

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[54] MAINTENANCE-FREE TYPE LEAD ACID

[75] Inventors: **Donald H. McClelland**, Littleton; **John L. Devitt**, Denver, both of Colo.

[73] Assignee: **The Gates Rubber Company**, Denver, Colo.

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[21] Appl. No.: **257,719**

Related U.S. Application Data

[63] Continuation of Ser. No. 62,227, Aug. 3, 1970, abandoned.

[52] **U.S. Cl.** **136/26,** 136/13
[51] **Int. Cl.** **H01m 39/00**
[58] **Field of Search** .... 136/26–27, 136/178–179, 176, 36, 13, 65, 67, 6, 3, 163, 6 R

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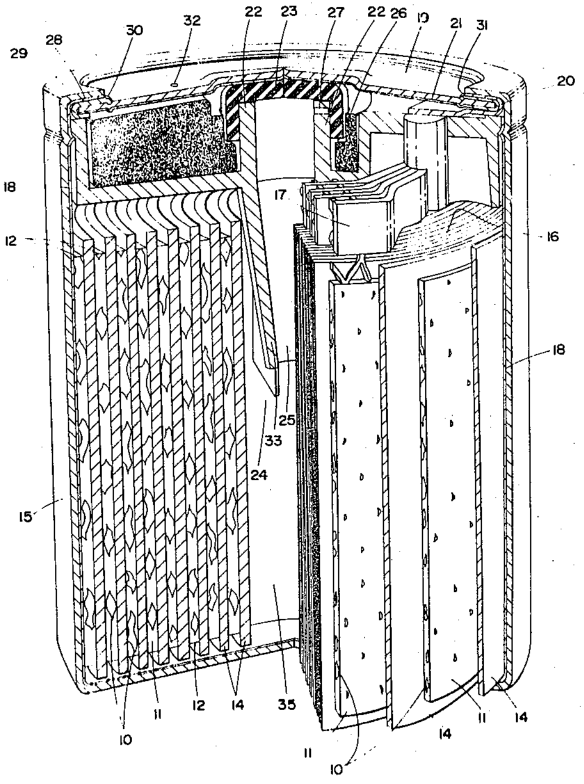
Primary Examiner—Anthony Skapars
Attorney, Agent, or Firm—Curtis H. Castleman, Jr.; Raymond Fink; H. W. Oberg, Jr.

[57] ABSTRACT

This invention concerns a maintenance-free type lead acid cell which is in a normally sealed condition. The cell is characterized by structurally free, non-self-supporting plates separated from one another with highly absorbent flexible separators containing electrolyte and constrained within a container such that mechanical integrity is imparted to obtain a unitary self-supporting structure. Means are provided for maximum recombination of evolved gases and for discharge of excessively high pressure gas. A centroid element allows for operation in any indiscriminate attitude.

23 Claims, 6 Drawing Figures



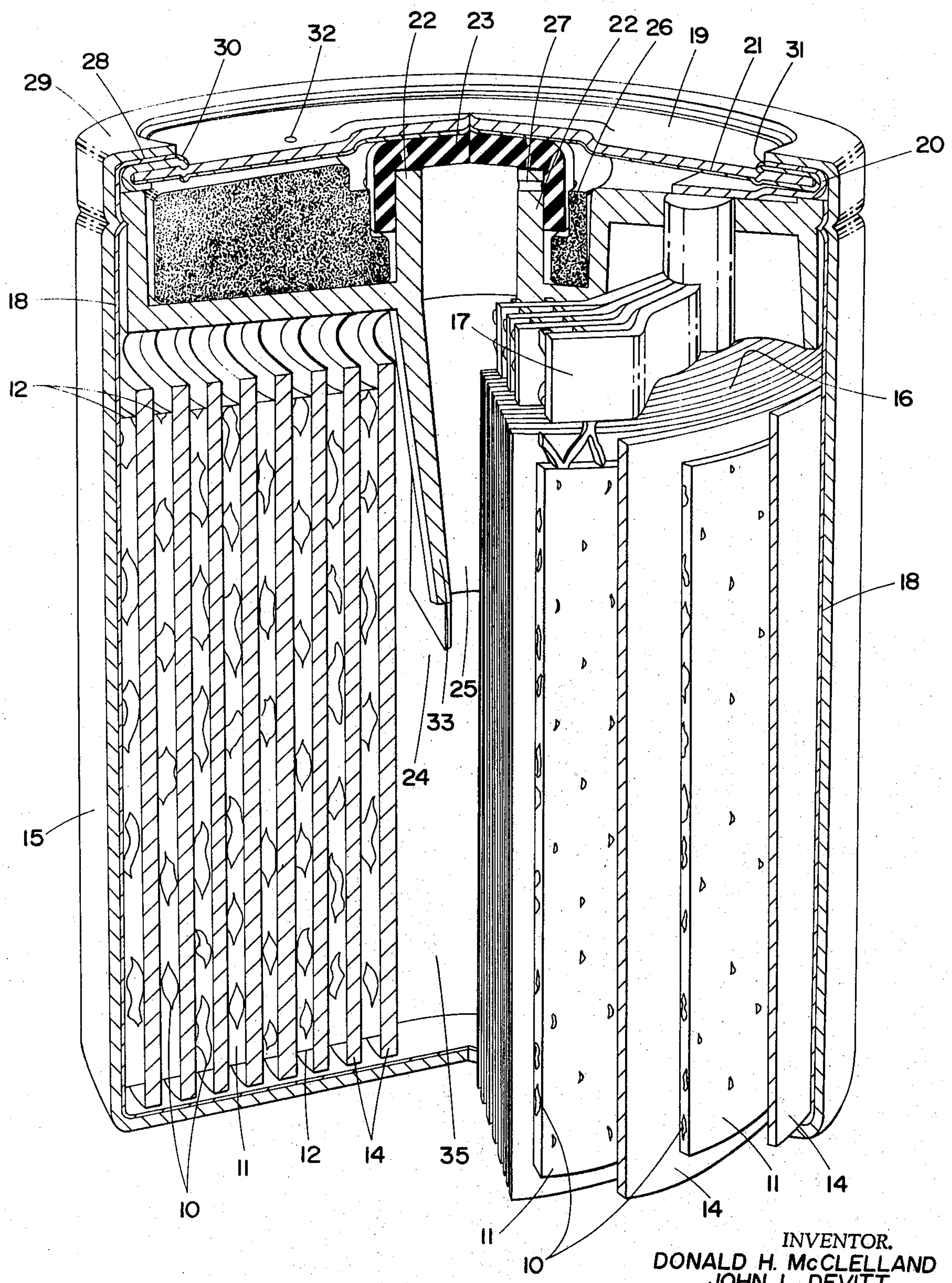


FIG. 1

INVENTOR.
DONALD H. McCLELLAND
JOHN L. DEVITT
BY Raymond Fink

ATTORNEY

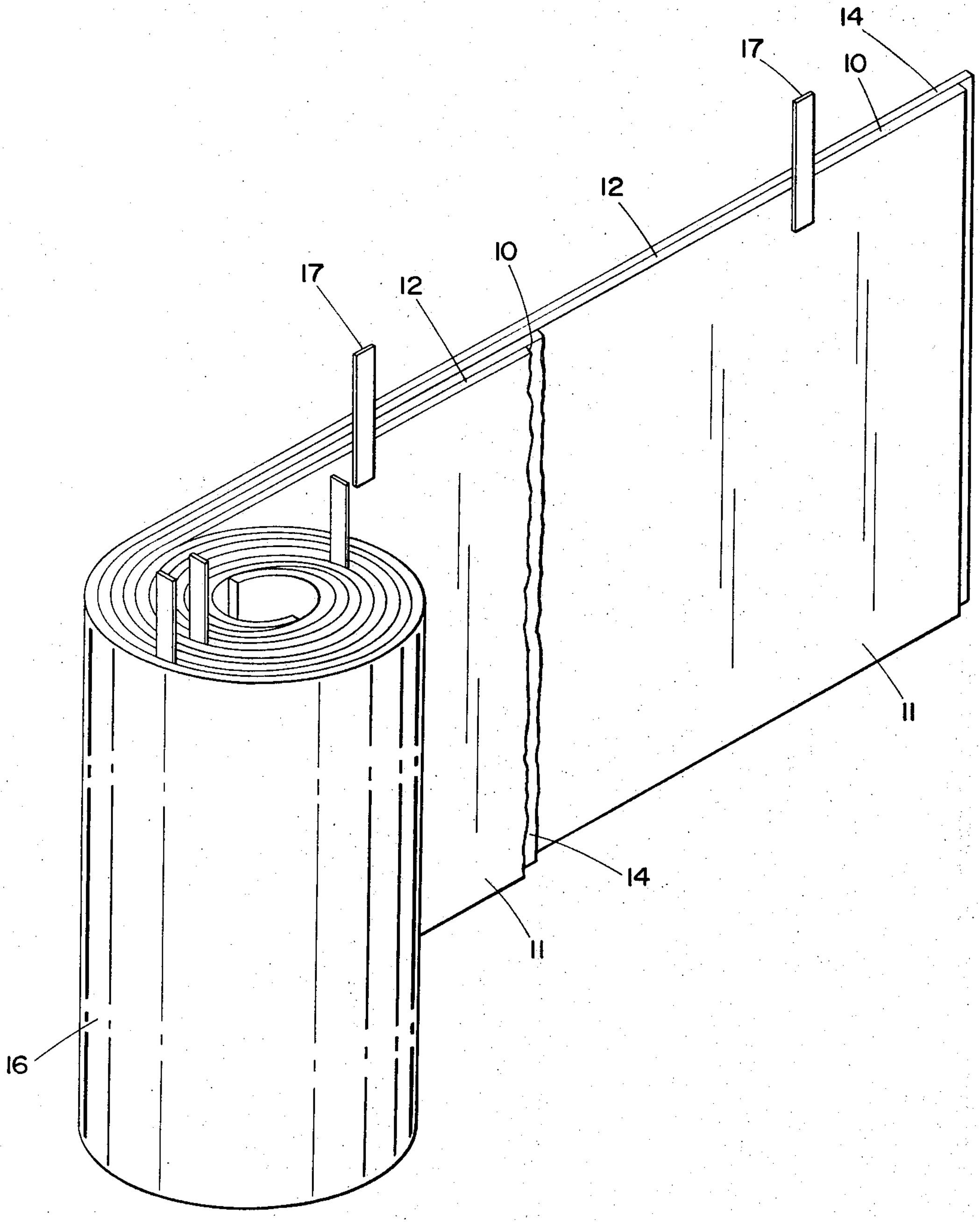


FIG. 2

INVENTOR.
DONALD H. McCLELLAND
JOHN L. DEVITT
BY Raymond Fink
ATTORNEY

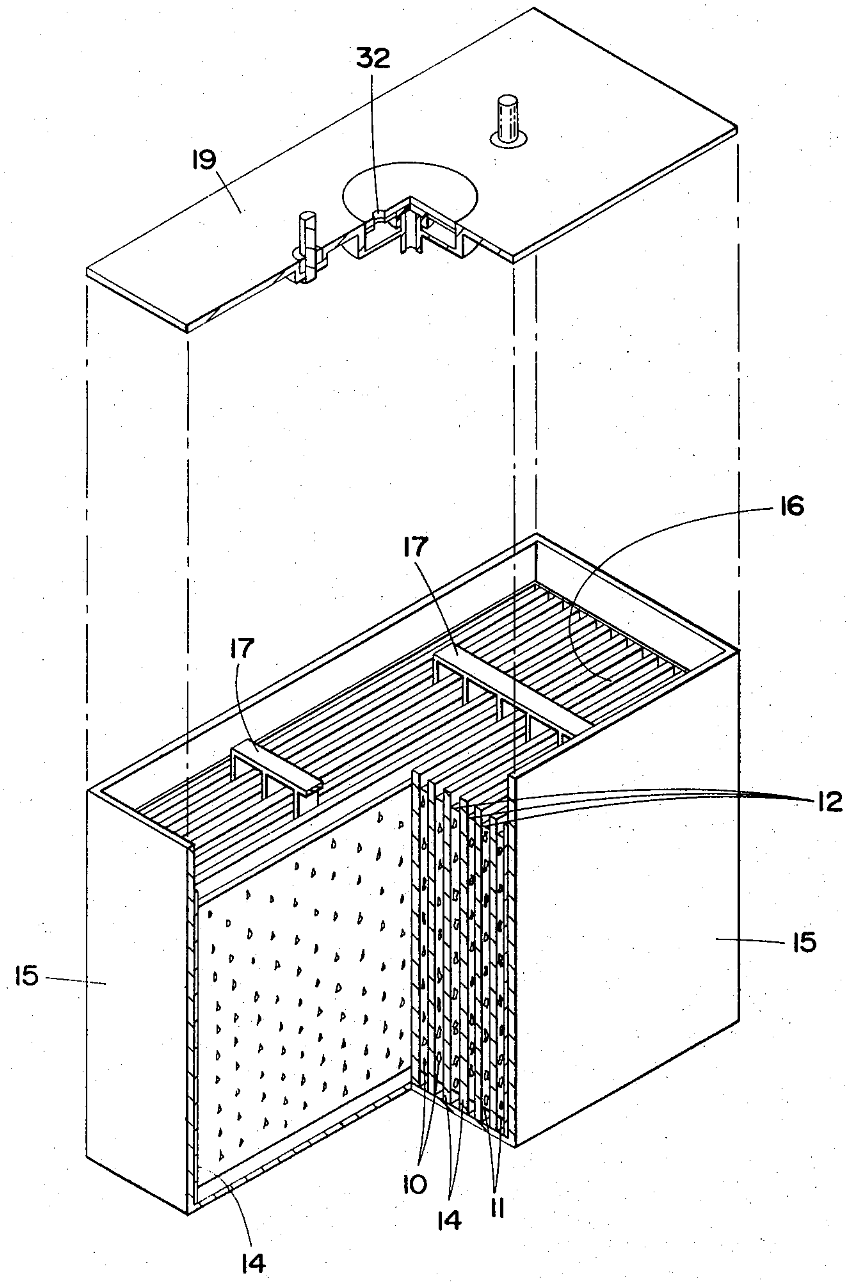


FIG. 3

INVENTOR.
DONALD H. McCELLAND
JOHN L. DEVITT
BY Raymond Fink
ATTORNEY

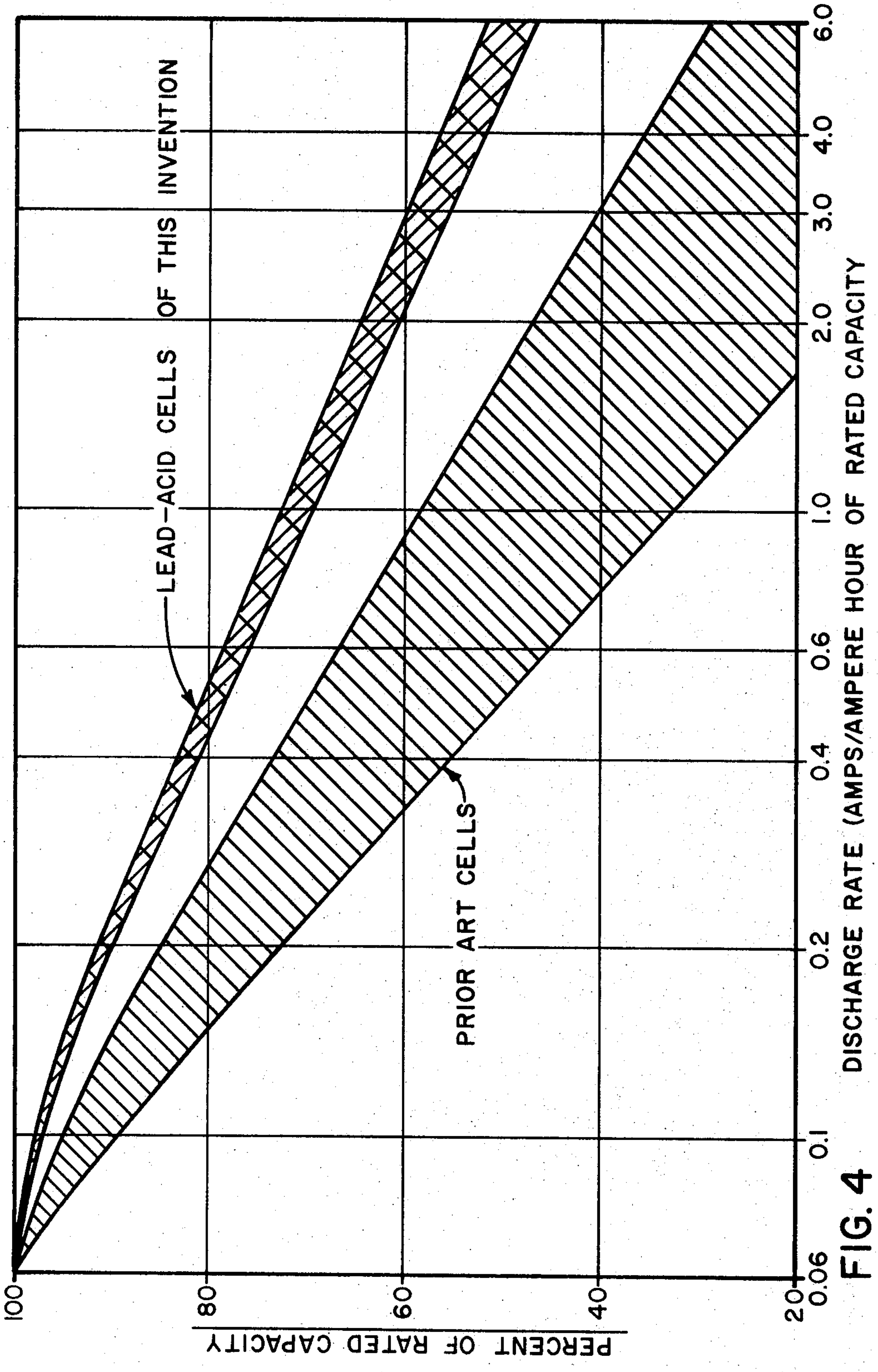
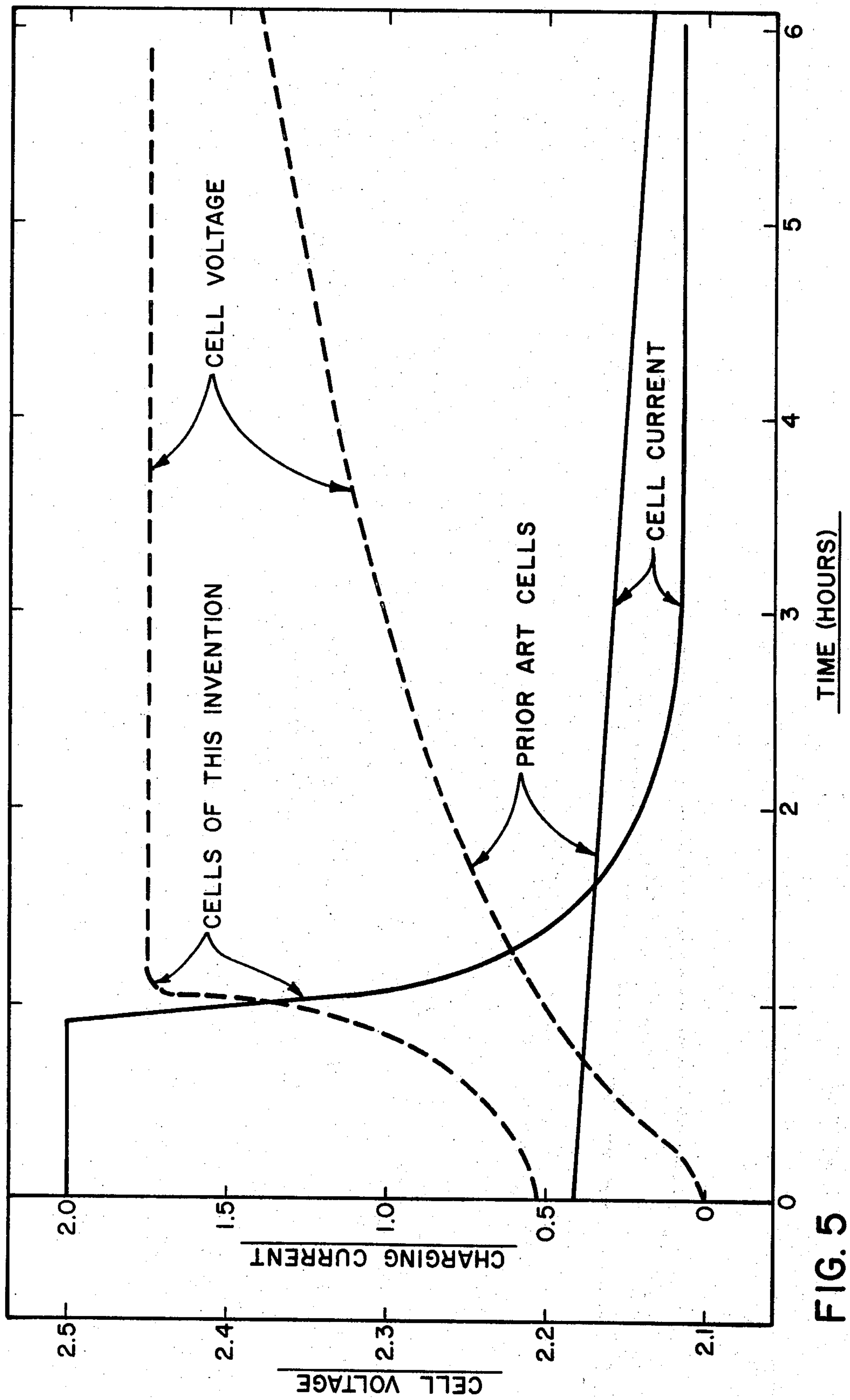

LEAD-ACID CELLS OF THIS INVENTION
PRIOR ART CELLS
DISCHARGE RATE (AMPS/AMPERE HOUR OF RATED CAPACITY
0.06
0.1
0.2
0.4
0.6
1.0
2.0
3.0
4.0
6.0
PERCENT OF RATED CAPACITY
100
80
60
40
20

FIG. 4



CHARGING CURVE FOR LEAD BATTERIES

FIG. 5

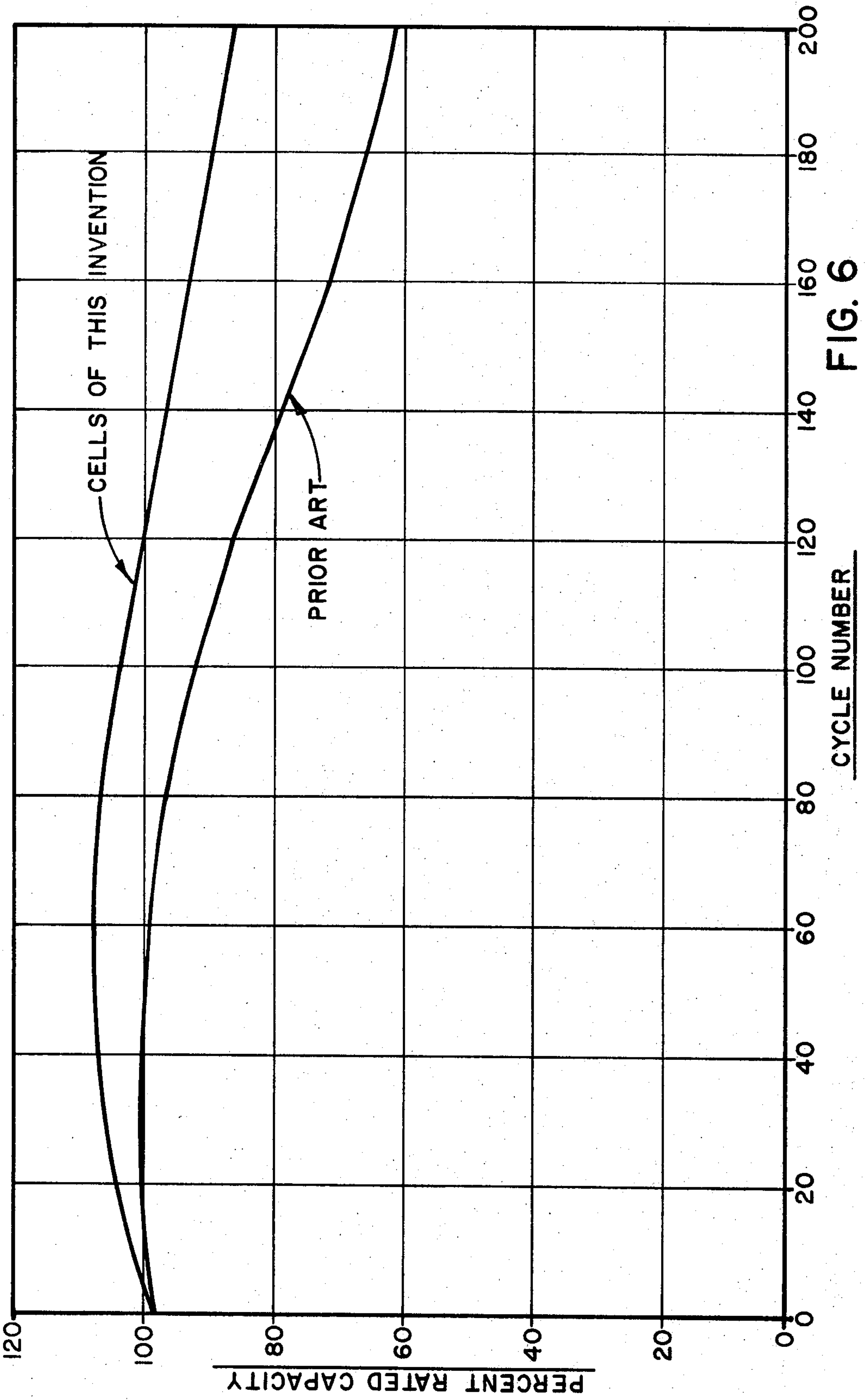


FIG. 6

CYCLE LIFE OF LEAD ACID CELLS

MAINTENANCE-FREE TYPE LEAD ACID

This is a continuation of application Ser. No. 62,227 filed on Aug. 3, 1970, now abandoned.

BACKGROUND OF THE INVENTION

Typically, the maintenance-free type of lead acid cell uses rigid cast self-supporting and sometimes structurally reinforced lead grids to which is generally added about 0.04 to 0.1 percent of calcium in the lead to impart additional rigidity. Though the use of calcium imparts decreased evolution of gas, these cells contain gas relief vents to release any evolved gas.

The plates are separated by materials which must be strong enough to separate the plates even when the plates are warped or distorted during charge/discharge cycles of the cell. The plates and separators generally are combined in a parallel plate manner and encased in a conventional type automotive lead acid battery case to which electrolyte is added, generally in a free liquid state. The container generally contains a pressure relief valve releasable at a very low differential pressure to allow the escape of evolved gases; yet attempting to minimize electrolyte evaporation. Loss of water accompanying the gas release imparts loss of ampere hour capacity of the cell.

Typically, plates of this type are fairly thick, sometimes being reinforced with frames and have low geometric area per unit ampere hour capacity. Utilization of the active material is, therefore, decreased particularly at high discharge rates. Thick separators must be provided with the heavy plates resulting in high internal resistance.

All known lead acid cells including maintenance-free type lead acid cells are fabricated to impart structural integrity to the plates in order to be self-supporting. consequently, grids in maintenance-free type lead acid cells generally contain at least 0.1 percent of calcium or some other impurity based on the weight of lead. The use of such impurities in amounts greater than this will impart structural integrity in order for the plates to be self-supporting. This is used in spite of the fact that with the presence of this much calcium or other impurity, the conductivity of the lead is decreased with a corresponding increase of the internal resistance. This, in turn, tends to result in passivation of the lead grid resulting in the formation of an insulating layer between the surface and the active material during prolonged charging.

Separators generally have been made to be rigid and strong in order to separate the plates. This is necessary since plates will sometimes warp and the separator must be capable of holding the plates apart. On the other hand, the separators are constructed to hold sufficient electrolyte to provide necessary hydrogen and bisulfate ion and water to maintain the electrochemical reaction. Sometimes a gelled electrolylte is used in combination with rigid, corrugated separators. Separation of the plates is maintained, but this construction increases the internal resistance of the cell because the gel reduces the rate of diffusion of the ions in the electrolyte. Gelled electrolyte also provides poor contact between the surface of the plates and the active electrolyte when gas is evolved at the plates.

Cycle life of maintenance-free cells is limited by water and electrolyte loss due to gas evolution since generally speaking, maintenance-free type cells have no provision for replenishment of water. Although an attempt has been made to minimize the loss by use of material having high hydrogen and high oxygen overvoltages and limiting the charge to prevent overcharge, it is known that some degree of overcharge is necessary at the positive plate in order to maintain utilization of the active material. During this overcharge, some gas is evolved and the typical maintenance-free cell, therefore, is provided with a vent above the separator and plate structure. Such venting does not allow the cell to operate in all indiscriminate attitudes. Furthermore, electrolyte loss from the cell may be experienced if operated in indiscriminate attitudes and also particularly during gas evolution.

To overcome the shortcomings of the conventional maintenance-free type lead acid battery, it is an objective of this invention to provide a maintenance-free lead acid cell having unique structural features allowing for relatively little contamination of high purity lead grids which are non-self-supporting.

It is a further object of this invention to provide a structure having improved high energy per unit volume and per unit weight over a wide range of discharge conditions and high power per unit volume and per unit weight with low impedance.

It is a further object of this invention to provide a maintenance-free lead acid cell having provisions for recombination of oxygen evolved at the positive plate and minimizing hydrogen evolution thereby allowing for significant overcharge.

It is a further object of this invention to provide a maintenance-free type lead acid cell operable in any position without leakage of electrolyte or change in electrical operational characteristics.

It is still another object of this invention to provide a maintenance-free cell having no need for additional or adjustment of electrolyte during its useful life.

SUMMARY OF THE INVENTION

The cells as provided for in this invention utilize very thin, flexible, structurally free, non-self-supporting grids which may be formed into various configurations. The lead utilized in the grids is of greater than 99.9 percent purity and contains no material to increase rigidity with accompanying degrees of reduction of hydrogen or oxygen overvoltage. The grids are pasted with material which has similarity to conventional pasted cells, however, unique variations are available for simplification of cell construction.

Highly retentive and porous flexible separators are placed between plates of opposite polarity which are capable of being stacked or formed or wound and confined within a container capable of a variety of configurations and shapes. The separators have high absorbent characteristics capable of retaining the electrolyte in intimate proximity to the plates regardless of the position of the cell. The cell may, therefore, be used in any indiscriminate attitude.

A central vent tube may be placed interiorly of the cell at close proximity to the centroid of the plate/separator mass. The vent is provided with a pressure relief valve normally biased in a closed position which is activated only during excessive gas pressure; for example during overcharge or excessively high temperature, but is closed during normal relatively high pressure operation. Neutralizing means may be provided to neutralize escape of acid droplets entrained in the vented gas. The cell operates in a starved condition with virtually no unabsorbed electrolyte. The plates have active edges exposed to gas volume. The ampere hour capacity of the negative plate is greater than that of the positive plate thereby allowing the positive plate to overcharge before the negative plate. Thus, oxygen which may be evolved during overcharge is thereby allowed to diffuse and recombine with the exposed portions of the negative plate.

FIG. 1 is a cutaway cell showing all of the components of an assembled cell in relative configuration with one another.

FIG. 2 is a partially unwound cell utilizing spiral configuration of the positive and negative grids separated by the separator which is a possible configuration according to this invention.

FIG. 3 shows a stacked plate cell assembly exploded apart.

FIG. 4 is a graph of discharge rate versus percent of rated capacity comparing prior art cells with the lead-acid cells of the invention.

FIG. 5 is a graph comparing the charging curves of the cell of the subject invention with that of prior art cells.

FIG. 6 is a comparison of the capacity of cells of the subject invention with that of prior art cells versus

TECHNICAL DISCLOSURE

Starting with the lead grid **10**, the grid in this invention is a flexible, non-self-supporting and non-reinforced structure. The preferred method of this invention is to use an expanded metal type of substantially pure lead which even further decreases the self-supporting capabilities of the grid and decreases the weight. Obviously, structurally speaking, other types of non-self-supporting grids such as thin flexible lead sheets or thin cast grids or lead foil could be used, however, the expanded lead grid is preferred.

The basic grid in this invention departs from the normal grid found in maintenance-free type lead acid cells. In this invention the grid is made from a very high purity lead. As was pointed out, lead in normal maintenance-free lead acid cells contains a sufficient amount of impurities to impart structural integrity to the grids in order to be self-supporting. This is neither necessary or desirable with the grids of this invention. In this invention, very high purity lead is used containing a very small amount of impurity such as calcium, present generally in an amount of less than 0.02 percent by weight based on the weight of lead. The low amount of impurity minimizes gas evolution at the plate, but it does allow for formation of nucleating points for a grain structure allowing for minimum grain size. This refinement of the grain structure is also beneficial in that there is a minimization of corrosion at the positive grid with such small grain size. Since the grids in this invention are not self-supporting, lead which is commercially available in purities of 99.99 percent purity or greater may be used. For this reason, though the cost is increased somewhat, it is possible to commercially obtain and use lead of purity of 99.999 percent and even as high as 99.9999 percent purity. The increased cost may be justified to minimize the other deleterious effects generally associated with impurities.

A preferred alloying agent is calcium with use of as little as 0.001 percent by weight in the lead. This small amount is possible since other means are utilized for imparting structural integrity to the grid. Though the smaller amount of as little as 0.001 percent by weight may be used, one strives to narrow the range to less than 0.03 percent by weight down to as little as 0.006 percent by weight, with an amount of 0.01 percent being quite acceptable. other materials such as silver, copper, arsenic and tellurium are effective as nucleating agents to refine the grain size. Silver may be used in amounts between 0.005 to 0.1 weight percent. If copper is used as the nucleating agent, amounts of from 0.001 to 0.1 weight percent are used. Arsenic is used in amounts of 0.002 to 0.1 weight percent and tellurium is used from 0.002 to 0.1 weight percent. A relatively small amount as compared to that found in the normal maintenance-free lead acid battery is used and effects minimization of likelihood of passivation as well as likelihood of corrosion.

Grids **10** for use in this invention may be made by means of casting, stamping, forging or perforating sheets of lead foil. A preferred method according to this invention is to expand chillcast lead sheet and subsequently cut it to the desired shape. Strand thickness of expanded grid lattice is of some importance especially in the positive plate since the plate must be as thin as reasonable but must be at least the thickness of the grid strands. The grid strands, however, in the positive plate, are slowly converted from lead to lead dioxide and if the strand thickness is too thin the strands will eventually be converted to oxide and the grid will no longer function properly as a current collector. Normally it is desirable to have a strand thickness of 0.020 to 0.45 inches with the plates **11** being from 0.020 to 0.60 inches in thickness. Additionally, thinner plates **11** may be utilized more effectively, particularly in higher discharge rates. Thinner plates also reduce the internal resistance of a cell of given ampere hour capacity since there is a corresponding increase in the geometric area of the plates. It is quite obvious that plates **11** of this cell differ drastically from plates of other cells in that the plates are non-self-supporting but yet give far improved characteristics.

Though conventional pasting methods may be used, some differences are helpful and lead to improved performance. A material of substantially 75 percent by weight of litharge (PbO) and 25 percent of red lead (Pb_3O_4) may be used for the positive plate. As is known in the art, additional components may be used such as some type of bulking agent, in the order of 0.05 percent to 0.2 percent by weight of the bulking agent. Paste density in this cell should be somewhat higher than for other types of maintenance-free type lead acid plates for best performance. A paste to grid weight of 1:06 to 1:1.5 is acceptable. As will be explained later, it is important that the plate paste should cover the edges **12** of the plates. Paste rather than solid grid must be exposed on the edges, especially in the negative plate. In the mixture defined above, sufficient water is added in the complete mixture to obtain a paste of 3.6 to 4.8 grams of paste per cubic centimeter of mixture.

The paste mixture is spread on to the lead grid to form a completely covered plate **11** and in the case of expanded lead grid, filling the holes therein as well as forming a coat on each side. A pasted grid still retains a non-self-supporting characteristic, either while the paste is wet or after it has dried.

The negative and positive plates **11** are essentially formed in the same manner utilizing a pliable, flexible lead for the grid. In this cell then the negative lead grid can be pasted with a similar type of paste comprised essentially of 80 percent litharge (PbO) plus essentially 17 percent by weight of small free lead particles. To this may be added about 1 to 3 percent by weight of expander type materials usually barium sulfate, carbon black and an expanding type material such as lignosulfonate. To this mixture is added concentrated sulfuric acid and water to obtain a paste material having a density of from 3.6 to 4.8 grams per cubic centimeter. The negative plate should have a slightly greater capacity than the positive plate but since the two plates normally have about the same utilization level, the negative plate should have 10 to 30 percent greater active material pasted thereto than does the positive plate.

A separator material **14** is utilized to not only separate adjacent plates from one another but must have a porosity and retention great enough to contain virtually all of the electrolyte necessary to support the electrochemical reactions. Consequently, an important part of this invention is the utilization of a separator material having a very high heat of wetting which aids in the retention of the electrolyte within the interstics of the separator except for a small amount of electrolyte contained in the pores of the plates **11**. It is of importance that in this cell there is essentially no free electrolyte except that which is retained within the separator material itself. As will be explained subsequently, various configurations have been described which will accommodate the possibility that some free electrolyte may be formed in the cell, either because of excessive gassing or forcing of the electrolyte out of the separator at attitudes of the cell other than at an up-right position. Therefore, one of the preferred embodiments of the cell is to have separator material **14** extending both above and below the plates to contact at least the upper or lower interior surface of the container or liner. Another configuration, therefore, would be to have separator material surrounding the outer-most layer of the plates and contact at least one interior surface of the container or liner. With such a configuration, freed electrolyte will be reabsorbed by the separators. Most of the well known separator materials such as microporous rubber, polyvinyl chloride, polyolefins and phenolic resin impregnated paper may be used with this cell.

The preferred separator material is made from a microfiber diameter, unwoven, short staple fiber glass material. Sheets of fiber glass manufactured from such material have extremely high surface area with correspondingly small fiber diameter capable of retaining the electrolyte within the separator itself. In order to obtain maximum heat of wetting, the micro-fine fiber filament with high surface area per unit weight or unoriented glass matting is utilized. This material has a high electrolyte retentivity per unit volume of material and is also very highly flexible. Fiber diameter of these materials is in the range of 0.2 to 10 microns and has surface area of approximately 0.1 to 20 square meters per gram of silica. Such material has a porosity of as high as 85 percent to 95 percent. This very high surface area together with the high heat of wetting by the sulfuric acid of the electrolyte on the glass results in a separator having a very high retentivity of volume of electrolyte per unit volume of separator. Though this separator material **14** is not so physically strong as the conventional maintenance-free type lead acid separators, it is sufficient for the novel cell according to this invention since the physical strength requirements for this separator are less than conventional cells since the plates do not tend to pull or warp during the cycle life nor are there associated problems related to conventional rigid grids and post structures.

The cell may be formed by preparing in a conventional manner, stacking plates and separators alternately of one another in the desired shape. Such plates and separators may be stacked and pressed to the desired pressure and placed in a container **15** resulting in the conventional parallel plate construction. However, it is preferred in this invention to use a unitary long, continuous, single strip of each plate **11** and separator **14** and spirally rolling or wound upon itself in order to provide electrical continuity within the plate. The rolling or winding is carried out under tension to maintain compression of the cell assembly though tension of as little as 5 pounds per square inch can be used. A winding tension of about 40 pounds is preferred to cause the separator **14** to compress slightly and to make the moist plate **11** conform to the separator. The assembly **16** is wound before the plates have had time to dry. The spirally wound components **16** can be formed into cylindrical, oval or rectangular shapes to accommodate any ultimate shape desired. Regardless of the shape into which the subassembly **16** is forced before the drying, the continuous plate structure is maintained. To the negative plate and the positive plate are then affixed separating current connector tabs **17**. A superior current distribution is available with the continuous strip fabrication. As will be explained later, it is preferred that separator material **14** extend both above and below the active edges of the positive and negative plates to aid in the recombination mechanism.

The next step in the process after the winding is to cure the plates **11** or as is commonly referred to in the art, the hydroset process. This can be conveniently done at a rather low temperature of 35°C. It is important, however, that this be done at a controlled humidity of essentially 100 percent. During the cure or hydroset process the PbO is transformed to lead hydroxide commonly thought to be $Pb(OH)_2$. In essence, however, it is a hydrated lead oxide in which the molar volume of the active components of both plates is significantly increased.

Subsequent to the curing process, the dried subassembly **16** of plates **11** and separators **14** under compression is stuffed into a container **15** resulting at this point in a transformation of a non-self-supporting feature of the fabricated components into a self-supporting, compact, integral structure. The constraint of the components with the container results in this self-supporting member in which the plates **11** are accurately spaced from one another while still being very close together. The constraint does not allow the plates **11** to move with respect to one another and allows for a very compact subassembly **16**. The compactness minimizes the ionic migration distance between the plates and tends to provide a consistent current distribution between the plates. In the spirally wound species, the winding is generally accomplished by utilizing a removable mandrel resulting in an open area **35** along the center axis which, as will be shown later, is useful for venting.

The container may be of an electrically inactive material; however, it has been found to be convenient to utilize electrically conductive containers and caps in which case the container is lined with an electrically insulating lining material **18** such as polyolefin, polyvinyl chloride or other similar inactive materials which are capable of rendering encapsulation and to electrically insulate the components from a constraining container **15** structure if it is electrically active such as sheet steel which may be formed into a desirable configuration. As was previously stated, it is convenient to form the cell into any desired geometric shape such as cylindrical, rectangular or oval shapes. It is an important factor, however, that the assembled components **16** are constrained within the container and if the container **15** itself is an electrically active material, then isolating the electrically active material with a liner **18** material disposed immediately within the cap **19** and container **15.**

Current connections **17** are made between the appropriate plates **11** and metal tabs through a top which is hermetically sealed to the container. If the container is of a non-electrically inactive material, a similar plastic top will be used; however, if an electrically active container is utilized then the top **19** will be lined with a similar material as the container liner **18** so that the liner material can be welded into a continuous structure. The top is made to fit down onto the plate/separator subassembly **16** so as to tightly constrain the pack along the axis of the winding and also to prevent any shifting of the pack or of the individual components in addition to minimize free gas volume in the cell.

The free gas volume is that volume of the cell within the cell liner which is occupied by gas. The plastic liner top **21** also contains a central vent tube **22,** if present, and part of the venting valve **23.** For this cell, a central venting tube **22** is preferred since by such means the venting exit can be placed in the approximate centroid **24** of the plate/separator pack **16** and further provide supporting means to the pack in the center **17** of the winding. In the event that gas venting occurs through the relief valve **23,** the gas must pass out through the centroid exit **25** regardless of the position or attitude of the cell. such an exit route will prevent the venting gas from carrying out any residual free electrolyte with it since free electrolyte cannot collect at the centroid but only at the gravitational bottom of the cell.

Of course, with a configuration such as is disclosed in the present invention, the addition of electrolyte must be handled differently. Normal types of electrolytes are utilized; however, the electrolyte content is in a more or less starved amount. In other words, it is important to control the amount of electrolyte placed in the cell. There must be enough hydrogen and sulfate ions together with water to support the electrochemical reaction but there should not be an excess of free electrolyte. Essentially, all electrolyte added is completely absorbed within the separator or within the plate pores. There is little or no free electrolyte not retained within the pores of the plates **11** or the interstices of the separator **14.** As will be explained later, it is important to maintain a starved electrolyte condition in order to maximize or enhance the recombination of oxygen with a negative plate sponge. Furthermore, free electrolyte will tend to move in the cell depending on the attitude of the cell.

To accommodate the addition of electrolyte, the addition is conducted essentially under a vacuum wherein the cell is essentially evacuated and electrolyte added through the central vent of the cap. Normally a sulfuric acid electrolyte of 1.3 density is satisfactory and can be added since the electrolyte is added under influence of vacuum. It substantially fills the interstices of the components but more important, is essentially completely absorbed by the separator material and the pores of the plates.

The cell is now electrolytically formed by application of a tapered or constant current charge. In essence, the cell is excessively overcharged. During the formation step, the $PbSO_4$ and the PbO in the positive plate are oxidized to form lead dioxide (PbO_2) with the evolution of oxygen gas occurring at the positive plate during the overcharge. At the negative plate, the $PbSO_4$ and PbO are reduced to the well-known spongy lead with evolution of hydrogen gas occurring at the negative plate during the overcharge.

Vacuum may once again be applied in order to remove the free oxygen and hydrogen gases. In essence the cell is at this point degassed. while maintaining the degassed condition, the cap is welded to the liner before which the central vent is capped with a relief valve **23** which may be of the Bunsen type capable of retaining at least 10 to 15 pounds of internal pressure. The Bunsen valve in essence is an elastomeric or yieldable cap of the central vent which may be biased outwardly during the relief operation but is normally biased in a closed position in order to retain a higher than atmospheric internal pressure. A neutralizing material **26** such as sodium bicarbonate is placed around the vent in order to absorb and neutralize any entrained droplets of electrolyte which may escape during any subsequent gas venting at excessively high pressures.

Referring to FIG. **1,** it is to be noted that in a preferred embodiment of the invention, the side flange of a plastic liner top has a niche **27** adjacent to the negative tab. separate from the negative tab is the positive tab which is brought out from the positive plate connector. At this point, however, there is no unbroken portion of the flange **28** of the plastic liner top adjacent to the positive tab. If a metal container **15** is used, a cell cap **19** or metal, preferably steel, is placed over and within the flange of the central vent mechanism; however, the inner surface of the cap is electrically insulated by means of a liner material **21** which may be similar to the liner **18** used within the container if a metal container is used. There is a break in the cap liner material **21** at which point the positive tab **31** can be connected with electrical continuity to the cap adjacent to the negative tab. The lining material is extended outward **28** to electrically insulate the negative tab from the cap. At this point, however, the negative tab is electrically connected to the container. Generally, if liner material is necessary, such as when a metal container is used, the cap liner and container liner are welded together and the upper edge **29** of the container is crimped over and around the cap to form a pressure-tight, sealed container. It is desirable and necessary to provide a vent hole **32** in the cap in case of serious malfunction of the cell in such cases as excessive generation of gas which may escape from the valving means. The venting hole **32** will allow escape and will prevent rupture of the container in case of excessive pressure build-up. However, because of the use of valving means **23,** the cell operates normally at greater than atmospheric pressure. The gases are retained within the cell, but quickly are recombined with the plate material.

An outstanding advantage of a configuration according to this invention is the improvement in the rate of recombination of oxygen with the lead sponge in the negative plate. Such recombination allows the cell to be overcharged without deleterious effects. In fact, overcharge is desirable in the battery operation to allow the positive plate to be charged to full capacity after each discharge. Excessive overcharge of the positive plate allows a balance of the state of charge of cells in series allowing also higher charging rates and greater flexibility in charging technique.

The configuration of this invention allows use of the so-called "oxygen" to be used in which only oxygen is evolved during overcharge and then reduced at the negative plate at the same rate so that there is no net change in the cell composition. The oxygen cycle requires: that only oxygen be evolved on an overcharge; and that the oxygen have free access to the active negative plate or metallic lead. It is known that oxygen does react very rapidly with lead on contact in the presence of sulfuric acid. The cell according to this invention, however, allows for use of very pure materials in the cell and, therefore, having more ampere hour capacity in the negative plate than in the positive plate since in this configuration the positive plate will go into overcharge before the negative plate is fully charged. It is for this reason that need for pure materials is particularly important in the grid composition. This cell is particularly adapted for use of pure grids since the plates need not be selfsupporting. The amount of hydrogen which is evolved during the cell life is small enough to be ignored for all practical purposes.

Finally, the cell adapted itself well for enhancement of free access of the oxygen to contact the lead. As was previously explained, the active lead sponge is exposed on the edges **12** of the negative plate and the edges **12** are not covered by an excess of free electrolyte. Since in this cell almost all the electrolyte is retained by the separator, it is only a thin layer of electrolyte on the lead sponge through which the oxygen must diffuse.

After the lead reacts with oxygen and bisulfate ion, it is reduced back to lead by the normal charge reaction. For this reason, it is important that the lead sponge in the exposed edges **12** have good ionic contact with the rest of the cell. The cell according to this invention has a distinct advantage over normal maintenance-free lead acid cells in that lead sponge is directly exposed to the oxygen. Other known cells require the use of heavy load supporting grids with structural members around the edge thereby precluding the use of the active edge as used in this cell. Incidentally, the cell according to this invention enhances the rate of recombination by operating under increased pressure. It is for this reason that the vent relief **23** should be biased to vent at as high a pressure as possible.

The cell according to this invention has the ability of self-adjustment of component balance within the cell to some degree. For instance, if too much electrolyte is placed into the cell, the negative plate sponge is covered by too thick of a layer of electrolyte thereby reducing the recombination rate. If this occurs, oxygen generated by the reaction is vented from the system and the electrolyte volume is thereby reduced. On the other hand, if there is too great a reduction in the electrolyte volume, thinner electrolyte thickness on the lead sponge increases oxygen diffusion to the sponge. In this manner, a self balance is maintained since electrolyte volume is decreased until the recombination rate can keep up with the overcharge. At the same time, if the state of charge in the negative plate is excessive, hydrogen is evolved and vented. The loss of hydrogen in turn lowers the state of charge in the negative plate and so brings the charge back into balance.

This cell is particularly adaptable to other constructions for increasing the rate of recombination by minimizing electrolyte film thickness surrounding the lead particles thereby reducing the diffusion rate of the oxygen through the electrolyte. The spiral configuration of this cell is particularly adaptable. The film thickness can be reduced by increasing the effective heat of wetting of the separator by adding a small amount of colloidal silica or colloidal polyfluoroethylene, commerically available as Teflon. Powder of polyfluoroethylene from a 1 percent water solution may be applied to the surface of the edges of the negative plate to increase the heat of wetting of the sponge. An 0.5 percent by weight of hydrophobic paste of polyfluoroethylene may be added directly to the negative plate paste. Such hydrophobic powders generally are added in the colloidal size from an aqueous solution.

Similar effect of edge area increase can be obtained by providing capillary gas means paths providing a path for the gas to wet the sponge surface. Hydrophobic rods of porous, non-wettable materials can be incorporated and interspaced between the negative plate and the separator. An effective path is provided for the oxygen so that the gas may again react with the surface of the plate. It has been found that polyfluoroethylene rods of as small as **30** mils diameter is sufficient to enhance gas recombination.

Previous mention was made of the central vent **22**, particularly in reference to the venting of excessive gas to the relief valve **23**. The central venting tube more efficiently allows operation of the cell at a positive pressure. The cap preferably comprises a stem which has an axial internal opening **25**. Preferably radially outward projecting vanes **33** are provided. The stem serves a dual purpose in allowing a path for the gas to be found only at essentially the centroid **24** of the cell. The cell may, therefore, be utilized in any position without a means of escape of entrained electrolyte particles. The vanes **33** also act as a foundation around which the plate and separator subassembly **16** can be wound. The foundation minimizes likelihood of internal collapse of the plate/separator subassembly.

The unique configuration of this cell leads to some remarkable characteristics as compared to maintenance-free type lead acid cells currently found in the art. Preferably, the highest rated maintenance-free lead acid cell having a rate capacity of 2.6 ampere hours at 6 volts had a weight of 1.3 pounds with a volume of 16.5 cubic inches. Such a battery has an energy density rating of 12 watt hours per pound and 0.95 watt hours per cubic inch. A cell constructed in accordance with the invention herein having a rated capacity of 2.5 ampere hours at 2 volts has a weight of 0.40 pounds with a volume of 3.42 cubic inches and an energy density of 12.5 watt hours per pound or 1.45 watt hours per cubic inch.

The relative capacity as compared to various discharge rates is equally as impressive and demonstrates well the advantages of the utilization of the invention herein described. FIG. **4** shows the relative capacity of typical maintenance-free lead acid cells compared to a maintenance-free lead acid cell made in accordance with this invention.

FIG. 5 shows quite dramatically the ability of the maintenance-free cell made in accordance with the present invention to maintain cell current over long periods of time, relatively speaking, as a function of the charging current. Basically, the cell current is maintained at a steady level over a long period of time, whereas the typical maintenance-free lead acid cell has a drastic drop in current capability falling far below the cell current of the cell according to this invention.

It was explained that the characteristics of the cell according to this invention were designed to withstand a relatively large number of charge/discharge cycles and yet maintain a consistent ampere hour capacity. FIG. 6 shows this capability as compared to a typical maintenance-free lead acid cell. Note that at a charge of 2.4 volts for 8 hours as compared to a typical maintenance-free cell at the same charge for 16 hours, that the cell according to the invention by the end of the 100th cycle maintains an ampere hour capacity of approximately 50 percent more than the typical cell.

what is claimed is:

1. A maintenance-free type lead acid cell which sustains substantial overcharge in any indiscriminate attitude of the cell, said cell operating in a normally sealed configuration utilizing an "oxygen" cycle, comprising:

non-self-supporting lead based grids having a high hydrogen overvoltage, said grids pasted with active material to form porous positive and negative plates;

an electrolyte absorbing and retaining separator material characterized by having a high heat of wetting and intimately contacting adjacnt, opposite polarity plates;

an electrolyte absorbed and retained by said separator and by said plates to the degree that no free unabsorbed electrolyte is present in the cell, said plates containing a thin layer of electrolyte on said active material sufficient to sustain electrochemical reactions at the plates and permitting oxygen transfer to and from the active material through a void volume formed in substantially all of the pores of said plates, said thin layer of electrolyte uniformly distributed throughout said plates and said void volume formed by virtue of the presence of only the thin layer of electrolyte on the active material, and

a container tightly constraining said plates, separator and absorbed electrolyte under firm stacking pressure to form a self-supporting integral cell.

2. A cell according to claim **1** in which the lead utilized in the grids is of greater than about 99.9 percent by weight purity and contains no material to increase rigidity with accompanying degrees of reduction of hydrogen or oxygen overvoltage.

3. A cell according to claim **1** in which each of said positive and negative plates comprises a continuous, unitary, pliable, structurally free lead sheet, forming a grid for said plates.

4. A cell according to claim **1** in which a gas venting means having a vent exit is inserted into the cell to a point such that the venting exit is disposed at substantially the centroid of the cell. is further a valving means disposed over said vent normally biased in a closed position to retain generated gas at a positive pressure within said cell.

5. A cell according to claim **3** in which separator material is disposed between each of said positive and negative plates prior to insertion within said container; said plates and separator material separating said plates tightly and spirally wound into a spiral configuration.

6. A cell according to claim **1** having additionally edge surfaces of active material on said plates to aid in the recombination of gas.

7. A cell according to claim **1** in which there is disposed between the container and the stacked plates, separator and electrolyte subassembly, an electrically insulated liner material electrically separating said plates, separator and electrolyte subassembly from said container.

8. A cell according to claim **1** in which a hydrophobic paste is incorporated within the negative plate to minimize the degree of wetting of the plate by the electrolyte.

9. A cell according to claim **6** in which separator material extends beyond the edge surface of the lead plates, said extended portion of the separator treated to be rendered hydrophobic thereby minimizing the degree of wetting of said extended to to allow for maximum portion to allow for maximum availability of generated gases to recombine with the edge surfaces of the plates.

10. A maintenance-free type lead acid cell operating under superatmospheric internal pressure and in a normally sealed configuration utilizing an "oxygen" cycle comprising:

lead based grids having a high hydrogen overvoltage and in which the lead utilized in the grids is of greater than about 99.9 percent by weight purity, said grids pasted with active material to form porous positive and negative plates;

an electrolyte absorbing and retaining separator material having a high heat of wetting, high surface area and porosity of about 85 to 95 percent, intimately contacting adjacent opposite polarity plates;

a liquid electrolyte absorbed and retained by said separator and by said plates to the degree that no free unabsorbed electrolyte is present in the cell; said plates containing a thin layer of electrolyte on said active material sufficient to sustain electrochemical reactions at the plates and permitting oxygen transfer to and from the active material through a void volume formed in substantially all of the pores of said plates, said thin layer of electrolyte uniformly distributed throughout said plates and said void volume formed by virtue of the presence of only the thin layer of electrolyte on the active material; and

a container encapsulating and tightly constraining said plates, separator and absorbed electrolyte under firm stacking pressure to form a self-supporting integral cell capable of use under any attitude.

11. A cell according to claim **10** in which the electrolyte is present in a relatively starved amount.

12. A maintenance-free type lead-acid cell operating in a normally sealed configuration utilizing an "oxygen" cycle including at least one porous positive plate, at least one porous negative plate, a liquid electrolyte in a starved amount, and a separator material, in firm pressure contact with the plates, which separator absorbs and retains all the electrolyte except for the presence of a thin layer of electrolyte distributed on the walls of substantially all of the pores uniformly throughout the active material of the cell plates, said pores which carry said thin film of electrolyte being free of electrolyte except for said thin film, allowing the cell to be utilized in any position without leakage of electrolyte and permitting the cell to sustain substantial overcharge rates by improved avenues for oxygen transport and recombination within the cell.

13. A cell according to claim **12** in which the separator is a non-woven, fiber glass matting having a high degree of wettability.

14. A cell according to claim **13** in which the fibers of the fiber glass have a diameter in the range of from about 0.2 to about 10 microns.

15. A cell according to claim **13** in which the fibers of the fiber glass have a surface area between about 0.1 to 20 square meters per gram of silica.

16. A cell according to claim **12** in which the separator material has a porosity in the range of 85 to 95 percent.

17. A cell according to claim **12** in which the separator is a non-woven, fiber glass matting having a porosity between about 85 and 95 percent and wherein the fiber diameter of the fibers of the fiber glass is in the range of about 0.2 to 10 microns and has a surface area in the range of about 0.1 to 20 square meters per gram of silica.

18. A cell according to claim **12** in which said positive and negative plates comprise non-self-supporting lead based grids having a high hydrogen overvoltage.

19. A cell according to claim **18** wherein said plates, separator and absorbed electrolyte are constrained tightly under firm stacking pressure to form a self-supporting integral cell.

20. A cell according to claim **18** in which the lead utilized in the grids is of greater than about 99.9 percent by weight purity and contains no materials to increase rigidity with accompanying degrees of reduction of hydrogen or oxygen overvoltage.

21. In a maintenance-free normally sealed lead-acid electrochemical cell operative without significant hydrogen evolution comprising at least one porous pasted negative plate, at least one porous pasted positive plate, both plates utilizing non-self supporting high purity lead grids, liquid acid electrolye, electrolyte absorbing and retaining separator, and a container encapsulating the plates, separator and included electrolyte under firm stacking pressure, the improvement comprising the following features:

a. electrolyte present in a starved amount so that there is no free electrolyte in the cell, substantially all of the electrolyte being absorbed within the interstices of the separator except for a small amount of electrolyte present as a thin layer on the surface of a substantial portion of the pores uniformly distributed throughout the plates producing an electrolyte-free void volume in said pores; and

b. porous separator material having a high heat of wetting and high surface area and in intimate contact with the plates, said properties of the separator together with the presence of only the starved amount of electrolyte and firm stacking pressure causing the separator to wick electrolyte from the plates whereby the thin layer of electrolyte in the plates is obtained, said substantial portion of the pores having said thin layer of electrolyte on the walls of the pores being sufficient in amount to enable improved oxygen access to the negative plate for recombination therewith at significant rates of overcharge.

22. A maintenance-free type lead-acid cell operating under the oxygen cycle capable of withstanding substantial rates of overcharge comprising:

lead based grids having a high hydrogen overvoltage and in which the lead utilized in the grids is of greater than about 99.9 percent by weight purity, said grids pasted with active material to form porous positive and negative plates;

a porous electrolyte absorbing and retaining separator composed of a matting of fiber glass in which the fibers have a diameter in the range of from about 0.2 to about 10 microns;

acid liquid electrolyte absorbed and retained by said separator and by said plates to the degree that no free unabsorbed electrolyte is present in the cell, said plates containing a thin layer of electrolyte on said active materials permitting oxygen transfer to the negative material from the positive active material through a void volume formed in substantially all of the pores of said plates, said thin layer of electrolyte uniformly distributed throughout said plates and said void volume formed by virtue of the presence of only the thin layer of electrolyte on the active material; and

a container encapsulating and tightly constraining said plates separator and absorbed electrolyte under firm stacking pressure to form a self-supporting integral cell capable of use under any attitude.

23. A maintenance-free normally sealed lead-acid electrochemical cell operative without significant hydrogen evolution comprising at least one porous pasted negative plate, at least one porous pasted positive plate, both plates utlizing non-self-supporting high purity grids, liquid acid electrolyte, electrolyte absorbing and retaining separator, and a container encapsulating the plates, separator and included electrolyte under firm stacking pressure, in combination therewith the improvement comprising:

a. electrolyte present in a starved amount so that there is no free electrolyte in the cell, substantially all of the electrolyte being absorbed within the pores of the separator except for a small amount of electrolyte present as a thin layer on the surface of the pores of the plate; and

b. separator material having a high heat of wetting and high surface area and in intimate contact with the plates.

* * * * *

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,862,861 Dated January 28, 1975

Inventor(s) Donald H. McClelland et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Title page, paragraph [54], "Maintenance-Free Type Lead Acid" should read -- Maintenance-Free Type Lead Acid Cell --.

Column 1, line 1, "Maintenance-Free Type Lead Acid" should read -- Maintenance-Free Type Lead Acid Cell --.

Column 1, line 36, "consequently" should read -- Consequently --.

Column 3, line 25, after "versus" insert -- cycle life --.

Column 4, line 5, "other" should read -- Other --.

Column 4, line 52, "1:06" should read -- 1:0.6 --.

Column 5, line 22, "interstics" should read -- interstices --.

Column 8, line 18, "while" should read -- While --.

Column 8, line 35, "separate" should read -- Separate --.

Column 9, line 11, after "oxygen" insert -- cycle --.

Column 11, line 21, "what" should read -- What --.

Column 11, line 32, "adjacnt" should read -- adjacent --.

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,862,861 Dated January 28, 1975

Inventor(s) Donald H. McClelland et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 11, lines 62 - 65, delete "is further a valving means disposed over said vent normally biased in a closed position to retain generated gas at a positive pressure within said cell."

Column 12, lines 21 - 22, delete "to to allow for maximum."

Signed and Sealed this

sixteenth Day of *September 1975*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks

REEXAMINATION CERTIFICATE (664th)

United States Patent [19]

McClelland et al.

[11] **B1 3,862,861**

[45] Certificate Issued **Apr. 7, 1987**

[54] MAINTENANCE-FREE TYPE LEAD ACID

[75] Inventors: **Donald H. McClelland**, Littleton; **John L. Devitt**, Denver, both of Colo.

[73] Assignee: **The Gates Rubber Company**, Denver, Colo.

Reexamination Request:

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Related U.S. Application Data

[63] Continuation of Ser. No. 62,227, Aug. 3, 1970, abandoned.

[51] **Int. Cl.**^{4} **H01M 2/14**; H01M 4/73; H01M 10/12

[52] **U.S. Cl.** **429/57**; 429/94; 429/245; 429/252; 429/225

[58] **Field of Search** 429/57, 94, 225-228, 429/245, 252

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Primary Examiner—Anthony Skapars

[57] ABSTRACT

This invention concerns a maintenance-free type lead acid cell which is in a normally sealed condition. The cell is characterized by structurally free, non-self-supporting plates separated from one another with highly absorbent flexible separators containing electrolyte and constrained within a container such that mechanical integrity is imparted to obtain a unitary self-supporting structure. Means are provided for maximum recombination of evolved gases and for discharge of excessively high pressure gas. A centroid element allows for operation in any indiscriminate attitude.

REEXAMINATION CERTIFICATE ISSUED UNDER 35 U.S.C. 307

THE PATENT IS HEREBY AMENDED AS INDICATED BELOW.

Matter enclosed in heavy brackets [ ] appeared in the patent, but has been deleted and is no longer a part of the patent; matter printed in italics indicates additions made to the patent.

AS A RESULT OF REEXAMINATION, IT HAS BEEN DETERMINED THAT:

The patentability of claims **12–20** is confirmed.

Claims **4**, **9** and **11** are cancelled.

Claims **1**, **10** and **21–23** are determined to be patentable as amended.

Claims **2**, **3** and **5–8**, dependent on an amended claim, are determined to be patentable.

New claims **24–32** are added and determined to be patentable.

1. A maintenance-free type lead acid cell which sustains substantial overcharge in any indiscriminate attitude of the cell, said cell operating in a normally sealed configuration utilizing an "oxygen" cycle, comprising:

[non-self-supporting] lead based grids *which do not support themselves in the cell* having a high hydrogen overvoltage, said grids pasted with active material to form porous positive and negative plates;

an electrolyte absorbing and retaining separator material characterized by having a high heat of wetting *and high surface area* and intimately contacting [adjacnt] *adjacent*, opposite polarity plates;

[an] *a liquid* electrolyte *present in a starved amount* absorbed and retained by said separator and by said plates to the degree that no free unabsorbed electrolyte is present in the cell, said plates containing a thin layer of electrolyte on said active material sufficient to sustain electrochemical reactions at the plates and permitting oxygen transfer to and from the active material through a void volume formed in substantially all of the pores of said plates, said thin layer of electrolyte uniformly distributed throughout said plates and said void volume formed by virtue of the presence of only the thin layer of electrolyte on the active material[,]*;* and

a container tightly constraining said plates, separator and absorbed electrolyte under firm stacking pressure to form a self-supporting integral cell.

10. A maintenance-free type lead acid cell operating under superatmospheric internal pressure and in a normally sealed configuration utilizing an "oxygen" cycle comprising:

lead based grids having a high hydrogen overvoltage and in which the lead utilized in the grids is of greater than about 99.9 percent by weight purity, said grids pasted with active material to form porous positive and negative plates;

an electrolyte absorbing and retaining separator material having a high heat of wetting, high surface area and porosity of about 85 to 95 percent, intimately contacting adjacent opposite polarity plates;

a liquid electrolyte *present in a starved amount* absorbed and retained by said separator and by said plates to the degree that no free unabsorbed electrolyte is present in the cell; said plates containing a thin layer of electrolyte on said active material sufficient to sustain electrochemical reactions at the plates and permitting oxygen transfer to and from the active material through a void volume formed in substantially all of the pores of said plates, said thin layer of electrolyte uniformly distributed throughout said plates and said void volume formed by virtue of the presence of only the thin layer of electrolyte on the active material; and

a container encapsulating and tightly constraining said plates, separator and absorbed electrolyte under firm stacking pressure to form a self-supporting integral cell capable of use under any attitude.

21. In a maintenance-free normally sealed lead-acid electrochemical cell operative without significant hydrogen evolution comprising at least one porous pasted negative plate, at least one porous pasted positive plate, both plates utilizing [non-self supporting] high purity lead grids *which do not support themselves in the cell,* liquid acid electrolye, electrolyte absorbing and retaining separator, and a container encapsulating the plates, separator and included electrolyte under firm stacking pressure *so that the grids and plates are supported within the cell by the constraint imposed by the firm stacking pressure, in combination therewith* the improvement comprising the following features:

a. electrolyte present in a starved amount so that there is *substantially* no free electrolyte in the cell, substantially all of the electrolyte being absorbed within the interstices of the separator except for a small amount of electrolyte present as a thin layer on the surface of a substantial portion of the pores uniformly distributed throughout the plates producing an electrolyte-free void volume in said pores; and

b. porous *compressible* separator material *formed of a microfine glass fiber mat having a surface area between about 0.1 to 20 square meters per gram of silica, and having a porosity between about 85 and 95 percent, and* having a high heat of wetting [and high surface area] and *being compressed and* in intimate contact with the plates, *and conforming to the surface of the plates,* said properties of the separator together with the presence of only the starved amount of electrolyte and firm stacking pressure causing the [separator to wick electrolyte from the plates whereby the] thin layer of electrolyte in the plates [is] *to be* obtained, said substantial portion of the pores having said thin layer of electrolyte on the walls of the pores being sufficient in amount to enable improved oxygen access to the negative plate for recombination therewith at significant rates of overcharge.

22. A maintenance-free type lead-acid cell operating under the oxygen cycle capable of withstanding substantial rates of overcharge comprising;

lead based grids having a high hydrogen overvoltage and in which the lead utilized in the grids is of greater than about 99.9 percent by weight purity, said grids pasted with active material to form porous positive and negative plates;

a porous electrolyte absorbing and retaining *compressible* separator composed of a matting of fiber glass in which the fibers having a diameter in the range of from about 0.2 to about 10 microns;

acid liquid electrolyte *present in a starved amount and* absorbed and retained by said separator and by said plates to the degree that no free unabsorbed electrolyte is present in the cell, said plates containing a thin layer of electrolyte on said active materials permitting oxygen transfer to the negative material from the positive active material through a void volume formed in substantially all of the pores of said plates, said thin layer of electrolyte uniformly distributed throughout said plates and said void volume formed by virtue of the presence of only the thin layer of electrolyte on the active material; and

a container encapsulating and tightly constraining said plates, separator and absorbed electrolyte under firm stacking pressure *to compress said separator into conforming contact with said plates and* to form a self-supporting integral cell capable of use under any attitude.

23. A maintenance-free normally sealed lead-acid electrochemical cell operative without significant hydrogen evolution comprising at least one porous pasted negative plate *sponge*, at least one porous pasted positive plate, both plates utilizing [non-self-supporting] high purity *lead* grids, *which do not support themselves in the cell,* liquid acid electrolyte, electrolyte absorbing and retaining separator, and a container encapsulating the plates, separator and included electrolyte under firm stacking pressure, *so that the grids and plates are supported within the cell by the constraint imposed by the firm stacking pressure,* in combination therewith the improvement comprising:

a. electrolyte present in a starved amount so that there is no free electrolyte in the cell, *the cell being capable of sustaining substantial overcharge,* substantially all of the electrolyte being absorbed within the pores of the separator except for a small amount of electrolyte present as a thin layer on the surface of the pores of the *negative* plate *sponge and the positive plate to effectively induce the diffusion of oxygen generated on overcharge through the thin layer of electrolyte*; [and]

b. *compressible porous* separator material *of silica base* having a high heat of wetting and *a* high surface area *of about 0.1 to 20 square meters per gram of silica* and *being compressed and* in intimate contact *and conformance* with the plates *along their mutual interface; and*

c. *the cell utilizing the oxygen cycle to allow the cell to be utilized in any position without leakage of electrolyte and permitting the cell to sustain substantial overcharge rates by improved avenues for oxygen transport and recombination within the cell.*

24. A cell according to claim 1 in which the separator is a non-woven, microfine fiber glass matting having a porosity between about 85 and 95 percent and a surface area in the range of about 0.1 to 20 square meters per gram of silica.

25. A cell according to claim 1 in which the interface between the container and constrained cell pack, defined as the stack of plates and separators, is free of air gaps.

26. A cell according to claim 12 in which the separator is formed solely of a mat or mats of microfine glass fibers having a surface area between about 0.1 to 20 square meters per gram of silica, and having a porosity between about 85 and 95 percent.

27. A cell according to claim 12 in which the plates and separator define a cell pack, and in which the cell pack is positioned within a container and forms an interface therebetween, and in which the interface is free of air gaps.

28. A cell according to claim 27 in which the cell pack is in direct contact with the container.

29. A cell according to claim 21 in which the lead utilized in the grids is of greater than about 99.9 percent by weight purity.

30. A cell according to claim 23 in which the lead utilized in the grids is of greater than about 99.9 percent by weight purity.

31. A cell according to claim 23 in which the separator is a non-woven, microfine fiber glass matting having a porosity between about 85 and 95 percent and a surface area in the range of about 0.1 to 20 square meters per gram of silica.

32. A cell according to claim 12 in which said plates comprise cast grids and the plates and separator are stacked together under compression in parallel plate configuration within the cell.

* * * * *