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SEALED LEAD ACID ELECTRIC STORAGE
BATTERIES OF RECOMBINATION TYPE

The present invention relates to lead acid electric storage batteries and is concerned with such batteries of sealed recombination type in which the gas evolved during operation or charging is induced

5. to recombine within the battery at the battery electrodes.

The invention is particularly applicable to, and will be described with particular reference to, miner's cap lamp batteries but is not limited in its applicability to such batteries.

10. Moreover, the invention, although described with reference to batteries, is not restricted to batteries but is also applicable to single cells e.g. spirally wound cells, and the claims to batteries thus include single cells within their scope.

15. According to the present invention there is provided a sealed lead acid electric storage battery of recombination type in which the positive and negative electrodes are separated by microfine glass fibre separator material, substantially all of the
20. electrolyte being absorbed in the electrodes and the separator material, the ratio of negative active material to positive active material (on the basis of the weight of active material calculated as lead) being less than 1:1 and the positive and negative electrodes
25. being separated by separators of electrolyte and gas permeable compressible fibrous material having an electrolyte absorption ration of at least 100%, the battery, at least when fully charged, having substantially no free unabsorbed electrolyte, whereby substantial
30. oxygen gas recombination occurs in the battery at charging rates not in excess of C/20. This is

contrary to what is conventional in recombinant batteries but we find that recombinant operation can be achieved at these ratios and they have the advantage of providing more positive active material for the same cell volume. We thus prefer to use ratios in the range 0.6:1 to 0.99:1 e.g. 0.7:1 to 0.9:1.

The current conducting elements may be made of pure lead or lead-calcium or lead-calcium-tin alloys or preferably any other material which can provide a strong self supporting readily handled and pasted electrode.

However, the current conducting elements of at least one of the electrode groups and preferably the positive electrodes preferably consist of antimonial lead alloy containing at least 1.0% by weight antimony.

The antimonial alloy may contain up to 12% by weight antimony but desirably contains 1 to 6% by weight e.g. 1% to 4% by weight, since the latter range achieves gas recombination whilst economising on expensive antimony. In addition in comparison with lower antimony content alloys the material can be more readily cast and is more resistant to grid growth.

Whilst the antimony content can be as low as 1% it is preferably in excess of this in order to achieve good hardness and pastability within reasonable periods after casting. In addition whilst the antimony content may be as high as 3% it is preferably less than 3% so as to keep the tendency of the plates to gas to a relatively low level as compared with the gassing tendency observed in flooded systems for such high antimony contents. Thus a preferred range is 1.01% to 2.99% e.g. 1.1 to 2.9 or 1.2 to 2.8% antimony.

- As mentioned above, it is preferred that the current conducting elements of only the positive electrodes are made from a lead-antimony alloy whilst those of the negative electrodes may be of a lead-calcium-tin alloy or a lead-calcium alloy or other mechanically strong alloy or grid material adapted to produce a strong self supporting readily handled and pasted electrode, or pure lead, though this material being soft can introduce problems in the assembly of the battery and high grid growth.
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 - 10.

- Another preferred antimonial alloy for use in the present invention contains 2.3 to 2.8% antimony, 0 to 0.5% by weight arsenic e.g. 0.2 to 0.49% or 0.25 to 0.4% arsenic, 0 to 0.1% by weight copper e.g. 0.02% to 0.5% copper, 0 to 0.5% by weight tin e.g. 0.002% to 0.4% tin and 0 to 0.5% by weight selenium e.g. 1.001% to 0.5% selenium and a particularly preferred alloy composition for the current conductors of the plates is 2.3 to 2.8% by weight antimony, 0.25 to 0.35% by weight arsenic, 0.10 to 0.14% by weight tin, 0.02 to 0.05% by weight copper, 0.002% to 0.05% by weight selenium, balance substantially lead.
- 15.
 - 20.

- The charging rate is desirably kept at not greater than C/15 and preferably less than C/20 e.g. C/20 to C/60.
- 25.

- The volume E of electrolyte in the battery after formation is desirably in the range 0.08 (X+Y) to 0.99 (X+Y) and is preferably at least 0.8 (X+Y) or 0.9 (X+Y) or even 0.95 (X+Y) where X is the total pore volume of the separators in the dry state and Y is the total pore volume of the active electrode material in the
- 30.

dry, fully charged state. These values enable the active material to be utilized more efficiently than when lower amounts of electrolyte are used.

5. It has also been found that recombination can still occur at the negative electrodes at these very high levels of saturation of the pores which is contrary to what is conventional in recombinant sealed lead acid cells.

10. The ratio of X to Y may be in the range 6:1 to 1:1 e.g. 5.5:1 to 1.5:1 or more preferably 4:1 to 1.5:1.

15. The electrolyte active material ratio is at least 0.05 e.g. at least 0.06 or at least 0.10 and is the ratio of H_2SO_4 in grams to the lead in the active material on the positive and negative electrodes calculated as grams of lead.

It is preferably in the range 0.10 to 0.60 e.g. 0.11 to 0.55 e.g. 0.20 to 0.50.

- As mentioned above the separator material is microfine glass fibre material which is compressible and absorbent e.g.
5. having an electrolyte absorption ratio of at least 100% e.g. 100 to 200% especially 110 to 170%. It is electrically non-conducting and electrolyte-resistant.

- Electrolyte absorption ratio is the ratio, as a percentage, of the volume of electrolyte absorbed by
10. the wetted portion of the separator material to the dry volume of that portion of the separator material which is wetted, when a strip of the dry separator material is suspended vertically above a body of aqueous sulphuric acid electrolyte of 1.270 SG
 15. containing 0.01% by weight sodium lauryl sulphonate with 1 cm of the lower end of the strip immersed in the electrolyte after a steady state wicking condition has been reached at 20°C at a relative humidity of less than 50%.
 20. The thickness of the separator material is measured with a micrometer at a loading of 10 kilopascals (1.45 psi) and a foot area of 200 square millimetres (in accordance with the method of British standard specification No. 3983). Thus the dry volume
 25. of the test sample is measured by multiplying the width and length of the sample by its thickness measured as described.

We also prefer that the separator material should

have a wicking height of at least 5 cms on the above test, namely that the electrolyte should have risen to a height of at least 5 cms above the surface of the electrolyte into which the strip of

5. separator material dips when the steady state condition has been reached, so that good electrolyte distribution is achieved in each cell.

We find that these two-requirements are met by fibrous blotting paper-like materials made from fibres

10. having diameters in the range 0.01 microns or less up to 10 microns, the average of the diameters of the fibres being less than 10 microns, and preferably less than 5 microns, the weight to fibre density ratio, namely the ratio of the weight of the fibrous material
15. in grams/square metre to the density in grams/cubic centimetre of the material from which the individual fibres are made-preferably being at least 20 preferably at least 30 and especially at least 50.

20. This combination of properties gives a material which is highly resistant to "treeing through", namely growth of lead dendrites from the positive electrode in a cell to the negative electrode producing short circuits, whilst at the same time even when containing large amounts of absorbed electrolyte, still
25. providing a substantial degree of gas transmission capability.

30. Recombinant lead acid batteries, in which gas recombination is used to eliminate maintenance during use, operate under superatmospheric pressure e.g. from 1 bar (atmospheric pressure) upwards and due to the

- restricted amount of electrolyte, the high electrolyte absorption ratio of the separator, and the higher electrochemical efficiency of the negative electrode, the battery operates under the so-called "oxygen cycle". Thus oxygen, generated during charging or overcharging, at the positive is transported, it is believed, through the gas phase in the separator to the surface of the negative which is damp with sulphuric acid and there recombines with the lead to form lead oxide which is converted to lead sulphate by the sulphuric acid. Loss of water is thus avoided as is excess gas pressure inside the battery.
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10. oxide which is converted to lead sulphate by the sulphuric acid. Loss of water is thus avoided as is excess gas pressure inside the battery.

- The higher electrochemical efficiency of the negative active material enables the negative electrode to effect recombination of the oxygen produced by the positive electrode even at the beginning of the charge cycle. Thus we have discovered that it is not necessary to have excess weight of negative active material compared to the positive active material and by working in accordance with the teachings of the present invention we can obtain increased capacities with the same cell volume.
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- However, recombinant operation of the battery may be facilitated by the use of a number of features in combination.
25. combination.

- Though the electrochemical efficiency of the negative electrodes is in general greater than that of the positive electrodes, it must be born in mind that the efficiency of the negative electrodes drops more rapidly than that of the positive electrodes both
30. rapidly than that of the positive electrodes both

as the cells undergo increasing numbers of cycles of charge and discharge and as the temperature of operation is reduced below ambient (i.e. 25°C). These factors must be taken into account for the specific cell use

5. envisaged. Thus for a miner's cap lamp battery, the temperature of use does not normally drop severely and the battery is subjected to a regular discharge recharge regime.

10. One should provide a restricted amount of electrolyte as described above and one should provide a separator, desirably having a high electrolyte absorption ratio as also described and defined above, which is compressible, so as to conform closely to

15. the surfaces of the electrodes, and which has wicking or capillary activity, whereby transmission of electrolyte and electrolytic conduction between the electrodes is facilitated and preserved independent of the orientation of the cell, whilst gas transmission
20. through the open spaces in the separator is maintained so that adequate and rapid gas transmission between the electrodes is also ensured.

25. Use of microfine glass fibre material having very small fibre diameters as the separator material ensures that the open spaces in the separator are highly tortuous thus fulfilling the requirement that the separator resist "treeing through" as described above.

30. If the charging conditions generate oxygen at a faster rate than it can be transported to the negative and react thereat, then the excess oxygen is vented from

the battery. The container of the battery is thus provided with gas venting means. The gas venting means preferably take the form of a non-return valve so that air cannot obtain access to the interior of the battery although excess gas generated therein can escape to atmosphere.

The lid of the container may be formed with filling apertures to permit electrolyte to be introduced into each cell. The filling apertures may be closed after the electrolyte has been added but the closures should provide gas venting means or separate gas venting means should be provided.

Further features and details of the invention will be apparent from the following description of various specific constructions of lead acid electric storage cells and batteries embodying the present invention which are given by way of example only with reference to the accompanying drawings in which:-

Figure 1 is a scrap perspective cut-away view of an experimental recombinant lead acid electric storage cell embodying the invention,

Figure 2 is a scrap cross sectional view on the line II - II of Figure 1 showing the gas vent,

Figure 3 is a scrap cross sectional view on the line III - III of Figure 1 showing the way in which the group bar and terminal post are sealed into the lid,

Figure 4 is a partly cut-away perspective view of a battery designed for use as a miner's cap lamp battery,

Figure 5 is an electron scanning photomicrograph of a preferred separator material at 1000 fold magni-

fication and

Figure 6 is a view similar to Figure 5 at 4000 fold magnification.

Example 1

5. The cell shown in Figure 1 has a capacity of 5 Ahr and is accommodated in a container 42 made as a single moulding of a polypropylene plastics material. The cell is sealed by a lid 46 which is connected to the walls of the container 42 by the method known as
10. "heat sealing" in which the edges to be joined are placed in contact with opposite surfaces of a heated tool which is subsequently withdrawn and the partially melted edges are pressed together.

15. The cell contains four positive plates 50 (which are not shown since they are hidden by the separator) interleaved with three negative plates 52 (which are normally also hidden by the separator). The plates are separated from one another by separators 14 of electrolyte and gas permeable compressible blotting
20. paper-like glass fibre material whose composition and function will be described below. A separator 14 is also placed on both outside faces of the cell. There are thus eight sheets of separator in each cell. The positive plates 50 and negative plates 52 are both 1.4mm
25. thick, 4.3 cms wide and 8.5 cm^s high and are each formed from a cast grid of lead alloy and carry positive and negative active electrode material respectively and each grid weighs 15.0 grams.

30. The grid alloy composition in % by weight is 2.43% antimony, 0.22% arsenic, 0.04% tin, 0.006% copper, 0.004% selenium, balance lead.

The positive active material had the following

- composition before being electrolytically formed:
 grey oxide 1080 parts, fibre 0.45 parts, water 142
 parts, 1.40 SG aqueous sulphuric acid 60 parts. The
 paste had a density of 4.2 gr/cc and a lead content
 5. of 79%. Each positive plate carried 15 grams of active
 material on a dry weight basis.

- The negative active material had the following
 composition before being electrolytically formed:
 grey oxide 1080 parts, fibre 0.225 parts, barium
 10. sulphate 5.4 parts, carbon black 1.8 parts, stearic
 acid 0.54 parts, Vanisperse^(registered Trade Mark) CB (a lignosulphonate)
 3.27 parts, water 120 parts, 1.40 SG aqueous sulphuric
 acid 70 parts. The paste had a density of 4.3 gr/cc
 and contained 79% lead. Each negative plate carried
 15. 16.0 grams of active material on a dry weight basis.

Vanisperse CB is described in British patent
 specification No 1,396,308.

- The separators 14 are of highly absorbent blotting
 paper-like short staple fibre glass matting about 2mm
 20. thick, there being fibres 61 as thin as 0.2 microns
 and fibres 60 as thick as 2 microns in diameter, the
 average of the diameter of the fibres being about 0.5
 microns. Figures 5 and 6 show this material at different
 magnifications, Figure 5 at 1000 fold and Figure 6 at
 25. 4000 fold.

- It will be observed that the material whilst
 highly absorbent still has a very large amount of open
 space between the individual fibres. When tested for its
 wicking and electrolyte absorption capabilities as
 30. described above it was found that the liquid had wicked

up to a height of 20 cms after 2 hours and this is the steady state condition. This 20 cms of material absorbs 113% of its own dry volume of electrolyte, and this is its electrolyte absorption ratio.

5. The separator 14 weighs 280 grams/square metre and has a porosity of 90-95% as measured by mercury intrusion penetrometry. The density of the glass from which the fibres of the separator are made is 2.69 gr/cc; the weight to fibre density ratio is
10. thus 100.

- Each sheet of separator material is 2mms thick, 5.3 cms wide and 9 cms high and weighs 280 grams/square metre. The total volume of separator for each cell before assembly in the cell is 76 cubic centimetres.
15. The separator in the cell is compressed by about 10% and thus the volume of separator in the cell is 68.7 cubic centimetres. Since the porosity is 90-95% the separator void volume is 61-65 ccs (this is the value of X). The weight of separator present in the cell
20. is 10.7 grams.

The separators being compressible conform closely to the surfaces of the plates thus facilitating electrolyte transfer and ionic conduction between the plates via the separator.

25. The total thickness of each separator should desirably be no thinner than about 0.6 mms since below this value we have found that growth of dendrites through the separator is liable to occur with the material shown in Figures 5 and 6. It may be as high
30. as 3 or more even 4 mms but a preferred range is 1.5 to

2.5 mms. The separator weight to fibre density ratio is preferably 90 to 120.

- The total geometric surface area of the positive plates in each cell is 2x2 square centimetres and of the negative plates 219 square centimetres. The dry weight of active material of the positive plates is 74 x 1.07 i.e. 79.2 grams (as PbO_2 i.e. 68.6 grams as lead) and that of the negatives is 48 x 0.93 i.e. 44.6 grams (as lead) an excess of 66% positive active material based on the weight of the negative active material (54% as lead) or a ratio of negative to positive active material (on a lead weight basis of 0.65:1. The total weight of the grids is 105 grams.

- Despite the excess of positive active material in grams, gas recombination still occurs as indicated below. This is thought to be due to the greater electrochemical efficiency of the negative active material enabling oxygen gas generated on charging at the positive to be recombined at the negative sufficiently rapidly for negative active material to remain available to deal with additional oxygen as it is generated at the positive.

- The true volume of the positive active material is 74 divided by 9 i.e. 8.2 ccs and its apparent volume is 74 divided by 4.2 i.e. 17.6 ccs; the void volume of the positive active material is thus 9.4 ccs.

The true volume of the negative active material is 48 divided by 10.5 i.e. 4.6 ccs; the pore volume of the negative active material is thus 6.3ccs.

The total pore volume of the active material is 15.7 ccs. which is the value of Y. The ratio of X to Y is thus 3.9:1 to 4.1:1 (X + Y) is 66.7 to 70.7

5. As the active material has sulphuric acid added to it its porosity decreases. When the active material is charged its porosity increases and in the fully charged condition is about the same as it is in the unformed state before addition of electrolyte.

10. The calculated true surface area for the positive active material is 74×2.5 i.e. 185 square metres and for the negative is 48×0.45 i.e. 21.6 square metres using a factor of 0.45 square metres gram for the dry weight of negative active material and 2.5 square metres/gram for the dry weight of positive active material.

15. The dry electrolytically unformed cell was evacuated to a high vacuum and had 56 ml i.e. 0.79 (X+Y) to 0.84 (X+Y) of 1.28 SG aqueous sulphuric acid i.e. 27 grams of H_2SO_4 added to the unformed cell. The cell was then allowed to cool to $40^\circ C$ (about 1 to 2 hours) and then electrolytically formed for 48 hours at 0.73 amps, i.e. 7C/5 Ahrs, and subjected to three cycles of charging at 0.34 amps for 14 hours and discharging at 0.38 for 10 hours, and was then charged for 60 hours at 0.2 amps. About 13 cc of electrolyte was electrolysed off, the specific gravity of the electrolyte thus rising to about 1.30 to 1.31.

The amount of electrolyte remaining is thus 0.64 (X+Y) to 0.61 (X+Y).

30. The battery characteristics indicate that at a C/15 charging rate substantial oxygen gas recombination

occurs and recombination still occurs at C/10.

The battery in the fully charged condition contained 0.39 grams of H_2SO_4 per gram of lead in the positive active material and 0.61 grams of H_2SO_4 per gram of lead in the negative active material. The electrolyte active material ratio was thus 0.24.

The battery had a capacity at 1.0 amps of 5 Ahr.

Gas recombination was demonstrated by subjecting the cell to 50 cycles of charging at 0.34 amps for 14 hours (125% of capacity) and discharging at 0.38 amps for 10 hours (80% of capacity). There was no detectable water loss. Even after 150 cycles the water loss was less than 0.5 ml i.e. less than 1%. On a Faradaic basis one would have expected the water loss to be $0.96 \times 150 \times 0.33$ i.e. 48 ml.

The positive and negative plates are interconnected by a respective positive and negative group bars 46 and 48. Integral with the negative group bar 48 is an upwardly projecting post 49 which is sealed into the lid 46 as shown in Figure 3. A tin plated brass terminal 47 is soldered to the top of post 49. The post passes up through a collar 70 in the lid the inside edge of which is dished so that a rubber 'O' ring 71 can nest tightly in it, whereby as shown the post 49 compresses the ring 71 in use. A ring of hot melt adhesive 72 seals around the 'O' ring and between the inside face of the lid and the top of the group bar 48. A further ring of hot melt adhesive 73 seals around the post 49 at the top of the collar outside the lid.

Polypropylene packing sheets 75 are positioned

between the ends of the electrode pack and the container to assist compression of the pack.

The cell or each cell of a battery is normally sealed, that is to say that during normal operation

5. a cell does not communicate with the atmosphere. However in case a substantial over-pressure should build up in a cell, for instance because the cell is exposed to a very high temperature or over-charged, so that oxygen gas is evolved at a faster rate than it

10. can be combined, a relief valve is provided to exhaust the excess gas. As can be seen in Figure 2 the valve is of the Bunsen type and comprises a passage 76 communicating with the interior of the cell and leading from inside the cell to atmosphere. The passage

15. 76 is within a boss 77 in a collar 78 in the lid, and the boss is sealingly covered by a resilient cap 80 having a depending skirt around the boss. The cap 80 normally seals the passage 76, but if an excessive pressure should occur in the battery the skirt of the

20. cap lifts away from the boss to vent the cell. A strip of adhesive tape (not shown) is secured over the cap 80 and the collar 78 thus ensuring that cap 80 is not blown off by the gas pressure.

Reference has been made above to cast lead alloy

25. grids. Whilst this is preferred the electrodes could be made from slit expanded sheet or be of wrought form e.g. perforated or punched sheet.

Alternative antimonial alloys include those disclosed in the United States patents Nos. 3,879,217

30. and 3,912,537.

- The electrolyte is added to each cell in a very limited quantity, that is to say much less is added than in the case of a conventional fully flooded cell. The electrolyte that is added is substantially all
5. absorbed and retained by the separators and the active material and there is substantially no free electrolyte in the cell at least in the fully charged condition.

- Thus, in use, the cell or each cell in a battery is normally sealed and is arranged so that essentially
10. only oxygen is evolved on over-charge. Any such oxygen recombines with a negative plate. The cell generally operates at superatmospheric pressure at least on charge, and the relief valves are arranged to open only if the pressure becomes excessive, say where
15. it reaches 1.1 bar i.e. 0.1 bar above atmosphere.

Example 2

Example 1 was repeated except that the negative grids consisted of 0.08% by weight calcium and 0.8% by weight tin, balance substantially lead.

20. The recombination performance was as described for Example 1.

Example 3

- Example 1 was repeated except that both grids used the calcium-tin-lead alloy used for the negative grids
25. of Example 2.

Example 4

- The battery shown in Figure 4 has a rated capacity 20 Ahr and is designed for use as a miner's cap lamp battery. It has two cells accommodated in a container 2
30. made as a single moulding of a polycarbonate plastics material and separated from one another by an integral

intercell partition 4. The two cells are sealed by a common inner lid 6 which is connected to the walls of the container 2 and the partition 4 by the method known as "heat sealing" in which the edges to be joined are placed in contact with opposite surfaces of a heated tool which is subsequently withdrawn and the partially melted edges are pressed together. The battery is capped by a further outer lid 8 which is secured to the container and locked into position by means which form no part of the present invention.

Each cell contains four positive plates 10 interleaved with three negative plates 12 separated from one another by double layer separators 14 of electrolyte and gas permeable compressible blotting paper-like glass fibre material whose composition will be described below. Each negative plate is wrapped in a U-shaped sheet with the separator enclosing the bottom of the plate. A sheet of separator 14 is also wrapped right around the sides of the electrode pack. There are thus eight thicknesses of the double layer separator and one double layer wrapping in each cell. The positive plates 10 are 2.1 mms thick, 5.5 cms wide and 13 cms high and are formed from a cast grid of lead alloy and carry positive and negative active electrode material respectively. Each positive grid weighs 38 grams and each negative grid weighs 33 grams. The grid alloy composition, positive active material composition, density, and lead content and the negative active material composition, density and lead content are the same as in Example 1.

19.

Each positive grid carries 50 grams of active material on a dry weight basis.

Each negative grid carries 45 grams of active material on a dry weight basis.

5. The separators 14 are the same highly absorbent blotting paper-like short staple fibre glass matting described for Example 1; but are about 1.2 mms thick, and are used as a double layer i.e. providing a total separator thickness between adjacent plates of 2.4 mms
10. before assembly.

Each 1.2 mm sheet of separator 14 weighs 200 grams/square metre and has a porosity of 90 to 95% as measured by mercury intrusion penetrometry. The density of the glass from which the fibres of the separator are made
15. is 2.69 gr/cc; the weight to fibre density ratio is thus 100.

Each sheet of separator material is 0.12 cms thick, 6.1 cms wide and 14.1 cms high. Each sheet of the outer wrapping is 32 cms by 6.4 cms by 0.12 cms thick.
20. The total volume of separator for each cell before assembly into the cell is thus 173.1 cubic centimetres, The separator in the cell is compressed by about 10% and thus the volume of the separator in the cell is 155.8 ccs. Since the porosity is 90 -95% the void volume is
25. 140 to 148 ccs (this is the value of X).

The weight of separator present in each cell is 31.6 grams.

The total geometric surface area of the positive plates in each cell is 572 square centimetres and of
30. the negative plates is 429 square centimetres. The dry

- weight of active material of the positive plates is 200×1.07 i.e. 214 grams (as PbO_2 i.e. 185 grams as lead) and that of the negatives is 135×0.93 i.e. 126 grams (as lead) or a ratio of negative to positive active material (on a lead weight basis) of 0.68:1.
5. The total weight of the grids is 251 grams.

- The true volume of the positive active material is 214 divided by 9 i.e. 23.8 ccs. and its apparent volume is 214 divided 4.2 i.e. 50.9 ccs; the pore
- 10 volume of the positive active material is thus 27.1 ccs

- The true volume of the negative active material is 126 divided by 9 i.e. 14 ccs and its apparent volume is 126 divided by 4.4 i.e. 28.6 ccs; the pore
15. ccs. The total pore volume of the active material is 43.7 ccs. which is the value of Y. The ratio of X to Y is thus 3.2:1 to 3.4:1. (X+Y) is 183.7 to 191.7.

- The calculated true surface area for the positive active material is 214×2.5 i.e. 535 square metres
20. and for the negative is 126×0.45 i.e. 56.7 square metres.

- Each dry electrolytically unformed cell is evacuated to a high vacuum and has 200 ml i.e. 1.09 (X + Y) to $1.04(X + Y)$ of 1.27 SG aqueous sulphuric
25. acid i.e. 91 grams of H_2SO_4 added to the unformed cell. The cell is then allowed to cool to 40°C (about 1 to 2 hours) and then electrolytically formed and about 30 cc of electrolyte is electrolysed off, the specific gravity of the electrolyte thus rising.

30. The electrolytic forming regime comprises 48 hours at 2.0 amps. i.e. 5 C/20 Ahrs.

The amount of electrolyte remaining is thus 0.93 (X + Y) to 0.89 (X + Y).

The battery in the fully charged condition contains 0.46 grams of H_2SO_4 per gram of lead in the positive active material and 0.72 grams of H_2SO_4 per gram of lead in the negative active material. The electrolyte active material ratio was thus 0.28:1.

The battery had a capacity at 1.0 amps of 15 Ahr.

The positive and negative plates are interconnected by respective positive and negative group bars 16 to 18. Integral with the negative group bar in the left hand cell as shown in Figure 4 is a laterally projecting portion which terminates in a "flag" or upstanding portion 20 which is adjacent to the intercell partition 4 and overlies a hole 22 in the partition. The positive flag in the left hand cell is connected to a similar negative flag in the right hand cell through the hole 22 so as to form an intercell connection.

The negative group bar in the left hand cell and the positive group bar in the right hand cell are also each provided with a flag 24 overlying a hole in the container 2. Each of the flags 24 is connected to a lug 26 outside the wall of the container 2 but within a space defined by the outer lid 8. The lugs 26 are connected to a respective connecting wire of a connecting lead 28 for connecting the battery to a miner's cap lamp.

Each cell is provided with a Bunsen type vent valve closely similar to that shown in Figure 2 and described for Example 1. Each valve comprises a passage 36 communicating with the interior of the cell and leading to the space between the internal and external lids 6 and 8. Each passage 36 is within a boss in a respective recess in the internal lid and the boss is sealingly covered by a resilient cap

40 having a depending skirt around the boss. A downwardly extending projection 42 on the outer lid 8 engages each cap 40, thus ensuring that it is not blown off by the gas pressure.

5. Example 5

This has the same structure and composition as the battery of Example 4 except that the negative grids consisted of 0.08% by weight calcium and 0.8% by weight tin, balance substantially lead.

10. Example 6

Example 4 was repeated except that both grids used the same calcium-tin-lead alloy used for the negatives of Example 5.

15. The battery of Example 6 was given 6 cycles of discharge across a 4.4 ohm. resistance to 3.4 volts from 4.0 volts and then recharged at a constant potential of 5 volts for 16 hours.

20. The battery was then subjected to an automatic cycling regime of discharge across a 4.4 ohm resistance for 12 hours (i.e. a nominal 12 Ahr discharge) followed by a recharge at 5 volts for 12 hours.

The battery had suffered no detectable water loss after 30 such cycles indicating a high level of gas recombination.

25. On a Faradaic basis one would have expected a water loss of $30 \times 2.4 \times 0.33$ i.e. ml. per cell.

CLAIMS

1. A sealed lead acid electric storage battery of recombination type in which the positive and negative electrodes are separated by microfine glass fibre separator material, substantially all
5. of the electrolyte being absorbed in the electrodes and the separator material, the ratio of negative active material to positive active material (on the basis of the weight of active material calculated as lead) being less than 1:1 and the positive and negative electrodes
10. being separated by separators of electrolyte and gas permeable compressible fibrous material having an electrolyte absorption ratio of at least 100%, the battery, at least when fully charged, having substantially no free unabsorbed electrolyte, whereby substantial
15. oxygen gas recombination occurs in the battery at charging rates not in excess of C/20.

2. A battery as claimed in Claim 1 in which the said ratio of negative active material to positive active
20. material is in the range 0.6:1 to 0.99:1.

3. A battery as claimed in Claim 1 or Claim 2 in which the positive and/or negative electrodes consist of antimonial lead alloy containing 1 to 4% by weight
25. of antimony.

4. A battery as claimed in Claim 3 in which only the positive electrodes consist of antimonial lead alloy containing 2.3 to 2.8% by weight antimony.



5. A battery as claimed in any one of the preceding claims in which the volume E of electrolyte in the battery after formation is at least $0.8 (X + Y)$, where X is the total pore volume of the separators in the dry state and Y is the total pore volume of the active electrode.

6. A lead acid electric storage battery substantially as specifically herein described with reference to either Figures 1 to 3 or Figure 4 in combination with Figures 5 and 6.

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