

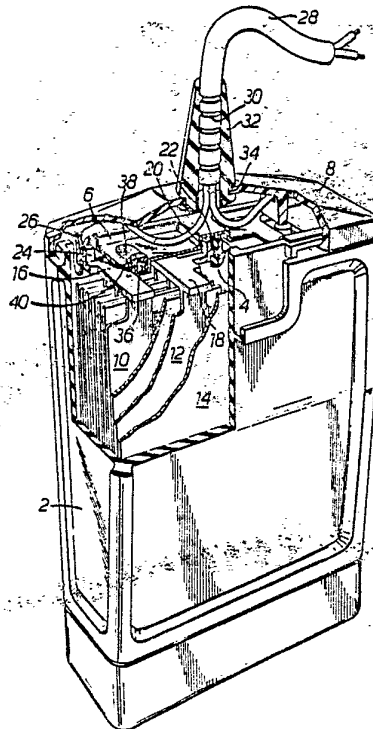


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(54) Title: ELECTRIC STORAGE BATTERIES



(57) Abstract

A recombinant lead acid electric storage battery in which the separator is an electrolyte and gas permeable compressible fibrous material having an electrolyte absorption ratio of at least 100% and a volume  $E$  of electrolyte of 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 material in the dry fully charged state, the battery at least when fully charged having no free unabsorbed electrolyte. Gas recombination at least at charging rates not in excess of  $C/20$  is achieved for miner's cap lamp, aircraft and automotive batteries which are described.

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ELECTRIC STORAGE BATTERIESTECHNICAL FIELD

5. The present invention relates to lead acid electric storage batteries, and is particularly concerned with such batteries of sealed or recombinant type in which the gas evolved during operation or charging is induced to recombine within the battery at the battery electrodes.

BACKGROUND ART

10. Recombinant lead acid batteries are known and teach the use of reduced amounts of electrolyte.

The present invention is based on the discovery that surprisingly gas recombination can be achieved at defined high degrees of saturation and this produces  
15. the advantage of more efficient utilization of the active material.

DISCLOSURE OF THE INVENTION

The invention can be used with a range of battery types including automotive batteries, aircraft  
20. batteries and electric storage batteries suitable for providing, in body portable form, the power needs of an individual, for example to power a miner's cap lamp.

The invention will be described with particular reference to miner's cap lamp batteries.

25. 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.

2.

Thus according to one aspect of the present invention there is provided a recombinant lead acid electric storage battery in which the positive and negative electrodes are separated by separators of electrolyte and gas permeable compressible fibrous material having an electrolyte absorption ratio of at least 100%, the volume E of electrolyte in the battery after formation being 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 material in the dry fully charged state, the battery at least when fully charged having substantially no free unabsorbed electrolyte, whereby substantial oxygen gas recombination occurs in the battery at charging rates not in excess of C/20.

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



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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 higher antimony contents. Thus a preferred range is 1.01% to 2.99% e.g. 1.1 to 2.9 to 1.2 to 2.8% by weight antimony.

Preferably the current conducting elements of only the positive electrodes are made from a lead antimony alloy and the negative is 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.

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 0.05% copper, 0 to 0.5% by weight tin, e.g. 0.02 to 0.4% tin and 0 to 0.5% by weight selenium e.g. 0.001% 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 0.005% by weight selenium, balance substantially lead.

5. 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.

- The volume of electrolyte is desirably in the range 0.8 (X+Y) to 0.99 (X+Y) and especially at least 10. 0.9 (X+Y) or even at least 0.95 (X+Y). These values enable the active material to be utilized more efficiently than when lower amounts of electrolyte are used.

15. 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.

20. 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.

25. 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 especially 0.11 to 0.55 e.g. 0.20 to 0.50.

The ratio of negative to positive active material on the basis of the weight of active material calculated

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as lead may be in the range 0.5:1 to 1.5:1 e.g. 0.6:1 to 1.4:1. The use of ratios below 1:1 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.

As mentioned above the separator material is a compressible absorbent fibrous material 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 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 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%.

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

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standard specification No. 3983). Thus the dry volume of the test sample is measured by multiplying the width and length of the sample by its thickness measured as described.

5. 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 separator material
10. drips 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
15. 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
20. 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.

- This combination of properties gives a material
25. 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,



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still providing a substantial degree of gas transmission capability.

- Recombinant lead acid batteries, in which gas recombination is used to eliminate maintenance during use,
5. 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
10. 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
15. 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.

- The higher electrochemical efficiency of the
20. 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 it may not be necessary to have an excess weight of negative active material compared to the
25. positive active material.

However recombinant operation of the battery may be facilitated by the use of a number of features in combination.

Thus firstly one desirably provides that, under



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the charge and discharge conditions, under which the battery is designed to operate, the capacity of the negative electrodes in each cell will normally and desirably always be in excess of that of the positive electrodes.

5. The electrochemical efficiency of the negative electrodes is in general greater than that of the positive electrodes but it must be born in mind that the efficiency of the negative electrodes drops more 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). Excess negative capacity may thus conveniently be ensured by providing an excess of negative active material (calculated as lead) compared to the positive active material in each cell.

10. Secondly one provides a restricted amount of electrolyte as defined above and thirdly one provides a separator, desirably having a high electrolyte absorption ratio as also described and defined above, which is compressible, so as to conform closely to 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 through the open spaces in the separator is maintained so that adequate and rapid gas transmission

between the electrodes is also ensured.

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

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.

#### BEST MODE OF CARRYING OUT THE INVENTION

Further features and details of the invention will be apparent from the following description of a number of specific constructions of lead acid electric storage 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 partly cut-away perspective view of



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a battery designed for use as a miner's cap lamp battery;

Figure 2 is an electron scanning photomicrograph of a preferred separator material at 1000 fold magnification; and

5. Figure 3 is a view similar to Figure 4 at 4000 fold magnification.

Example 1 (miner's cap lamp battery)

- The battery shown in Figure 1 has a rated capacity of 16 Ahr and is designed for use as a miner's cap lamp
10. battery. It has two cells accommodated in a container 2 made as a single moulding of a polycarbonate plastics material and separated from one another by an integral inter-cell partition 4. The two cells are sealed by a common inner lid 6 which is connected to the walls of
15. 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
20. 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 three positive plates 10 interleaved with four negative plates 12 separated from one
25. another by double layer separators 14 of electrolyte and gas permeable compressible blotting paper-like glass fiber 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

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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.

10. 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:

15. 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 of 79%.

The negative active material had the following composition before being electrolytically formed:

20. grey oxide 1080 parts, fibre 0.225 parts, barium sulphate 5.4 parts, carbon black 1.8 parts, stearic acid 0.54 parts, Vanisperse 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.

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

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

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

5. The separators 14 are of highly absorbent blotting paper-like short staple fibre glass matting about 1.2 mm 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 2 and 3 show this material at different magnifications, Figure 2 at 1000 fold and Figure 3 at 4000 fold.

10. 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 described above it was found that the liquid had wicked  
15. 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.

20. A double layer of separator is used between the plates i.e. providing a total separator thickness between adjacent plates of 2.4 mms before assembly.

25. 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 is 2.69 gr/cc; the weight to fibre density ratio is thus 74.

Each sheet of separator material is 0.12 cms thick, 6.1 cms wide and 14.1 cms high. Each sheet of

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the outer wrapping is 32 cms by 6.4 cms by 0.12 cms thick.

5. 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 cubic centimetres. Since the porosity is 90-95% the void volume is 140 to 148 ccs (this is the value of X).

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

15. 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.

20. 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 2 and 3. It may be as high as 3 or more even 4 mms but a preferred range is 1.5 to 2.5 mms. The separator weight to fiber density ratio is preferably 70 to 160 or 200.

25. The total geometric surface area of the positive plates in each cell is 429 square centimetres and of the negative plates 572 square centimetres. The dry weight of active material of the positive plates is 150 x 1.07 i.e. 160.5 grams (as  $PbO_2$  i.e. 139 grams as lead) and that of the negatives is 180 x 0.93 i.e.  
30. 167.4 grams (as lead) an excess of 4.3% negative active

14.

material based on the weight of the positive active material (20% as lead) or a ratio of negative to positive active material (on a lead weight basis) of 1.20:1. The total weight of the grids is 246 grams.

5. The true volume of the positive active material is 160.5 divided by 9 i.e. 17.8 ccs and its apparent volume is 160.5 divided by 4.2 i.e. 38.2 ccs; the void volume of the positive active material is thus 20.4 ccs. The true volume of the negative active
10. material is 167.4 divided by 10.5 i.e. 15.9 ccs and its apparent volume is 167.4 divided by 4.4. i.e. 38.0 ccs. The pore volume of the negative active material is thus 22.1 ccs. The total pore volume of the active material is 42.5 ccs, which is the value of
15. Y. The ratio of X to Y is thus 3.3:1 to 3.5:1. (X+Y) is 182.5 to 190.5 ccs.

- 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
20. charged condition is about the same as it is in the unformed state before addition of electrolyte.

- The calculated true surface area for the positive active material is 160.5 x 2.5 i.e. 401.3 square metres and for the negative is 167.4 x 0.45 i.e. 75.3 square
25. metres using a factor of 0.45 square metre/gram for the negative active material and 2.5 square metres/gram for the positive active material.

Each dry electrolytically unformed cell is evacuated to a high vacuum and has 200 ml i.e. 1.10 (X+Y) to



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1.05 (X+Y) of 1.27 SG aqueous sulphuric acid i.e. 91 grams of  $H_2SO_4$  added to the unformed cell.

The cell is then allowed to cool to  $40^\circ C$  (about 1 to 2 hours) and then electrolytically formed and about 5. 30 cc of water is electrolysed off, the specific gravity of the electrolyte thus rising.

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 10. (X+Y) to 0.89 (X+Y).

The battery in the fully charged condition contains 0.61 grams of  $H_2SO_4$  per gram of lead in the positive active material and 0.55 grams of  $H_2SO_4$  per gram of lead in the negative active material. The electro- 15. lyte active material ratio was thus 0.29.

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 and 18. Integral with the negative group bar 20. in the left hand cell as shown in Figure 1 is a laterally projecting portion which terminates in a "flag" or upstanding portion 20 which is adjacent to the inter-cell partition 4 and overlies a hole 22 in the partition. The positive flag in the left hand 25. cell is connected to the 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 30. 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 but within a space defined by the outer lid 8. The lugs 26 are connected to a respective connecting wire of a

5. connecting lead 28 for connecting the battery to a miner's cap lamp.

The cell or each cell of a battery is normally sealed, that is to say that during normal operation a cell does not communicate with the atmosphere.

10. 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 can be combined a relief valve is provided to

15. exhaust the excess gas.

Each cell is provided with a Bunsen type vent valve. 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

20. 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

25. thus ensuring that it is not blown off by the gas pressure.

Reference has been made above to cast lead alloy 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 and 3,912,537.

5. Example 2

The battery in this example has the same structure as that described in Example 1 except that it has four positive plates and three negative plates. It has a rated capacity of 20 Ahr. Each positive  
10. plate is wrapped in a U-shaped sheet of separator with the separator enclosing the bottom of the plate. A sheet of separator is also wrapped right around the sides of the electrode pack as in Example 1.

The plate dimensions and grid weight, active  
15. material composition and density and weight per plate for the positive and negative plates are the same as in Example 1.

The separator composition, volume and weight are also the same as in Example 1.

20. The total geometric surface area of the positive plates in each cell is 572 square centimetres and of the negative plates is 429 square centimetres. The dry weight of active material of the positive plates is  $200 \times 1.07$  i.e. 214 grams (as  $PbO_2$  i.e. 185 grams  
25. as lead) and that of the negatives is  $135 \times 0.93$  i.e. 126 grams (as lead) an excess of 70% positive active material based on the weight of negative active material (47% as lead) or a ratio of negative to positive active material (on a lead weight basis) of

0.68:1. The total weight of the grids is 251 grams.

The true volume of the positive active material is  $214 \div 9$  i.e. 23.8 ccs and its apparent volume is  $214 \div 4.2$  i.e. 50.9 ccs; the pore volume of the positive active material is thus 27.1 ccs.

The true volume of the negative active material is  $126 \div 9$  i.e. 14 ccs and its apparent volume is  $126 \div 4.4$  i.e. 28.6 ccs; the pore volume of the negative active material is thus 14.6 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  $214 \times 2.5$  i.e. 535 square metres and for the negative is  $126 \times 0.45$  i.e. 56.7 square metres.

Each dry electrolytically unformed cell was evacuated to a high vacuum and had 200 ml i.e. 1.09 (X+Y) to 1.04 (X+Y) of 1.27 SG aqueous sulphuric acid i.e. 91 grams of  $H_2SO_4$  added to the unformed cell.

The cells were then formed as described for Example 1.

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 to 1.

#### Examples 3 and 4

These have the same structures and compositions as the batteries of Examples 1 and 2 except that the negative grids consisted of 0.08% by weight calcium

and 0.8% by weight tin, balance substantially lead.

Example 5 (aircraft battery)

The cell in this example has a rated capacity of 25 Ahr at 25 amps i.e. the 1 hr rate and is designed for use in an aircraft battery. The cell is accommodated in a container made as a single moulding of a polystyrene plastics material. The cell is sealed by a lid which is connected to the walls of the container by cementing with an appropriate conventional cement. The cell is provided with a vent of the type described for Example 1 and the terminal posts are sealed into the end walls of the container as is conventional for flooded aircraft batteries. The cell contains six positive plates interleaved with seven negative plates separated from one another by separators of the same material used in Example 1. Each negative is wrapped in a single U shaped layer of the 1.2 mm thick material (which weighs 200 gr/square metre) with the separator enclosing the bottom of the plate.

The positive plates are 0.15 cms thick, 8.25 cms wide and 14.5 cms high, the negative plates are 0.13 cms thick, 8.25 cms wide and 14.8 cms wide. They are formed from a cast grid of lead alloy and carry positive and negative active electrode material respectively. Each positive grid weighs 43 grams and each negative grid weighs 37 grams.

The grid alloy composition is 6% by weight anti-mony, balance substantially lead.

The positive active material had the following composition, before being electrolytically formed: grey oxide 1080 parts, fibre 0.45 parts, water 140 parts, 1.400 SG aqueous sulphuric acid 76 parts. The  
5. paste had a density of 4.1 gr/cc.

The negative active material had the following composition, before being electrolytically formed: grey oxide 1080 parts, fibre 0.255 parts, barium sulphate 5.4 parts, carbon black 1.8 parts, stearic  
10. acid 0.56 parts, Vanisperse CB (a lignosulphonate) 2.25 parts, water 126 parts, 1.40 SG aqueous sulphuric acid 66 parts. The paste had a density of 4.35 gr/cc.

Each positive grid carried 55 grams of active material on a dry weight basis (65 grams of wet paste).  
15. Each negative grid carried 49.5 grams of active material on a dry weight basis (62 grams of wet paste).

The plates were dry charged before assembly into the cell by immersion as pairs of positives alternating with pairs of negatives, the pairs being spaced  
20. apart by 1 cm, in a tank of aqueous sulphuric acid having an SG of 1.010 (measured at 15°C) for 20 hours at 1.39 amps per plate.

Each sheet of separator material is 0.12 cms thick 8.8 cms wide and 31.3 cms long. The total  
25. volume of separator in the cell before assembly is thus  $7 \times 0.12 \times 8.8 \times 31.3$  i.e. 231 ccs. The separator in the cell is compressed by 5% and thus the volume of the separator in the cell is 219.4 ccs. Since the porosity of the separator is 90-95% the

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separator pore volume is 197.5 to 208 ccs (this is the value of X).

5. The total geometric surface area of the positive plates in the cell is 1435.5 square centimetres and of the negative plates is 1709.4 square centimetres. The dry weight of the active material of the positive plates is  $55 \times 6 \times 0.83$  i.e. 274 grams (as  $PbO_2$  i.e. 237 grams as lead) and that of the negatives is  $49.5 \times 7 \times 1.00$  i.e. 346.5 grams (as lead) an excess of 26% of negative active material based on the weight of positive active material (46% as lead) or a ratio of negative to positive active material (on a weight of lead basis) of 1.46:1. The total weight of the grids is 517 grams.

10. The true volume of the positive active material is  $274 \div 9$  i.e. 30.4 ccs and its apparent volume is  $274 \div 4.2$  i.e. 65.2 ccs; the pore volume of the positive active material is thus 34.8 ccs.

15. The true volume of the negative active material is  $346.5 \div 10.5$  i.e. 32.4 ccs and its apparent volume is  $346.5 \div 4.4$  i.e. 78.8 ccs; the pore volume of the negative active material is thus 46.4 ccs. The total pore volume of the active material is thus 81.2 ccs, which is the value of Y. The ratio of X to Y is thus 2.9:1 to 2.6:1. (X+Y) is 278.7 to 289.2.

20. The calculated true surface area for the positive active material is  $274 \times 2.5$  i.e. 685 square metres and for the negatives is  $346.5 \times 0.45$  i.e. 156 square metres.

Each dry charged cell was evacuated to a high vacuum and had 300 ml i.e. 1.08 (X+Y) to 1.09 (X+Y) of 1.30 SG aqueous sulphuric acid i.e. 156 grams of  $H_2SO_4$  added to it.

5. The cell was then discharged to 1.667 volts and if the discharge time was in excess of 55 minutes it was used. If it was less the cell was recharged at 2 amps for 16 hours (i.e. 25 Ahr or 125% of the cells capacity) and then discharged at 1.5 amps to 1.667
10. volts once or twice after which time the discharge time had risen to 60 minutes in almost all cases.

- Despite the amount of electrolyte seeming by calculation to exceed the pore volume of the system in the fully charged state recombination still
15. occurred as can be seen from the performance in the following tests.

- The cell was recharged at 2 amps for 16 hours and then subjected to 25 cycles of discharge at 6
20. amps across a 0.33 ohm resistance (80% depth of discharge) and then recharged at 4 amps for 8 hours. After this the cell had lost 2.9 cc of water. The cell was then taken at top of charge and discharged at 25 amps (1 hour rate) to 1.667 volts (i.e. 100% depth of discharge). The discharge duration was
25. in excess of 48 minutes.

- The cell was then given 30 more cycles as in the first 25 cycles after which it had lost a further 1.7 ccs of water. On a Faradaic basis one would have expected the cell to have lost 110 ml over this
30. period.



The cell survived this regime, with discharge at 79 and 104 cycles at which the further water losses were 1.5 and 1.1 ccs respectively, to in excess of 125 cycles.

5. Example 6

Example 5 was repeated except that the grids were made from the alloy described for Example 1.

The cell was subjected to the same test regime as the cell of Example 5 and the water loss after 28  
10. cycles was 1.7 ccs, after 54 cycles was 1.4 ccs after 84 cycles was 1.0 ccs and after 112 cycles was 0.9 ccs, the cell surviving in excess of 125 cycles.

Testing of the cells of Examples 5 and 6 on constant potential recharging at 2.37 volts also  
15. indicated good cycle lives with even lower water losses than those quoted for the constant current recharging regime described above.

Example 7 (automotive battery)

The battery has a capacity of 24 Ahr and has six  
20. cells accommodated in a container made as a single moulding of polypropylene plastics material and separated from each other by integral intercell partitions. The cells are sealed by a common lid which is connected to the walls of the container and partitions by the  
25. 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 lid is provided with a vent of the type described  
30. for Example 1. Intercell connectors and terminal

posts are provided in conventional manner as for a flooded automotive battery.

- Each cell contains three positive plates interleaved with four negative plates separated from one another by separators of electrolyte and gas permeable compressible blotting paper-like glass fibre material whose composition and function will be described below. A sheet of separator is also placed on both outside faces of each cell. Each positive is wrapped in a sheet 23 cms by 16 cms by 1.2 mms thick weighing 200 grams/square metre with the separator enclosing the bottom of the plate. A single sheet of separator 0.6 mms thick by 11.5 cms high by 16 cms wide weighing 100 grams/square metre is placed against the outside face of the two end negative plates. The positive plates are formed from a cast grid of the antimonial alloy of Example 1 and the negative plates are formed from a cast grid of lead alloy containing 0.07% calcium and 0.7% tin and carry positive and negative active electrode material respectively.

- The positive and negative plates are 1.27 mms thick 15.0 cms wide and 10.7 cms high and are held in intimate contact with the separators by solid polypropylene packing pieces. Both faces of all plates are covered by separator material which extends out above and below and on each side of the plates.

More broadly the plates may be 1 to 2 mms thick e.g. 1.2 to 1.9 or 1.2 to 1.6 mms thick. In another alternative the positive is 1.4 mms thick and the

negative is 1.2 mms thick.

The positive and negative active material compositions, densities and lead contents are as described in Example 1.

5. Each positive grid carried 75 grams of active material and each negative 74 grams, both on a dry weight basis.

The separators are as described in connection with Example 1.

10. The interplate separators weighed 200 and the end separators 100 grams/square metre respectively and have 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 thus 74.

- Each sheet of the three sheets of interplate separator material is 1.2 mms thick by 23 cms by 16 cms. Each of the two sheets of end separator is 0.6 mms thick by 11.5 cms by 16.0 cms. The total volume of separator for each cell before assembly is 154.6 cubic centimetres. The separator in the cell is compressed by 10% and thus the volume of the separator in the cell is 139.1 cubic centimetres. Since the porosity is 90-95% the separator void volume is 125 to 132 ccs (this is the value of X). The weight of the separator present in each cell is 25.8 grams.

The total geometric surface area of the positive plates in each cell is  $6 \times 15 \times 10.7$  i.e. 963 square

centimetres and of the negative plates 8 x 15 x 10.7 i.e. 1284 square centimetres. The dry weight of active material of the positive plates is 75 x 3 x 1.07 i.e. 240.8 grams (as  $PbO_2$  i.e. 208 grams as lead) and that of the negatives is 74 x 4 x 0.93 i.e. 275.3 grams (as lead) an excess of 14% negative active material based on the weight of the positive active material (32% as lead) or a ratio of negative to positive active material (on a lead weight basis) of 1.32:1.

10. The true volume of the positive active material is  $240.8 \div 9$  i.e. 26.8 ccs and its apparent volume is  $240.8 \div 4.2$  i.e. 57.3 ccs; the void volume of the positive active material is thus 30.5 ccs.

The true volume of the negative active material is  $275.3 \div 10.5$  i.e. 26.2 ccs and its apparent volume is  $275.3 \div 4.4$  i.e. 62.6 ccs; the void volume of the negative active material is thus 36.4 ccs. The total void volume of the active material is 66.9 ccs which is the value of Y. The ratio of X to Y is thus 1.9:1 to 2.0:1. (X+Y) is 191.9 to 198.9 ccs.

20. The calculated true surface area for the positive active material is  $240.8 \times 2.5$  i.e. 602 square metres and for the negative is  $275.3 \times 0.45$  i.e. 124 square metres, using a factor of 0.45 square metre/gram for the negative active material and 2.5 square metres/gram for the positive active material.

25. Each dry electrolytically unformed cell was evacuated to a high vacuum and had 240 ml of cold ( $5^\circ C$ ) 1.270 SG aqueous sulphuric acid i.e. 1.21 (X+Y)

- to 1.25 (X+Y) i.e. 109 grams of  $H_2SO_4$  added to the unformed cell. The cells were electrolytically formed within two hours of filling and 20 cc of water was electrolysed off, the specific gravity of the electrolyte rising to 1.310.
- 5.

The electrolytic forming regime comprised 72 hours at 1.67 amps i.e. 5  $C_{20}$  Ahrs; the  $C_{20}$  capacity being 24 Ahr.

- The amount of electrolyte remaining is thus 1.15 (X+Y) to 1.11 (X+Y) and would thus appear by calculation to exceed the pore volume of the system in the fully charged state.
- 10.

However the battery characteristics indicate that at a C/15 charging rate substantial oxygen gas recombination occurs and recombination still occurs at C/10.

15.

Example 8

Example 7 was repeated except that the negative grids were made of the same antimonial alloy as the positive grid.

20. Example 9

Example 7 was repeated except that the positive grid was made of an alloy of 6% by weigh antimony, balance substantially lead.

Example 10

25. Example 9 was repeated except that the negative grids were made of the same 6% antimonial alloy as the positive grids.

Continuous overcharge tests at 2 amps for 193 hours indicated that the batteries of Examples 7, 8, 9 and 10 are all achieving a high level of gas

30.

recombination in the light of the water loss incurred, which was less than 5 ml per cell.

On a Faradaic basis one would have expected the water loss to be  $386 \times 0.33$  i.e. 127 ml per cell.

5. Example 11

Example 5 was repeated using a lead calcium, tin alloy of 0.07% calcium, 0.7% tin, balance substantially lead for the positive and negative grids.

Gas recombination as good as for the cell of Example 5 was obtained.

Example 12

Example 2 was repeated using the same lead, calcium tin alloy as Example 11 for both positive and negative grids.

15. Gas recombination as good as for the battery of Example 2 was obtained.

INDUSTRIAL APPLICABILITY

The invention is applicable to recombinant lead acid electric storage batteries and cells.

CLAIMS

1. A recombinant lead acid electric storage battery in which the positive and negative electrodes are separated by separators of electrolyte and gas permeable compressible fibrous material having an electrolyte absorption ratio of at least 100%, the volume E of electrolyte in the battery after formation being 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 material in the dry fully charged state, the battery at least when fully charged having substantially no free unabsorbed electrolyte, whereby substantial 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 current conducting elements of at least one of the electrode groups consist of antimonial lead alloy containing 1% to 4% by weight antimony.

3. A battery as claimed in Claim 2 in which the antimonial lead alloy contains 1.01% to 2.99% by weight antimony.

4. A battery as claimed in Claim 1, 2 or 3 in which the volume of electrolyte is in the range  $0.8 (X+Y)$  to  $0.99 (X+Y)$ .

5. A battery as claimed in Claim 1, 2, 3 or 4 in which the volume of electrolyte is at least  $0.95 (X+Y)$ .

30.

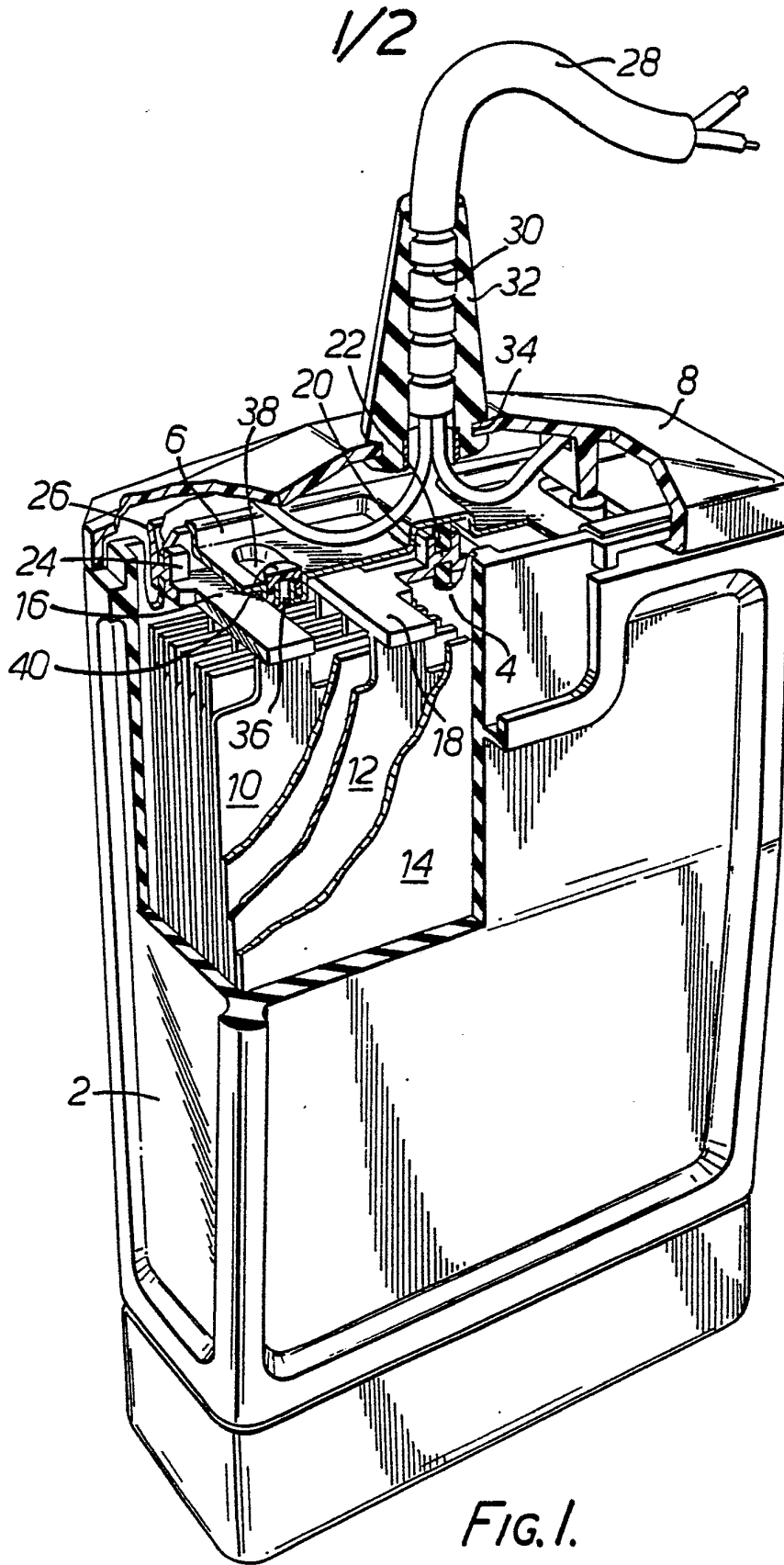
6. A battery as claimed in any one of Claims 1 to 5 in which the ratio of X to Y is in the range 6:1 to 1:1.

7. A battery as claimed in Claim 6 in which the ratio of X to Y is in the range 4.0:1 to 1.5:1.

8. A battery as claimed in any one of Claims 1 to 7 in which the electrolyte active material ratio is in the range 0.20 to 0.50.

9. A battery as claimed in any one of Claims 1 to 8 in which the ratio of negative active material to positive active material is in the range 0.6:1 to 0.99:1.





2/2

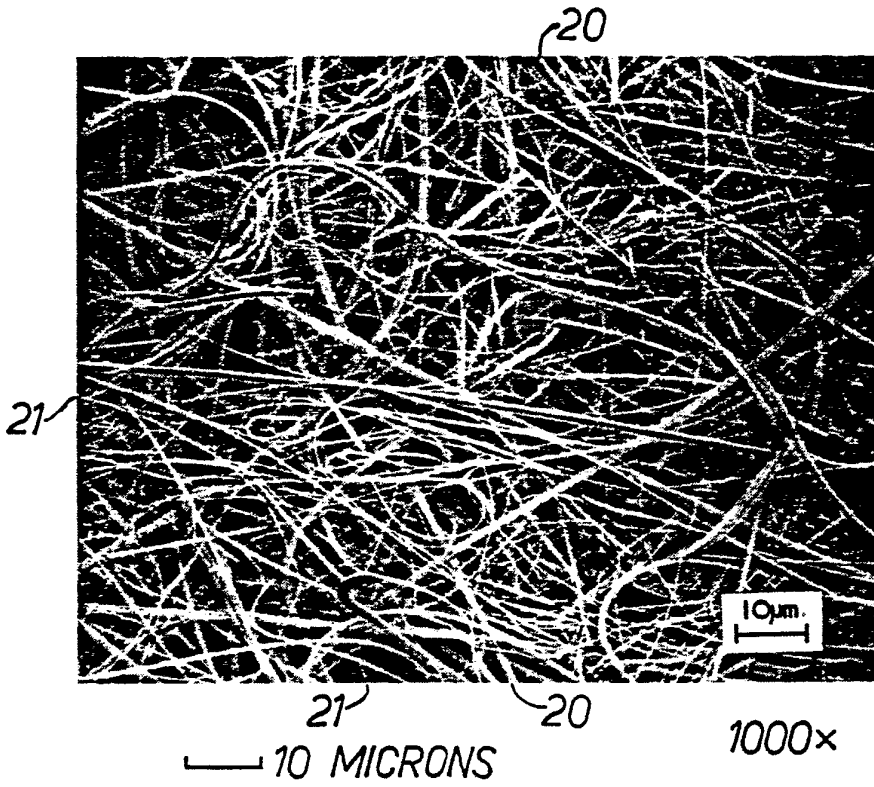


FIG. 2.

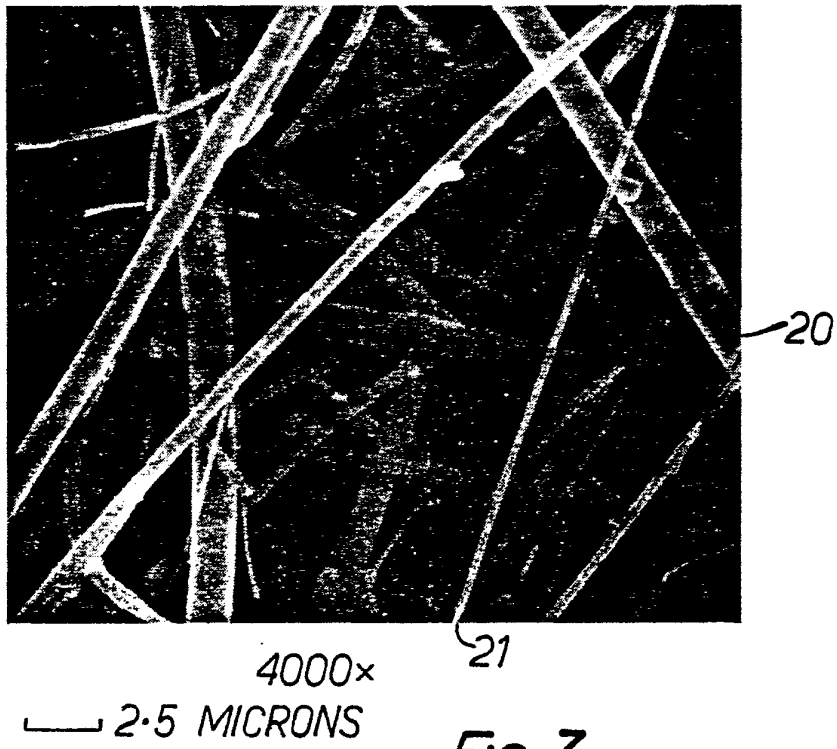


FIG. 3.

# INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 80/00082

**I. CLASSIFICATION OF SUBJECT MATTER** (if several classification symbols apply, indicate all) <sup>3</sup>

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. Cl. <sup>3</sup>: H 01 M 10/34

**II. FIELDS SEARCHED**

Minimum Documentation Searched <sup>4</sup>

Classification System

Classification Symbols

Int. Cl. <sup>3</sup>

H 01 M 10/34; H 01 M 10/06

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched <sup>5</sup>

**III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>14</sup>**

Category <sup>*</sup>	Citation of Document, <sup>15</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No. <sup>18</sup>
X	FR, A, 2101193, published March 31, 1972 see page 2, lines 30-40, page 3, page 4, page 7, lines 9-40, page 8, lines 1-22, The Gates Rubber Co. corresponding to US, A, 3862861 DE, A, 2137908 ---	1
X	GB, A, 1032852, published June 15, 1966, see page 1, lines 29-65, page 2, lines 11-51, The Electric Storage Battery Co. ---	1
X	DE, A, 2149660, published April 12, 1973, see page 2, last paragraph, page 3, page 8, paragraphs 2.3 and 4, page 9, page 10, claim 1, Robert Bosch ---	1
X	Revue Générale de L'Electricité, volume 84, nr. 6, June 1975, G. Dalibard "L'accumu- lateur au plomb sans entretien", pages 463-472, see page 472, left-hand column ---	1, 2, 4
	US, A, 4053695, published October 11, 1977 see abstract, column 3, lines 9-68, column 4, lines 1-26, column 7, lines 55-68, column 12, example 1, Kenneth	1, 6, 8. ./.

<sup>\*</sup> Special categories of cited documents: <sup>15</sup>

"A" document defining the general state of the art  
"E" earlier document but published on or after the international filing date

"L" document cited for special reason other than those referred to in the other categories

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but on or after the priority date claimed

"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention

"X" document of particular relevance

**IV. CERTIFICATION**

Date of the Actual Completion of the International Search <sup>1</sup>

August 7, 1980

Date of Mailing of this International Search Report <sup>2</sup>

August 18, 1980

International Searching Authority <sup>1</sup>

European Patent Office

Signature of Authorized Officer <sup>20</sup>

G. L. M. KRUYDENBERG

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

Peters

FR, A, 2303388, published October 1st, 1976  
 see page 1, lines 1-5, page 2 lines 28-40, page 3, lines 1-15, page 5, Varta  
 corresponding to NL, A, 7602114  
 DE, A, 2509779  
 US, A, 4031293

1, 9

FR, A, 2376529, published July 28, 1978  
 see page 1 lines 18-24, page 3, lines 23-26, C.E.G.  
 corresponding to NL, A, 7800079

1, 2

./.

V.  OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE <sup>10</sup>

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1.  Claim numbers \_\_\_\_\_, because they relate to subject matter <sup>12</sup> not required to be searched by this Authority, namely:

2.  Claim numbers \_\_\_\_\_, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out <sup>13</sup>, specifically:

VI.  OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING <sup>11</sup>

This International Searching Authority found multiple inventions in this international application as follows:

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

Remark on Protest

- The additional search fees were accompanied by applicant's protest.
- No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

Derwent Japanese Patents Reports, volume 74, nr. 27, August 8, 1974, (London GB), Ref. J7-4025575 (Japan Storage Battery)	2, 3
Chemical Abstracts, volume 91, issued 1979, (Columbus, Ohio, US) see page 151, the abstract no. 41974t, corresponding to JP, A, 7942629 (Yuasa Battery Co., Ltd.) 04 April 1979	2, 3
AU, A, 407845, published December 11, 1969 see page 5, page 6, page 13, Yuasa Battery Co.	1, 2
	./.

V.  OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE <sup>10</sup>

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- 1.  Claim numbers \_\_\_\_\_, because they relate to subject matter <sup>12</sup> not required to be searched by this Authority, namely:
  
- 2.  Claim numbers \_\_\_\_\_, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out <sup>13</sup>, specifically:

VI.  OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING <sup>11</sup>

This International Searching Authority found multiple inventions in this international application as follows:

- 1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
- 2.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
- 3.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

Remark on Protest

- The additional search fees were accompanied by applicant's protest.
- No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A DE, A, 1943183, published April 23, 1970,  
Matsushita

V.  OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE <sup>10</sup>

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1.  Claim numbers ..... because they relate to subject matter <sup>11</sup> not required to be searched by this Authority, namely:

2.  Claim numbers ..... because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out <sup>12</sup>, specifically:

VI.  OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING <sup>13</sup>

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1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

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3.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

Remark on Protest

The additional search fees were accompanied by applicant's protest.

No protest accompanied the payment of additional search fees.