

SPECIFICATION

Electric storage batteries

5 The present invention relates to lead acid storage batteries of recombinant type.

Recombinant batteries are known, but it is an object of the invention to provide a battery that is simpler and/or more economical to manufacture than those known hitherto.

According to one aspect of the present invention a recombinant electric storage battery has two or more cells each including a cell pack comprising one or more positive electrodes and one or more negative electrodes interleaved with separator material, each cell pack being substantially enclosed by a bag of flexible plastics film material, and at least the opposed surfaces of adjacent cell packs being close fits with the said films of plastics material.

20 The provision of a close fitting shroud of plastics film material in accordance with the present invention permits the cell packs to be a relatively tight fit within the battery thereby minimising the effects of vibration and in addition enabling the available space to be used more economically. It is not generally possible to slide a cell pack into a cell compartment unless the plate pack is substantially smaller than the compartment due to frictional forces. It has in the past been proposed to overcome this by slightly compressing the leading edge of the plate packs during their introduction into the cell compartments, and it has also been proposed that a plastics shim be placed against each flat face of each cell pack to facilitate its sliding in to its respective compartment. However, shrouding the cell packs in plastics film, for example a heat shrunk film or a plastics bag, substantially reduces the friction of the cell pack with the battery container very much more simply. The plate straps and intercell connectors may be formed before the cell packs are inserted into the battery container, or afterwards. In the latter case the provision of the shroud of plastics film has the additional advantage that it tends to hold each cell pack together before and during insertion into the container since it is a close fit at least against the opposed surfaces of the cell pack. This is particularly so when the shrouding is heat shrunk against the plates of the cell pack.

Batteries of so called "sealed" or "recombinant" type are batteries in which the amount of electrolyte present is restricted so that there is no free unabsorbed electrolyte in the cells, and the gases evolved during operation or charging are induced to recombine within the battery. Such batteries utilise separators of compressible fibrous absorbent material, and it is believed to be important that in such batteries the separators be maintained in intimate contact with the electrodes so that the entire surface of the electrodes has adequate electrolyte for its electrochemical requirements. Thus, in such batteries it is necessary either that the cell packs are under a compressive stress or that they are at least a relatively tight fit within the container to ensure the necessary close contact between the electrodes and separators. The provision of the plastic film around

the cell packs facilitates the introduction of the cell packs into the container at the requisite degree of tightness and since the film is flexible the pressure exerted by the container is transmitted to the cell packs.

In one preferred embodiment of the invention the cell packs are spaced apart by intercell partitions which terminate short of the battery lid. Thus not only is it not necessary to ensure the provision of a seal between the intercell partitions (which are now provided by the walls of the bags) and the intercell connectors, but it is possible to arrange the intercell connectors so that they merely pass over the intercell partitions, thus simplifying the assembly procedure.

According to a further aspect of the present invention a recombinant electric battery has a container and two or more cells each including a cell pack comprising one or more positive electrodes and one or more negative electrodes interleaved by compressible fibrous absorbent separator material, each cell pack being substantially enclosed by a bag of flexible plastics film material, at least the opposed surfaces of adjacent cell packs being close fits with the said films of plastics material, the cells containing substantially no free unabsorbed electrolyte, and the cell packs being spaced apart by the film walls of the said bags which are not sealed to the battery lid.

The flexible plastics film bags constitute the intercell partitions. This enables a much simpler battery container to be used than previously, by virtue of the fact that no integral intercell partitions need to be moulded, and permits the achievement of a higher capacity from a battery of the same external dimensions by virtue of the fact that virtually no space is occupied by the intercell partitions.

In addition the bags, being flexible and a close fit against the surfaces of the plates, at least in use in the cell pack, ensure that the plates and the separators are held in the necessary intimate contact by the pressure exerted by the container.

In the heat shrunk embodiment the bags also assist by exerting pressure even before introduction of the shrouded cell packs into the container.

As mentioned above the cells contain essentially no free unabsorbed electrolyte, and in the most preferred condition of the cells the amount of electrolyte is not sufficient to saturate the pores in the electrodes and in the separators. The electrolyte absorption ratio of the separator material is preferably greater than 100%.

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% 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 measurement at least for the electrolyte absorption ratio measurement is carried out

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 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 separator material dips when the steady state condition has been reached.

We find that these two requirements are met by fibrous blotting paper like materials made from fibres 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 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 30 and especially 50.

Moreover this combination of properties give a material which is highly resistant to "treeing through", namely growth of lead dendrites from the positive electrode of a lead acid battery to the negative electrode producing short circuits, whilst at the same time, even when containing large amounts of absorbent electrolyte, still providing a substantial degree of gas transmission capability.

This combination of properties is ideally suited to use in so-called "sealed" or "recombinant" lead acid batteries in accordance with the invention in which the amount of electrolyte present is restricted so that there is no free unabsorbed electrolyte in the cell.

The amount of electrolyte added is typically in the range 7 to 12 mls of sulphuric acid of 1.270 SG per cell in the discharged state of the cell, per Ampere hour of capacity of the cell.

Recombinant lead acid batteries operate under superatmospheric pressure e.g. from 1.1 bars upwards and due to the restricted amount of electrolyte, the high electrolyte absorption ratio of the separator, and there being at least as much negative active material capacity as positive active material capacity and the higher electrochemical efficiency of the negative electrode, the cell operates under the so-called "oxygen cycle" in which oxygen 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 cell. 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 cell.

The cells may be located in the container in the dry state a lid sealed on, and the electrolyte injected into the cells e.g. through filling holes provided in the lid

above each cell.

The amount of electrolyte added is not highly critical since it is observed that if a slight excess of electrolyte is added above that required to saturate the porosity of the cell components the recombination mechanism is suppressed and electrolyte is lost by electrolysis until the electrolyte volume has reached the correct amount for the cell in question, i.e. the cell porosity has reached the correct degree of unsaturation, when the recombination mechanism comes into operation again and a steady state recombination condition related to the rate of charging which is used is established.

The electrodes may be prismatic or may be spirally wound. Prismatic electrodes may be separate rectilinear plates e.g. cast grids, or cast or rolled sheets, slit and expanded to make expanded mesh grids or cast or rolled sheets punched to produce perforated grids. The prismatic electrodes may be folded and interleaved or arranged in interleaved zig zag relationship, the longitudinal axes of the plates being parallel to each other or at right angles to each other.

Spirally wound electrodes are preferably made from expanded mesh grids or perforated grids and these are preferably provided with unexpanded selvages from which the current take offs are made or to which they are connected.

Conventional grid alloys may be used to make the current conducting supports for the electrodes but for the folded or wound embodiments, softer materials such as pure lead or lead/calcium alloys e.g. with up to 0.1% calcium or lead/calcium/tin alloys e.g. with up to 0.1% calcium and up to 1.0% tin are preferred.

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 gas generated therein can escape to atmosphere.

The plastics film must resist degradation by the electrolyte. Thus it may be polyethylene or polypropylene or polyvinyl chloride film for a lead acid battery, and may have a thickness of less than 0.010 inches (0.25 mms) e.g. 0.001 to 0.005 inches (0.025-0.125 mms).

The invention may be put into practice in various ways and two specific embodiments will be described by way of example to illustrate the invention with reference to the accompanying diagrammatic drawings in which:

Figure 1 is a perspective view of a first embodiment of a recombinant multicell battery having flat plates in accordance with the present invention;

Figure 2 is a similar view of a second embodiment of a recombinant battery with one corner cut away;

Figure 3 is a view similar to Figure 2 showing part of the battery lid and the single vent;

Figure 4 is an electron scanning photomicrograph of a preferred separator material at 1000 fold magnification; and

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

Referring first to Figure 1, the battery has a container 10 of plastics material such as polypropylene integral with which are five intercell partitions

12 which divide the container into six equally sized compartments, each of which receives a cell pack. A single cell pack 14 is shown above the container prior to insertion into a compartment.

- 5 A cell pack is made up by assembling a stack of positive and negative plates, each of which has a plate lug 16, interleaved with compressible adsorbent microfine glass material which will be described in more detail below. The stack is then
- 10 inserted into a bag 18 of plastics film, which has less than 0.010 inches (0.25 mms) wall thickness, of for instance polypropylene, which is seamed at 20. The plastics bag extends up above the plates and separators, but not as far as the tops of the plate lugs
- 15 16. Six such cell packs are slid into respective compartments, and the relatively low coefficient of friction between the bags and the container enables the cell pack to be a relatively tight fit in the compartment, the flexibility of the bags ensuring
- 20 intimate contact between the plates and the separators. The negative and positive plates within each cell pack are connected together by respective plate straps which are fused to the plate lugs 16 in any conventional manner. Every alternative plate strap
- 25 passes over an intercell partition 12 to form an intercell connector in the usual manner. A reduced amount of electrolyte is added to each cell, either prior to sealing, e.g. hot plate welding a lid to the container or after such sealing, e.g. by injecting
- 30 through holes in the lid.

In the embodiment illustrated in Figure 1, the intercell connectors can therefore pass over, and if desired rest on, the intercell partitions. However, in a modified construction, the container is of more

35 conventional construction with the tops of the intercell partitions sealed to the lid. In this case the intercell connectors pass through the intercell partitions, and may be sealed thereto if required.

The embodiment illustrated in Figure 2 is very

40 similar to that illustrated in Figure 1, and similar features are identified with the same reference numerals. In Figure 2 the cell packs 14 are shown within the container 10, plate straps 22 which also comprise the intercell connectors are shown and one

45 corner of the container is shown cut away.

The cell packs are made up as before, and placed in the container. However the container has no intercell partitions and the bags 18 of plastics film, again having a wall thickness of less than 0.010

50 inches (0.25 mms), serve the function of the partitions. As mentioned above the plastics bag extend above the tops of the separators and plates and this is important since it ensures that the separator material in adjacent cells cannot come into contact. It

55 is not critical if the bags should extend slightly above the plate lugs, since the flexible plastics material will simply be depressed by the mould in which the plate straps are formed, or by the plate straps themselves.

The remaining assembly steps may be similar to

60 those described in connection with Figure 1 above.

The fact that the intercell partitions afforded by the bags are not sealed to the lid means that any gas evolved within the battery can pass from cell to cell. This permits the provision in the preferred embodiment of the invention of only a single vent which

communicates with a common head space below the battery lid and thus vents all the cells. Such a construction is illustrated in Figure 3 in which the battery lid 24 is provided with a single vent 32. This

70 vent is of Bunsen type and comprises an aperture 34 in the floor of a well in the lid, the aperture being surrounded by an upstanding open-topped tube 33. The tube is covered by a rubber cap 35 which lifts away from the wall of the tube when the pressure

75 rises within the battery thus venting excess gas to the atmosphere.

In each embodiment the electrode supports are cast prismatic grids made from a lead, 0.07% calcium, 0.7% tin alloy. The grids are 1.2 mms thick

80 and are rigid and self supporting and resist deformation even under load. They have good creep resistance.

The separators are highly absorbent blotting paper-like short staple fibre glass matting about 1 mm

85 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 diameters of the fibres being about 0.5 microns. Figures 4 and 5 show this material at different magnifications, Figure 4 at 1000 fold and

90 Figure 5 at 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. The material when tested for its wicking and electrolyte absorption capabilities as described above absorbs electro-

95 lyte so that the liquid has 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

100 electrolyte absorption ratio.

The separator material weighs 200 grams/square metre and has a porosity of 90-95% as measured by mercury intrusion pentrymetry. The density of the glass from which the fibres of the separator are

105 made is 2.69 g/cc; the weight to fibre density ratio is thus 74.

The arrangement shown in Figures 1, 2 and 3 may be assembled by stacking the interleaved pasted plates and separators shrouded in their bags in a jig, and then inserting the complete assembly into the

110 container, or the shrouded cell packs may be inserted sequentially into the container. The electrolyte is added to the cells and the plate straps/intercell connectors are formed after the cell packs have been

115 inserted into the container. The battery terminals are then connected to or formed on the plate straps and the lid sealed to the container.

After electrolytic forming the cell may then be brought to a gas recombination steady state (if it is not already in that state) by appropriate charging to electrolyse off any excess electrolyte.

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CLAIMS

- 125 1. A recombinant electric storage battery having two or more cells each including a cell pack comprising one or more positive electrodes and one or more negative electrodes interleaved with separator material, characterised in that each cell pack is substantially enclosed by a bag of flexible plastics film
- 130



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material and at least the opposed surfaces of adjacent cell packs are close fits with the said film of plastics material.

2. A recombinant electric storage battery having
- 5 a container and two or more cells each including a cell pack comprising one or more positive electrodes and one or more negative electrodes interleaved with compressible fibrous absorbent separator material, characterised in that each cell pack is
- 10 substantially enclosed by a bag of flexible plastics film material, and at least the opposed surfaces of adjacent cell packs are close fits with the said films of plastics material, the cells contain substantially no free unabsorbed electrolyte, and the cell packs are
- 15 spaced apart by the film walls of the said bags which are not sealed to the battery lid.

3. A battery as claimed in Claim 1 or Claim 2 in which the wall thickness of the bags of plastics film material is less than 0.010 inches (0.25 mms).

- 20 4. A battery as claimed in Claim 1, 2 or 3 in which the amount of electrolyte is not sufficient to saturate the pores in the electrodes and in the separator material.

5. A battery as claimed in any one of the
- 25 preceding claims in which the electrolyte absorption ratio of the separator material is greater than 100%.

6. A battery as claimed in any one of the preceding claims in which the separator material comprises glass fibres having an average diameter
- 30 of less than 10 microns.

7. A battery as claimed in any one of the preceding claims including a single vent which communicates with a common head space below the battery lid and thus vents all the cells.

- 35 8. A recombinant electric storage battery substantially as specifically herein described with reference to Figure 1 or Figures 2 and 3 of the accompanying drawings.