Study of valve-regulated lead/acid batteries manufactured with different separator papers

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Abstract

The separator paper is a key component within a valve-regulated lead/acid (VRLA) battery. Here we describe an experimental program aimed at elucidating how separator papers influence battery performance. Identical batteries were manufactured using three different types of separator paper and subsequently cycled to failure. The failed batteries were then subjected to a series of tests, which included measurements of electrode potentials, compositional analysis of active materials, separator paper saturation and stratification measurements. Results indicated that separator paper type significantly influences battery performance. It is believed that subtle changes in the separator structure caused changes in the rate at which imbalances between the cells in each test battery developed, which led to subsequent changes in failure. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

In a battery, the individual electrodes must be physically separated so that the electrolyte forms the only conduction path between them. In order to ensure separation of the electrodes in valve-regulated lead/acid (VRLA) batteries, a separator material is used. Separators need to be porous in order to allow the penetration of electrolyte and movement of gases produced during battery operation [1]. Over recent years, development has led to the wide acceptance of an absorptive borosilicate glass microfibre separator material [2]. This material has a very high porosity, approximately 95% is inert, and has a contact angle of $0°$ with sulphuric acid [3]. It was originally used by the Gates Rubber Company in 1972 with a flat plate design [4]. In addition to the above functions, separators also absorb excess electrolyte and reduce the risk of dendrite formation, which can develop short circuits between plates resulting in a damaged cell.

Although battery separator papers do not themselves react chemically during battery operation, they have a significant influence over the charge and discharge reactions and are not inactive barriers, as is the case for flooded cells. In recent years, research has been conducted on separators in order to investigate how they influence battery operation [2,3].

In addition to their obvious role as a material to absorb and immobilise electrolyte, subtle changes in porosity and compression characteristics can have significant effects on battery performance. The importance of the various separator properties is dependent on operational characteristics such as the depth of discharge and number of cycles to which the battery will be subjected.

A number of properties that are desirable in a good separator have been identified by Zguris [5]. In addition to immobilising the electrolyte and allowing the battery to operate at an angle, a separator that applies a consistent and uniform compression on the plates during the life of the battery is required. A number of key points, which must be considered when designing a separator, are summarised as follows.

- Retention of separator thickness during saturation is important as this maintains plate compression when the separator is wetted.
- As variations in temperature have been observed to result in changes in compression force of up to 10%, it is important that the separator is insensitive to the

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effects of draughts impinging on the outside of the battery case.

- Resiliency of the separator, when subject to a crushing force is important, as failure to recover can lead to changes in the active material pore structure, resulting in a decline in battery performance.
- Studies have shown that as a stack of plates is compressed into a cell, not all separators deform equally. Uniform stack compression is important to ensure active mass consistency between plates.

This paper describes work to identify the effect of separator type on battery operation. The approach adopted was to build a number of batteries of similar design using the same components such as electrodes, case, etc., but with different separator materials. Each battery was cycled to failure and subsequently examined using a range of techniques.

2. Construction of test batteries

The batteries used in this study were all 40 Ah, 12 V monoblocs. Pure lead grids were used for both positive and negative electrodes. The positive and negative active materials were formed from a paste containing grey oxide. Batteries containing the different separator materials were manufactured for testing. In this study three different separator materials were compared, details of which are given in Table 1.

3. Cycling of test batteries

Cycling was carried out automatically using Digitron charging units. Each cycle consisted of a constant current discharge at 7.05 A to 10.2 V followed by a constant voltage recharge at 14.7 V for 16 h. This was repeated until the capacity after charging reduced to less than 80% of the starting capacity. The cells that showed the greatest and least voltage difference between end of discharge and end of charge were examined, these are referred to as the "bad" and "good" cells, respectively.

Table 1
Types of separator paper used in the construction of test batteries

Separator type	Weight (g/m^2)[a]	Composition $(\%)$[b]	
		Glass	Polyester
A	146.56	100	0
B	144.44	100	0
C[c]	181.96	92	8

[a] Measured value.

[b] Manufacturers value.

[c] Due to shortage, it was not possible to conduct all the tests carried out on this separator type.

4. Experimental methods

4.1. Examination of separator material

Data on separator saturation and acid specific gravity at different heights within the battery cell was obtained using the following procedure. After the cell had been removed from the battery case, it was split exposing a sheet of separator paper. The paper was cut into five horizontal strips, each approximately 1 in. in width, and each strip was then weighed to an accuracy of 0.0001 g. Distilled water was used to remove residual acid from the strips before drying in an oven. After the strips had been washed and dried, they were re-weighed allowing the weight of acid in each strip to be calculated. This procedure was then repeated on a new separator sheet, except that instead of weighing the strips, the specific gravity was measured. Three sets of five strips were examined using this method from a good and bad cell from each test monobloc. Care was taken to weigh the strips as quickly as possible to reduce the errors caused by evaporation and the strips being held in the horizontal position, i.e. cell on its side. After cutting, the order in which the strips were weighed was randomised to remove the possibility of introducing systematic errors into the results. Finally, the area of each strip was measured to allow the separator saturation to be calculated. Separator thickness was calculated from the electrode thickness and cell dimensions of the experimental batteries.

4.2. Examination of active materials

Active materials obtained from the "good" and "bad" cells of batteries were characterised using a number of techniques. However, before tests could be conducted, it was necessary to stabilise the active materials by soaking in distilled water for 30 min to remove the acid and then drying in a vacuum oven at 70 °C for 15 h, or until dry.

Values for BET surface area were obtained using a Micromeritics Gemini 2360 VS.OO. analyser. The stabilised active material was broken into small pieces prior to the analysis to allow insertion into the sample tube.

Compositional information was obtained using X-ray diffraction (XRD) and a wet chemical analysis technique. Wet chemical analysis was used to determine the amount of lead in the sample, as this cannot be obtained accurately using XRD. The analysis technique used a solution of sodium hydroxide, mannitol sugar and hydrazine sulphate, commonly referred to as mannitol solution. When a sample of active material is boiled in the solution, all lead compounds are dissolved leaving only metallic lead. By measuring the sample weight before and after reaction, the weight percentage of metallic lead can be determined.

XRD was conducted on a Philips PW1730/00 diffractometer using Cu Kα radiation. Samples were scanned over a range of 5–90° at a speed of 0.5 s per step with a step size of 0.01°.

A quantitative analysis of the active materials was determined by entering the results from the wet chemical analysis and XRD into the PEAKS program. The PEAKS program was developed by the CSIRO in the Division of Mineral Products under sponsorship from Pasminco Metals Ltd. [6]. PEAKS is capable of determining the relative abundance of the lead phases commonly found at different stages of lead acid battery manufacture and service. Characteristic intensities from the XRD patterns are entered into the "input screen" of the program and the relative abundance of each phase is calculated. Initial corrections are made for background radiation and peak overlap before average intensities are calculated for up to three of the peaks from each phase present. Data is then normalised for differences in scattering power using pre-determined calculated reference intensity ratios [7].

5. Results and discussion

5.1. Electrical testing of batteries

Plotting the discharge time against cycle number (Fig. 1), allows the performance of each battery type to be compared. From the figure it can be seen that there is a significant difference in performance between the batteries containing each separator type. The battery containing type C separator paper was the first to fail at approximately 35 cycles. The second to fail was the battery containing type A separator paper at approximately 70 cycles. The final battery to fail was that containing type B separator paper at over 160 cycles. Previous tests indicated similar trends in performance to those described above with respect to separator type [8].

Voltages of the cells in each battery type were monitored during a C1 capacity discharge to 4 V in order to identify the good and bad cells. Results indicated that all the batteries failed due to the degradation of a number of cells rather than a single failed cell.

During battery operation, the potential of the positive and negative electrodes can vary depending on the diffusion of ions through the electrolyte and oxygen gas through pores in the separator. The potential of the positive and negative plates in the good and bad cells of each battery examined were measured relative to a mercury sulphate reference electrode for a discharge (7.05 A to 6 V) per charge cycle. Variations in potential of the electrodes in each cell examined are given in Figs. 2–4.

It can be seen that as the batteries are discharged, the cell potentials decrease until the failure point is reached. This reduction in cell potential is the result of a decrease in the potential of the positive electrode and an increase in the potential of the negative electrode.

From Figs. 2–4, the time between the start of reduction in potential of the bad cell and recharging of the battery varies for each of the batteries tested. The greatest time is observed for the battery containing type C separator paper, which sustained 35 cycles to failure, and the least time for the battery containing type B separator paper, which sustained 160 cycles.

The reduction in cell voltage observed in the bad cells from each of the batteries tested is a result of a reduction in potential of the positive electrode. No significant increase in potential of the negative electrode was observed for any of the batteries. This indicates that failure is due to the positive rather then the negative electrode.

5.2. Analysis of active materials

Compositional analysis and BET surface area measurements were carried out on the active materials from all batteries tested. This was done to determine whether any significant changes were present which would suggest different failure mechanisms.
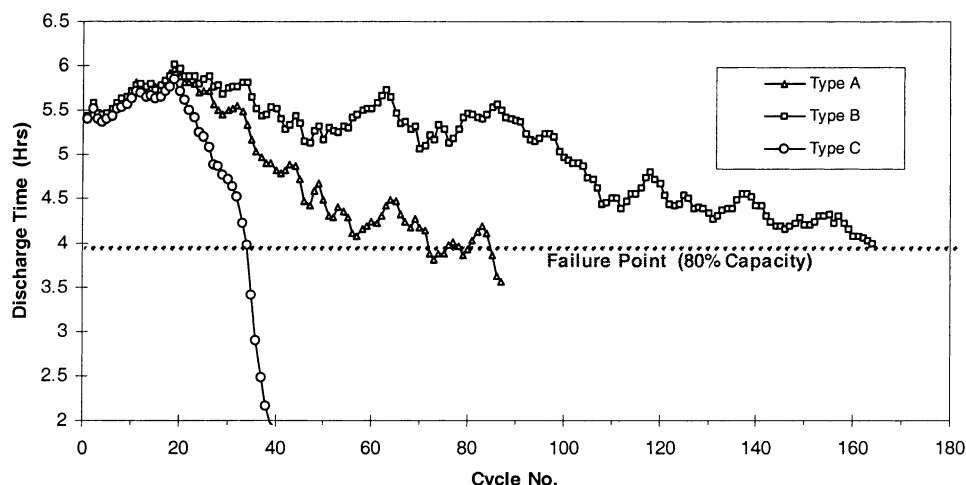

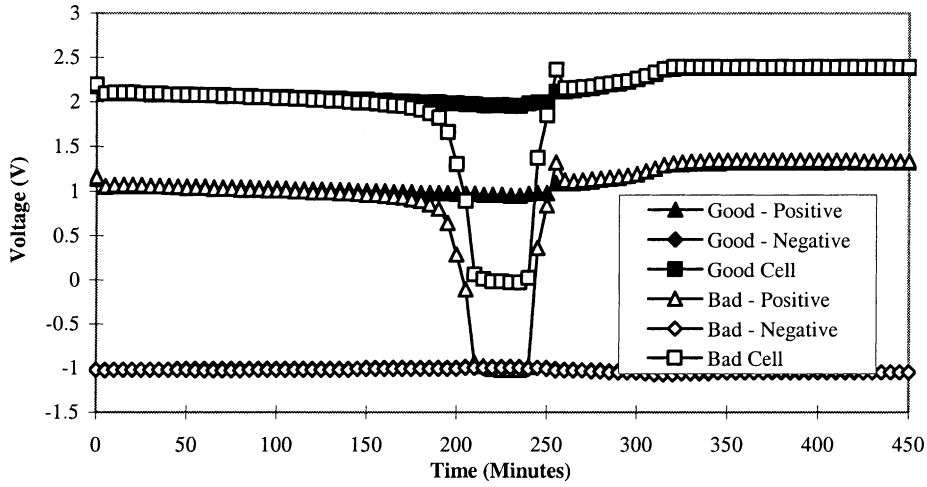Fig. 1. Discharge time vs. cycle number.

Fig. 2. Potential of the individual electrodes in the battery containing type A separator.
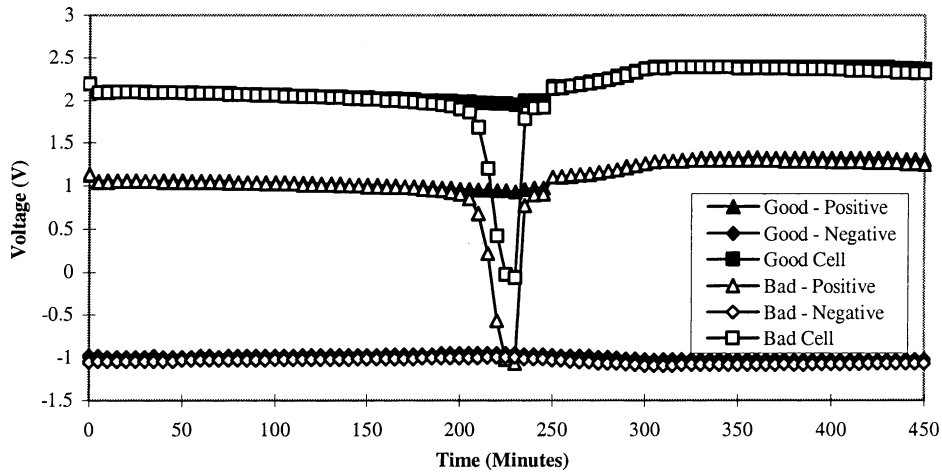

Fig. 3. Potential of the individual electrodes in the battery containing type B separator.
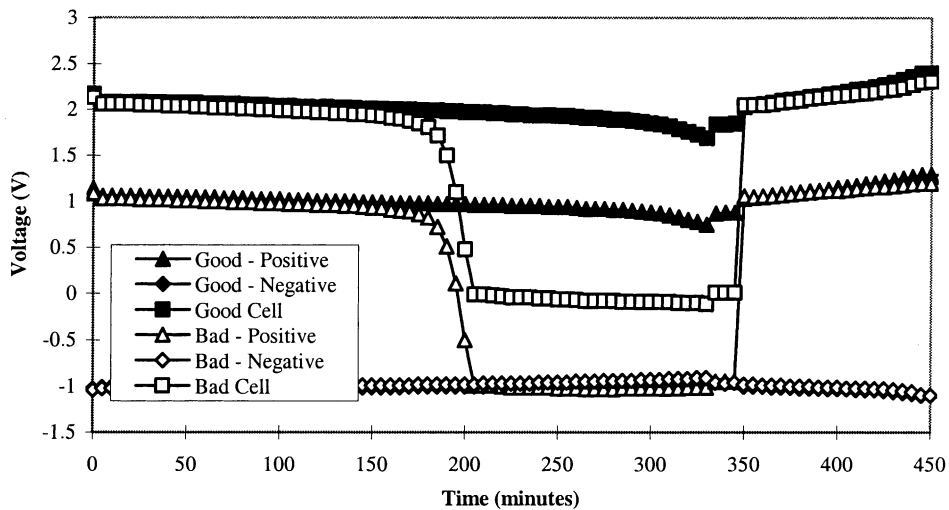

Fig. 4. Potential of the individual electrodes in the battery containing type C separator.
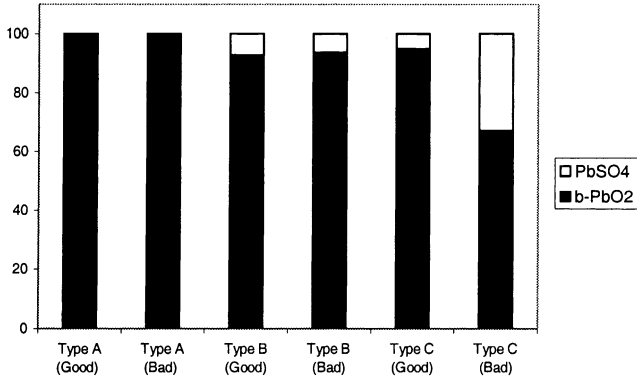
Fig. 5. Composition of positive active materials in all test batteries.

Composition of the active materials was determined using XRD and wet chemical analysis. This was done for both positive and negative plates from good and bad cells. A compositional analysis of the positive electrodes from the good and bad cells examined is given in Fig. 5.

Examination of the positive electrodes revealed the presence of a small amount of sulphation in the positive plates from the batteries containing separator types B and C. This was less than 10%, except for the bad cell of the battery containing type C separator paper, which contained approximately 30% lead sulphate. These results correlated with the values of BET surface area (Fig. 6), which show a reduction in surface area where lead sulphate is present.

Analysis of all negative active materials revealed that the composition was 100% lead. Measurements of BET surface area for these materials are given in Fig. 7. These results do not show any significant variation in the negative active materials from the batteries tested.

5.3. Separator saturation and specific gravity measurements

During operation of a lead acid battery, variations in acid concentration are observed at different positions within the cell. This phenomenon is commonly referred to as acid stratification and can be determined by measuring specific gravity. There are several mechanisms which contribute to stratification, such as uneven discharge of the active material throughout the electrodes and the force of gravity.

Gases produced during charging can cause the movement of acid around the separator and electrodes, thereby reducing the extent of stratification. The effectiveness of this process is influenced by the separator properties and for this reason stratification measurements have been taken for the cells examined from the test batteries.

The specific gravity of the electrolyte in five equally spaced strips positioned between the top and bottom of the cells taken from the batteries containing separator paper types A and B was measured. Results obtained are shown in Figs. 8 and 9.
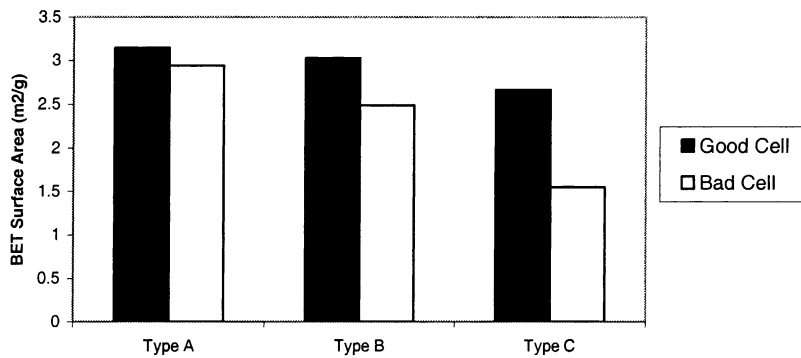

Fig. 6. BET surface areas of positive active materials in all test batteries.
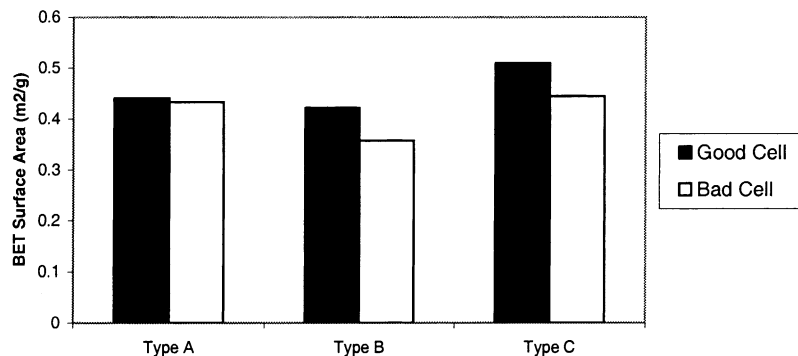

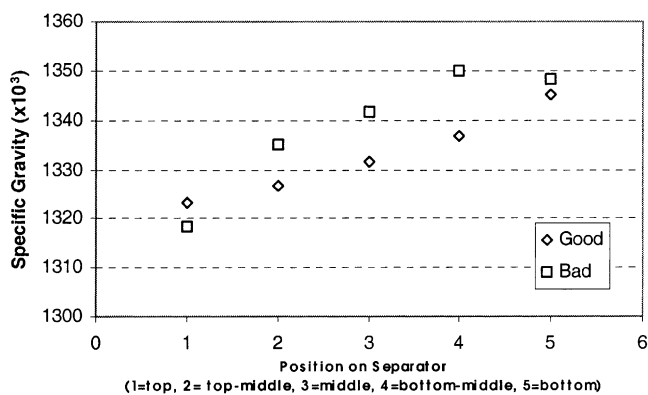Fig. 7. BET surface areas of negative active materials in all test batteries.

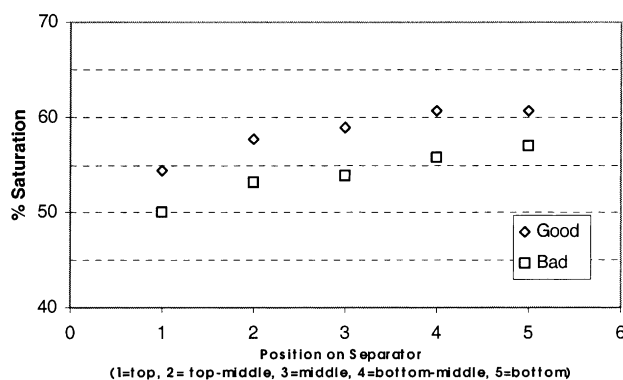Fig. 8. Variation of electrolyte specific gravity with cell height for separator type A.
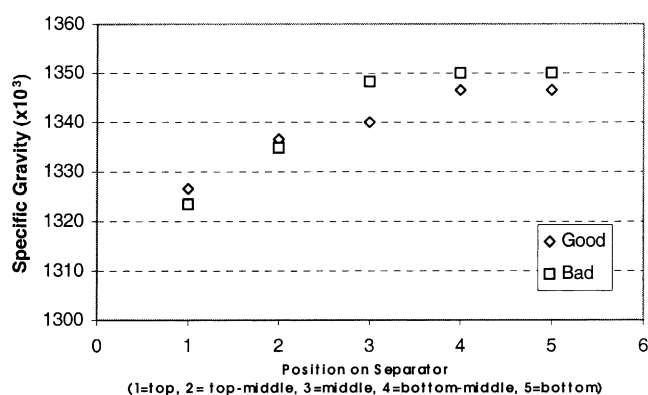

Fig. 9. Variation of electrolyte specific gravity with cell height for separator type B.

Fig. 10. Variation of electrolyte saturation with cell height for separator type A.

Fig. 11. Variation of electrolyte saturation with cell height for separator type B.

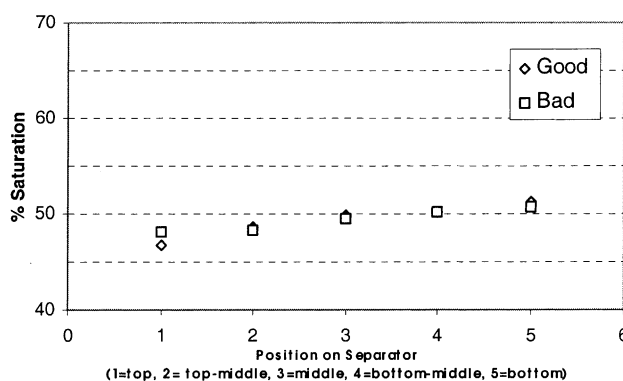Table 2
Average separator saturations for cells from batteries containing separator types A, B and C

Separator type	Separator saturation (vol.%)	
	Good cell	Bad cell
A	58.42	54.02
B	49.33	49.34
C	57.57	40.75

The results in Figs. 8 and 9 show the specific gravity of the electrolyte decreases with cell height. The smallest stratification was observed in the battery containing type B separator paper, which achieved the greatest number of cycles. This battery also showed the smallest difference in acid specific gravity between the good and bad cells.

To determine separator saturation, the weight of acid in five equally spaced strips positioned between the top and bottom of the cell was measured. The acid specific gravity at the corresponding positions was then used to determine the volume of acid and therefore saturation. Measurements of percentage saturation versus separator height for batteries containing types A and B separator papers are shown in Figs. 10 and 11. Average saturations for the total cell for batteries containing separator types A, B and C are given in Table 2.

Both figures show an increase in separator saturation towards the bottom of the cell. This is likely to be due to the gravitational forces and gases escaping through the top of the cell during charging. The presence of a separator paper decreases the gravitational effect significantly compared to a flooded cell without the separator paper. From Table 2, separator paper type B has a lower saturation compared to types A and C. However, this is to be expected as this battery sustained the greatest number of cycles and

would therefore have lost the greatest amount of water from the electrolyte. Differences in total cell saturation between the good and bad cells is least in the battery containing type B separator paper compared to types A and C. The implication of this is that, during battery operation, the bad cells in batteries containing separator types A and C sustained a greater amount of water loss.

6. General discussion

This study shows that battery cycle life is influenced by the choice of separator paper. The low cycle life exhibited by the battery containing type C separator is probably a consequence of lower wicking rates. This is a result of the higher

contact angle between the electrolyte and polyester fibre surface compared to the other separator papers.

Separator types A and B were very similar in weight and composition, both containing 100% glass fibres, however, a significant difference in cycle life was observed. Subtle differences in the separator papers' structures resulted in variations in acid stratification and saturation between the different test batteries. The separator papers influenced the rate at which variations in specific gravity and saturation between cells within a battery developed, which inevitably resulted in the monobloc, becoming unbalanced and premature failure resulting. Consequently, the results in this paper have been able to highlight the importance of choice of separator when designing a battery and the need for consistency of saturation and stratification between cells on cycle life.

Acknowledgements

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