



# A broad look at separator material technology for valve-regulated lead/acid batteries

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## Abstract

Recent research has proved the importance of a constant force of 40 kPa or greater on the paste solidus–grid interface. This has led to increased interest in re-examining the microglass separator and the system that the plate–separator interaction forms. This renewed interest has resulted in new separator ideas and the revisiting of concepts tried in the early days of valve-regulated lead/acid (VRLA) technology. The paper is divided into two parts. The first part examines some past separator developments that have been tried but are presently not accepted by the general VRLA community. This is due to the excellent performance of the microglass separator used so successfully during the last 20 years. Many fundamental questions that need to be asked regarding the selection of a new separator system have long ago been forgotten. The second part of the paper reviews some fundamental aspects of separator selection, and some important attributes that the separator must provide based on current knowledge of the separator system. Attributes such as toughness, corrosion resistance, compression, wicking, stratification, porosity and conformability are discussed. © 1998 Elsevier Science S.A. All rights reserved.

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## 1. Introduction

Separator selection is very important. The process is interesting, since it must balance cost with the quality and functionality of the separator. Separator selection must be looked at very carefully. The ideal case is to have the lowest cost separator at the highest quality for the given battery application. The quality–cost parameters are usually on opposite ends of the design spectrum, and trade offs must be made. To optimize the design, manufacturers have typically adjusted microglass separator properties such as the composition, density (porosity), and surface area (microglass fibre diameters). The separator manufacturing method and materials have also been explored. The separator selection process must be looked at as a system. Important factors are the case material, the draft of the battery case, the group compression, how the separator is wrapped around the plates, and the designed separator fringe area. This paper will first examine some early separator history, and then some aspects which must be

considered in the selection of the separator for the overall battery system.

## 2. Background

This section will briefly examine the quest for the elusive ‘perfect’ separator [1]. The battery industry has always searched for a better performing separator at a lower cost or for that matter just a lower cost separator. The microglass separator, since its discovery by J. Devitt, has been the material of choice for valve-regulated lead/acid (VRLA) designs. The earliest separators tried by Devitt were the more traditional separator materials used at the time. The highly favourable attributes of the subsequently discovered microglass mat significantly contributed to making 100% recombinant lead/acid technology a reality. It should be noted that before the ‘Gates’ cell, several batteries existed that were to some extent recombinant. Examples of these batteries were Yuasa’s NP cells or the old Variety aircraft battery.

Glass fibres for lead/acid batteries have many benefits, e.g.:

- excellent acid resistance;

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- extremely wettable with sulfuric acid (long term, will not de-wet);
- excellent corrosion resistance;
- glass fibres can be manufactured in small diameters and thus give high porosity separators;
- inorganic, thus very high temperature stability;
- cost effective.

This explains why glass fibres have been used in lead/acid batteries for more than 60 years. In 1935, US Patent 2015006 sited the use of a multi-layer, bonded glass mat. Shortly after this patent, British patent 479390, by Chloride Electric Storage, discussed a separator made by mixing a diatomaceous earth and a binder, moulding to shape, and setting the binder. It sited the use of fibrous materials such as spun glass.

During the 1950s, glass was again being used to develop the perfect separator. Vinal in US patent 2511887 used cellophane attached to a sheet of fibrous glass floss. Giles and Scott in US patent 2578534 revealed a separator with glass fibres in the 8 to 15  $\mu\text{m}$  range. US patent 2653985 discussed the impregnation of a glass mat with a slurry of diatomaceous earth mixed with a bonding agent. In US Patent 3085126, a separator was claimed using a mix of very fine microglass in the 0.25–0.50  $\mu\text{m}$  (5–15%) and 2–3  $\mu\text{m}$  range, and a binder of colloidal silica.

In 1968, Globe-Union in US Patent 3846175 revealed as a very useful separator material an ultra-fine fibre mat of randomly oriented borosilicate glass, free of any binders and having a void volume of approximately 90%. By the end of 1970, Gates Rubber applied for the famous foundation patent 3862861 for the maintenance-free lead/acid cell using pure-lead grids, i.e., the 100% recombinant battery. As mentioned earlier, the separator of choice was a glass-fibre sheet with an extremely high surface area, and thus composed of fibres with small diameters. These earlier sheets were essentially 100% fine glass in the 0.6–0.8  $\mu\text{m}$  range using flame-blown glass fibres. In some earlier attempts, mainly to avoid US Patent 3846175, around 10% of chopped glass strand fibres, in the 13 to 19  $\mu\text{m}$  range were used along with these fine flame-blown microglass fibres.

In today's market, the use of a high percentage of fine glass is not often used. This is due to the higher cost of this type of separator, as compared with the separators being used today that contain as low as 10% fine glass. The battery manufacturers have learned to adjust for the changes in properties, such as lower tensile strength, as the fine-fibre content has been decreased. Another concern in the earlier days was lead dendrite growth. High separator tortuosity was felt to be necessary to reduce this problem. The need for high tortuosity was overcome by the discovery that a small amount of a salt, such as sodium sulfate, would decrease the problem of dendrite formation.

As this technology developed through its childhood in the 1970s, many materials were considered to provide the elusive 'perfect' separator. Efforts invariably lead back to

a pure microglass separator. British patent 1461388 assigned to W.R. Grace detailed a synthetic, non-glass, melt-blown material that had a pore size in the 7 to 20  $\mu\text{m}$  range. In French patent 2403651, issued to Yuasa, a mixture of fine and coarse glass was sited along with a small percentage of an organic fibre or binder. Chloride claimed, in British patent, a separator for a sealed cell that was principally a non-woven material such as polyester, in which the fibres were fused to each other. This patent also mentioned that glass fibres could be used. Companies also explored multi-layer separators e.g., Gates' British patent 1569745. In the 1980s, Chloride's British Patent 2051463 sited a multi-layer separator in which one layer had weldable fibres. Gates' US patent 4414295 disclosed the benefits of having a middle layer of glass that has only 70–85% the surface area of as the outer glass layers. All these approaches used microglass fibres.

During the adolescence of this technology in the 1980s, efforts were still being undertaken to develop the perfect separator. Gates and Johns Manville worked on a separator that was a mixture of Perlite© with 30–50% glass fibres of 0.3 to 1.0  $\mu\text{m}$  (US patent 4233379). In the mid 1980s, Matsushita's Act© Battery used a glass-fibre separator which contained 40% of a special polyester fibre developed for thermal bonding non-woven webs. This allowed the separator to be enveloped and provided increased separator toughness. In the early 1980s, the Dexter had products containing small levels of organic and 5–10% of long, large diameter, chopped, strand glass fibres. These fibres were 6–12 mm in length. Also, binders such as silane, organic fibres, silicates and silica gels were tried during this period. In making the microglass sheet, an acid is used to etch the fibre for improved strength. During the early days, different acids were tried.

As the 1980s progressed, the focus of separator development shifted toward cost reduction. Materials such as melt-blown webs and needled polyester batts were tried again, although permanent wettability was, and still is, a major area of concern with these materials. Another concern was the high-temperature stability of the mats. Organic non-woven webs, such as melt-blown materials, were used and testing gave acceptable results. For various reasons, such as the fibres becoming less wettable and/or oxidation of the organic fibres, the batteries' recombination efficiency can increase and result in thermal runaway. With thermal runaway or high battery temperature, the low-temperature stability of the melt-blown polyethylene will result in melting of the separator. This can give rise to catastrophic failure, at least in accelerated testing. Even with a moderate level of hydrophobic fibres, thermal runaway could happen as the result of increase recombination efficiency.

In the 1990s, history continues to repeat itself, although fortunately with some advancements in fibre technology. The use of VRLA in automotive and other applications that use expanded metal grids and continuous strip require

tougher separators and separators that can be enveloped. Composite separators have emerged and are composed of microglass and advanced polyester fibres. The increased interest in VRLA batteries for automotive applications will accelerate development efforts in this area.

### 3. Aspects of separator selection

#### 3.1. Plate / separator interaction

The manufacturing method of the grid is an important consideration in selecting a separator. A 100% microglass separator has shown itself to be an excellent separator for moulded plates. The need for thinner plates and lower manufacturing cost has resulted in the use of expanded metal, continuous strip and other methods for making thinner plates. A plate made by the expanded-metal process requires a separator that has higher puncture strength than a separator that uses a moulded grid. Separators are available that provide increased toughness and puncture strength. These separators provide increased toughness through the use of advanced non-woven organic fibres.

#### 3.2. Electrode saturation / fringe area

The quantity of acid that will be absorbed by the plates and the separator must be accurately calculated when precision acid filling is used to make the VRLA battery. The acid requirement of the plates is directly related to the weight and the porosity of the active materials. Likewise, correct oxygen recombination with a 100% microglass separator requires the separator material to be approximately 90–95% saturated. This correlates to the separator (in the area between the plates) holding around 6 g of acid for every 1 g of the separator.

The battery design should also consider the fringe area of the separator. The fringe area is the area not between the plates and not compressed. If the battery is precision filled, the amount of acid that the fringe area will hold must be considered. Larger fringe areas allow for additional acid and thermal capacity in the battery. This will help in the thermal management of the cell. Additional fringe acid allows for added low-rate capacity by providing extra acid for the reaction. This has been reported by Badger [2]; fringe acid was found to contribute to the reaction, at least for the 20-h rate.

#### 3.3. Separator thickness and total acid quantity

VRLA batteries are usually designed for an acid gravity between 1.290 and 1.320 at full charge. Many batteries are manufactured with a full charge acid gravity of 1.300 and contain from 9 to 11 ml of acid per A-h as measured at the 20-h discharge rate. Fully discharged, the acid gravity can be around 1.08.

At high discharge rates, such as starting a car, acid diffusion is not sufficiently rapid to use the acid stored in the centre of the separator. The acid used in high rates is the acid stored in the plate's pores and perhaps at the separator/plate interface. Consequently, a high-rate discharge is not dependent on the acid stored within the separator. For this type of application, a thin separator is possible. This provides a lower resistance and cost. A thinner separator results in closer plate spacing and the opportunity for additional plates inside the battery. On the other hand, thicker separators are needed to provide the acid required for the reserve capacity.

Discharging at a low or intermittent rate depends upon diffusion of acid from the separators into the plates. The acid required in a cell is directly related to the acid specific gravity and the battery's application. A high-rate application often requires a separator that has a larger pore structure than a battery designed for low-rate applications. A separator designed with a larger pore structure or a distribution with some large pores within the separator may allow the plates to absorb the acid from the separator more quickly. This process is also dependent upon the pore size of the plate.

The pore structure of the separator will influence the wicking characteristics. A smaller pore structure will wick fluid to a higher height in a bottom-up wick test. Most batteries are filled from the top however, with the acid flowing down the plates. Increasing the pore structure will increase the rate of wicking, but decrease the amount absorbed at various heights. The pore structure will influence stratification inside the battery, a smaller pore structure due to the use of fine fibres will help decrease stratification inside the cell. Larger pore structures could allow for easier acid filling.

#### 3.4. Filling of batteries

The filling of a VRLA battery is more costly than that of a flooded battery. In a flooded battery, the plate and separator interface operates in an uncompressed state. The electrolyte is added to the system without experiencing any real resistance to fluid flow. Additionally, with flooded batteries, the separator saturation is not a concern, since the battery is totally flooded.

In a VRLA battery, the electrolyte is generally precision filled to allow for the designed saturation level. In some cases, companies practice a 'fill-and-spill' approach. The battery, after spilling out the extra electrolyte, is overcharged to reach the correct saturation level for recombination. With the use of Hovosorb® II technology, however, overcharging to drive off the excess electrolyte is not needed. The hydrophobicity of the Hovosorb® II fibre structure allows for the presence of excess electrolytes without compromising the recombination process.

Additionally, in a VRLA battery system, the pore structure of the separator provides for a highly tortuous path.

This helps prevent dendrite growth and minimizes the size of any dendrite if formed. Unfortunately, this also creates a tortuous path for acid and air movement. The acid does not instantly flow into the separator. Therefore, the time to fill the battery becomes longer, especially if only one or a few filling stations are used. This dynamic also creates a very high resistance to air flow within the system, especially between the plates with high compression designs. At times and with poor practices, dry spots within the separator can occur. This is a result of getting air or CO<sub>2</sub> (from the plates) trapped within the acid as it drips toward the bottom of the case while air is trying to escape from the top. Since most of the time the acid is added from the top, care should be taken to ensure this problem does not arise.

For the filling process, the following factors should be considered in selecting a separator.

- Porosity of the separator between the plates;
- System compression design; higher compression will general result in slower fill rates;
- Surface area of the separator, i.e., pore structure; higher surface area correlates to a smaller pore structure and will result in a slower fill rate;
- Wettability of the material; for example, microglass wicks much faster than a synthetic non-woven material.

Other factors beside the separator can affect filling. For example, additives used in the active material can have an influence. The expander or reinforcing fibres used in the paste may interact and result in excess gassing during acid addition. This results in longer fill time or for that matter in totally unacceptable batteries. These ingredients can also interact with the glass fibre surface. Care needs to be taken when any new material is used since the VRLA battery should be considered as a system and all the ingredients do interact.

### 3.5. Porosity of separator

The glass used to manufacture microglass fibre has a high density, about 2.5 g cm<sup>-3</sup>. The microglass is also produced with a very fine fibre structure. These two facts allow the microglass separator to have a very high porosity, namely, in the 92–96% range. This high porosity allowed the VRLA technology to be realized.

When selecting a new separator, the average material density of the separator's raw materials must be considered. To examine this point, consider a sealable separator that has 40% organic loading, as compared with a 100% glass separator. The 40% organic level allows the separator to be sealed. Typical densities of organic fibres are between 0.9 and 1.5 g cm<sup>-3</sup>. Assume, an organic density of 1.0 g cm<sup>-3</sup> and that the remaining portion is glass with a density of 2.5 g cm<sup>-3</sup>. The average separator density is 1.9 g cm<sup>-3</sup>.

Compared with an all-glass separator with a porosity of 94.6%, at the same grammage and thickness, the sealable separator has a porosity of 92.6%. Compressing the all-glass separator 20% (based on BCI thickness) results in a porosity between the plates of 93%. This porosity is still higher than the sealable separator with no compression. In fact, the all-glass separator would have to be compressed to 24%, to equal the porosity of the sealable separator with no compression. Conversely, a separator manufactured with 100% microglass allows for higher compression levels for a given volume of acid. What this says is that the all-glass material can be filled with more acid than the sealable separator for a designed level of compression. This highlights one aspect that must be considered when separators are being selected.

### 3.6. System compression

Compression is one of the most important variables for a VRLA Battery. Moseley [3] has stated the following:

... both fall within a couple of hundred of cycles if they are constructed with a low level of compression but when they are assembled with a high level of compression, then their cycle life is very much longer. Before we leave the subject of compression and separator compression, it is important to mention that the maintenance of compression within a stack depends upon the use of adequate separator materials.

As Moseley stated, the compression used is an important consideration. Work by ALABC and CSIRO [4] has shown the importance of having at a minimum, 40 kPa force against the paste/plate interface. As separator com-

Table 1  
Compression vs. possible acid addition

Percent compression	Spacing between plates (mm)	Available volume (cm <sup>3</sup> )	Separator solid volume (cm <sup>3</sup> )	Available acid volume in separator (cm <sup>3</sup> )	Grams of acid (1.3 g)	Acid/separator ratio
10	1.539	15.39	0.94	14.45	18.78	7.83
20	1.368	13.68	0.94	12.74	16.56	6.90
30	1.197	11.97	0.94	11.03	14.34	5.98
40	1.026	10.26	0.94	9.32	12.12	5.05
50	0.855	8.55	0.94	7.61	9.89	4.12

Assumptions: plates are 10 × 10 cm; separator is 240 g m<sup>-2</sup>, BCI thickness, 1.71 mm.; density of glass is 2.55 g cm<sup>-3</sup>.

Table 2  
Some factors that influence compression

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1. How is thickness measured
2. Variation in the separator
3. Variation of the plates
4. Draft of battery case
5. Percent compression used
6. Acid saturation level
7. Density of the separator
8. Surface area of the separator
9. Case material used
10. Uniformity of compression between the plates

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pression is increased, the amount of acid that can be added between the plates decreases, as shown in Table 1. This factor is an extremely important system consideration.

Many aspects influence compression, see Table 2. The saturation level is a major influence. Nakamura et al. [5] have reported on this process. As the level of saturation changes, the force exerted by the separator also changes. This behavior has been reported by Hollingsworth and Vose in many papers, the latest is given in Ref. [6]. The modification of the separator compression force from dry to wet can be compensated with the proper separator compression, density of the separator, and grade of separator.

Further key influences on battery system compression are the degree of separator saturation and the resulting compressive force the separator applies to the plates. The separator's saturation level will influence the separator thickness under load. This is one reason why, when acid is added to the battery, a relaxation of the case is sometimes observed. A dry separator will exert a higher force than a partially saturated separator. The resultant relaxation seen when acid is added to the battery is a direct result of the subsequent force reduction. The compression remaining inside the battery after the acid is added is a critical factor: insufficient compression and the separator may lose contact with the plates. This lack of plate-to-separator contact may develop during the battery life as the battery dries out. This is especially true if the design compression did not account for the saturated recovery curve of the glass separator at the lower saturation levels.

In developing a test to examine the separator and compression dynamics, it is important that the separator be first compressed, held under the load, and then saturated with acid. Pre-wetting the separator, and then compressing the separator will lead to a lower measured thickness/force. The first condition simulates a real battery system. Compressing the separator in a dry condition first locks the

fibres in place. Pre-wetting the separator and then exposing the separator to a compressive force can provide a lubricant for which will allow the unbounded microglass fibres to move more freely.

The density of a given fibre blend is also an important consideration for system compression. A lower density separator may cost less per linear metre but the end wet compression force will usually be less than a denser version with the same fibre blend. Other areas to examine are the temperature to which the battery is exposed. At high group compression, the creep of the plastic case might be the weak link in the system. What happens to the plastic case during high temperature operation and while the groups are under high compression? In laboratory work, that examines the influence of high temperature and force retention of separator systems, a major problem is having a 25-mm thick block of Plexiglass® or Lexan® hold up to the stress. In one experiment, the glass separator under force extruded the Lexan, embedding the separator into the plastic. These studies show a lower retained force in the system when exposed to a higher temperature environment.

#### 4. Conclusions

Throughout the evolution of the VRLA battery, many excursions from 100% microglass separator have been investigated. The benefits imparted by the microglass separators have repeatedly proven to be of more value than the attributes realized by other materials.

Separator selection must be considered as part of a system approach in a VRLA battery.

A high group compression is needed for improved performance, and with such compression, the battery case may become the weak link in the system.

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