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Development of a novel synthetic loaded separator paper for VRLA batteries

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Abstract

Absorbent glass material made of 100% microglass fibre is a well-known separator for valve regulated lead acid (VRLA) batteries and has been in use for around 20-year period. As the VRLA battery market and demands of the customer continue to grow; electrical performance, productivity and reliability of VRLA batteries are being enhanced. This is achieved through a combination of process, quality assurance, materials and electrochemical engineering. Reliability and electrical performance of the battery is linked to the AGM glass material. Properties of the AGM material impact the assembly route, defect rates, productivity, product cyclability, life, reliability and recharge performance.

Bernard Dumas in partnership with Enersys has developed a specific product containing 8% synthetic fibres for thin plate application. Enough data have now been gathered to guarantee that this type of separator is giving electrical performance equal to or better than 100% glass AGM and has increased battery productivity. The electrical performance of the batteries manufactured with synthetic loaded separator paper was equal or better than the AGM counterpart as demonstrated by capacity testing, cycling and accelerated float life (AFL) tests. Tear-down investigation after accelerated float life testing at 55 °C showed no degradation of the synthetic separator paper.

Keywords: Valve regulated lead acid batteries; Synthetic fibre; Absorptive glass mats

1. Introduction

Standard valve regulated lead acid (VRLA) batteries have been manufactured for many years with 100% microglass fibre separators, also called AGM. Glass fibres are resistant to sulphuric acid at various battery operating temperatures and have got excellent acid wetting property (near zero contact angle). Strength of 100% microglass fibre AGM is provided by physical interlacing of the fibres achieved by the wet paper machine process. For standard application, 100% microglass fibre AGM, is strong enough to have good processability, but, enhanced physical and mechanical properties are sometime desirable for more robust manufacturing and defect-free processing.

Bernard Dumas has developed a specific separator containing 8% synthetic fibres in order to improve mechanical strength. The synthetic fibres used have shown very good behaviour in contact with acid and very good tensile and puncture resistance to avoid any structural degradation in acid. This synthetic fibre is a bicomponent fibre where the inner fibre core is providing strength and stiffness and outer core is binding by melting on the glass fibre during drying process on paper machine. Puncture resistance can be doubled by the addition of 8% of this specific synthetic fibre. As a consequence, short circuit during assembling the plates has been decreased. On the other hand standard AGM characteristics concerning capillarity rise and pore size distribution are more or less unchanged with 8% synthetic fibres.

This paper describes the development of the 8% synthetic loaded separator paper, prototype build and electrical testing of VRLA batteries utilising this separator.

2. Synthetic fibre loaded AGM separator characteristics

2.1. Synthetic fibre structure

Absorbent glass material is made on paper machine. Fibres are dispersed in water and then all the process consists

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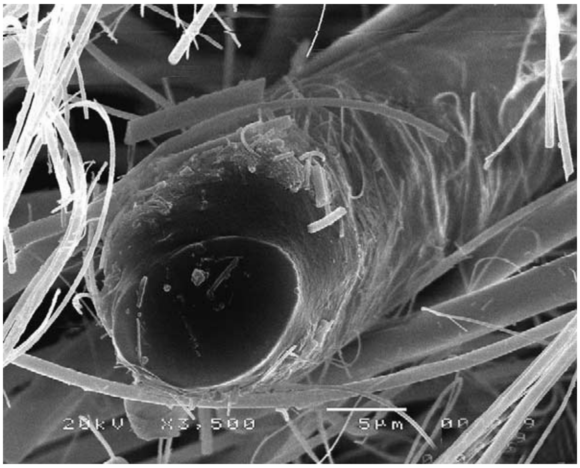

Fig. 1. SEM micrograph showing bicomponent nature of synthetic fibre materials.

in removing water from paper sheet formed on paper machine head.

Standard Bernard Dumas 100% AGM separators are made off a mixture of microfibre glass:

- fine microfibres with diameter <1 μm;
- coarse microfibre with diameter <5 μm;
- chopped strand fibre with diameter ~11 μm.

All these glass fibres are mainly bound together by mechanical interlacing strength. In wet condition (acid or water absorbed), the water is going between the fibres, if external force is applied, the fibres slip one to each other much more easily than when AGM is dry.

Synthetic fibres used in this development are bicomponent as shown in Fig. 1.

Fibre core is a strong polymer that does not change in shape and structure in acid and hot conditions. Outer fibre part is a polymer that can melt in the paper drying process, this melting makes synthetic fibres bind on any glass fibre that touches them as shown in Figs. 2 and 3. When temperature is going back under 90 °C this melted part becomes hard again and reinforce glass mixture structure.

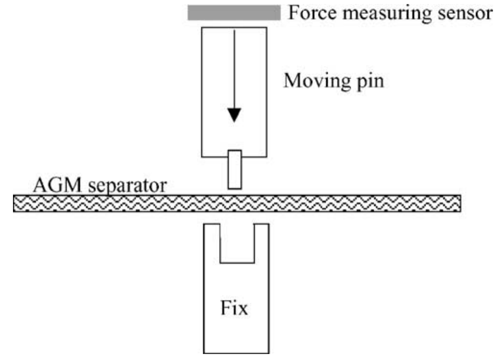

Fig. 4. Puncture resistance measurement.

2.2. Puncture resistance and short circuit

Puncture resistance is the measurement of a pin strength going through the separator as described in Fig. 4 [1].

Puncture resistance is the highest strength measured while the pin is going through the separator at 20 mm/min. Standard range of products are known to be little different in strength by the fine fibre content. The more fine fibres, better is the fibre links and stronger is the AGM.

Addition of synthetic binding fibres enhanced the physical and mechanical characteristics. By adding 8% of this fibre, puncture resistance is more than doubled in dry state and almost tripled in wet state (water saturated) as show in Fig. 5.

This test is representative of potential defects during manufacturing. During the battery making process, AGM separator is pressed on to the plates. If burrs are present on plates they have, under pressure, the potential to cut through the separator. Synthetic loading resists this and avoid short circuits to appear as shown in Fig. 6.

During cycle life, plates size have the tendency to change in volume depending on charge and discharge states. AGM,

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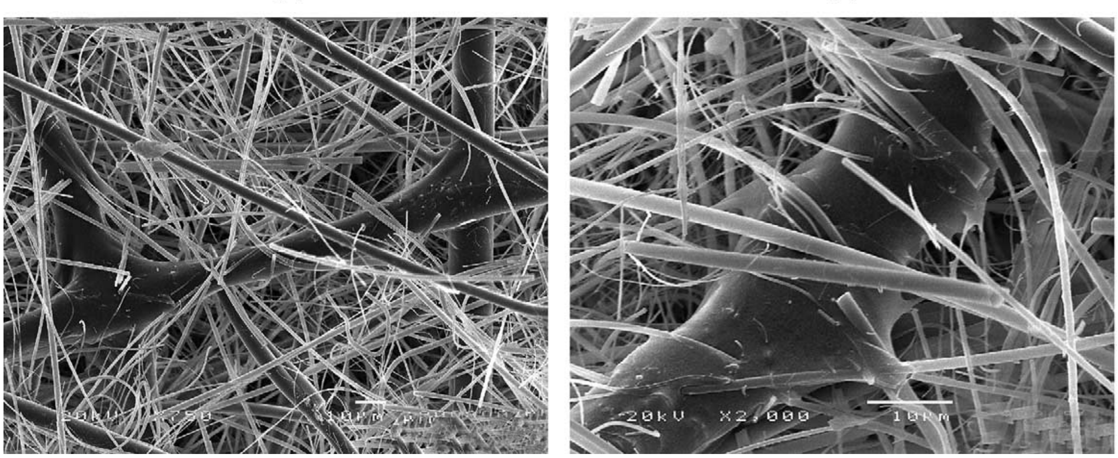

Figs. 2 and 3. SEM micrographs showing glass fibres bound log ether by melted polymeric material.

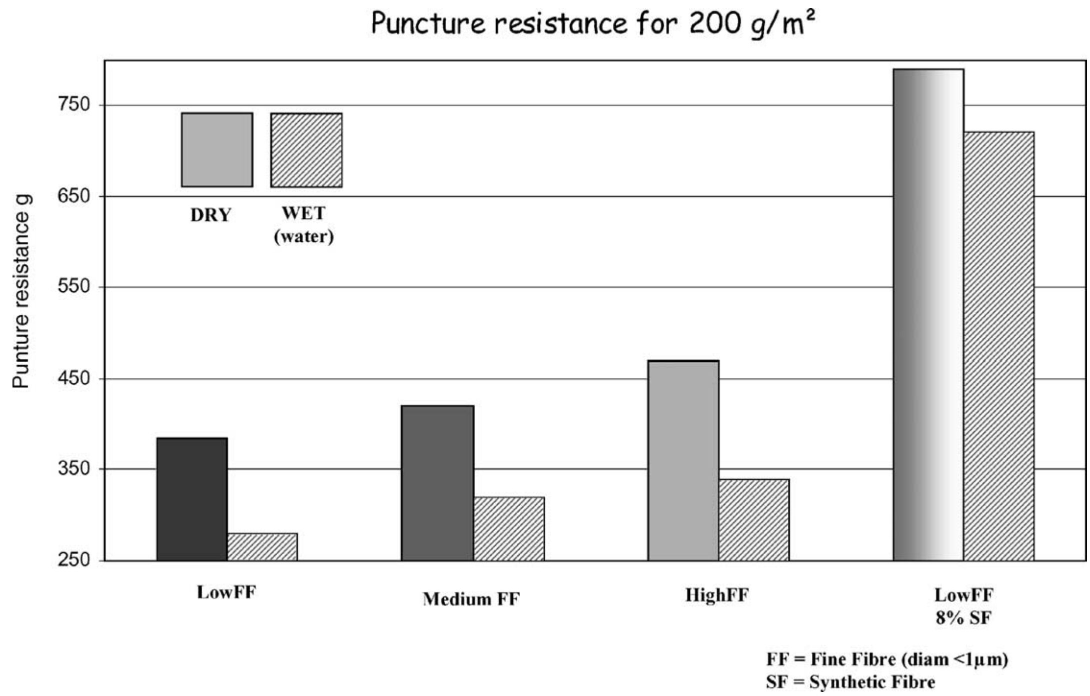

Fig. 5. Puncture resistance vs. AGM composition.

as an elastic material, is able to follow these sizes changes during cycling. If plate surfaces are not smooth enough, surface irregularities can makes compressed "zone" when plates are occupying the biggest volume. On these zones, AGM structure is mechanically stressed:

- "compressed" where there is a "bump";
- "stretched" around this "bump".

Without synthetic fibre reinforcement, the stretched zone makes an irreversible more open structure, more prone to have short circuit. With synthetic fibre reinforcement, these stretching zones are held together firmly by the fibre structure. This phenomenon is described in Fig. 7.

2.3. Effect of synthetic fibre on capillarity rise and separator pore structure

2.3.1. Capillarity rise in sulphuric acid

An important AGM parameter is its wetability with sulphuric acid. Glass fibres and more generally glass are known to have very good wetability in sulphuric acid (contact angle near to zero). This wetability has some importance for acid filling but more concerning acid stratification in the separator. For any glass separator, it is known that stratification occurs after aging making more corrosion at the bottom than at the top of the plate. It is also known that higher the fine fibre content, lesser the stratification.

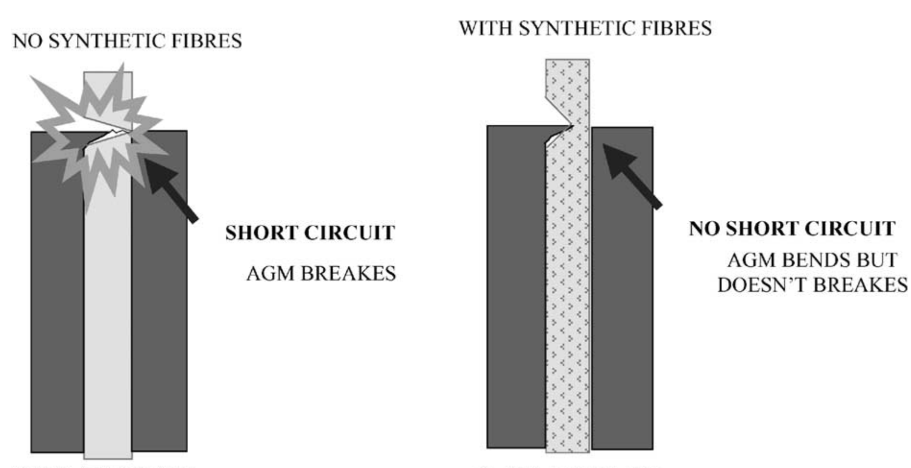

Fig. 6. Battery assembling short circuit.

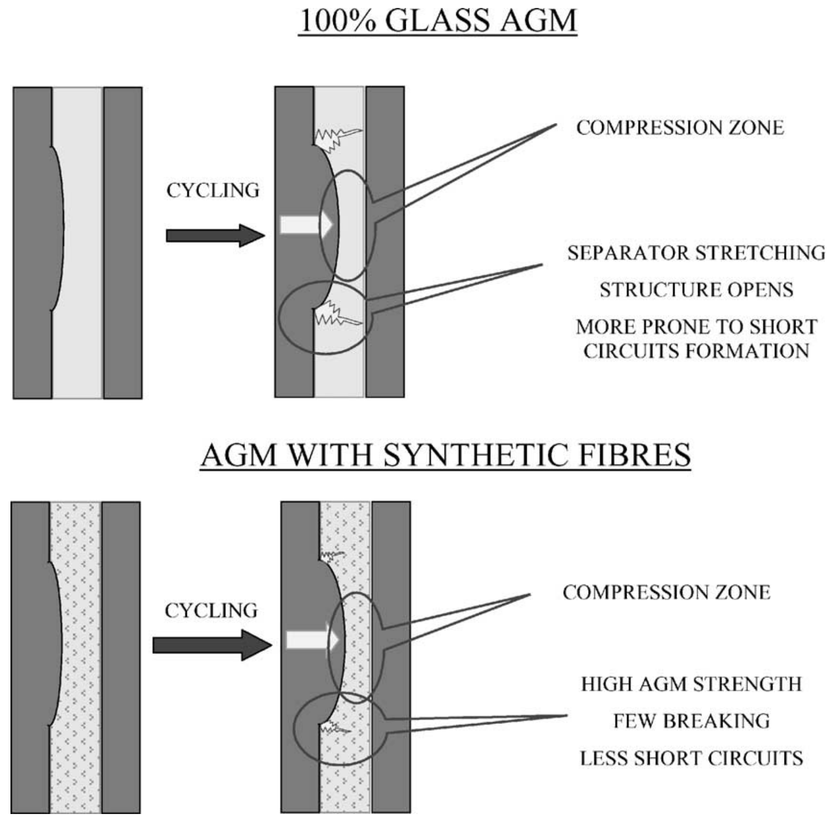

Fig. 7. Battery cycling short circuit.

Synthetic fibre polymer used in the new separator presented here have less wetability than glass, thus the AGM loaded with synthetic fibre should have a behaviour in acid not as good as what 100% glass material has. This wetability can be measured by *capillarity rise*.

This test consists in an AGM strip dipped by 10 mm in acid bath at room temperature. After 24 h, 50 mm length pieces are weighted from the bottom to the top. Then absorption percentages of each 50 mm length pieces are calculated independently.

After this absolute absorption percentages are calculated, the maximum is set at 100% and relative absorptions are calculated, this step is to make all different separators comparable one to each other.

The results reported in Fig. 8 are capillarity rise in sulphuric acid $d = 1.30$ after 24 h of standard 100% Glass mat and the same material (in terms of glass types ratio) but with 8% synthetic fibres.

The two curves obtained are remarkably similar. Minor difference occurs above 600 mm where acid is reaching higher point for 100% glass material (around 750 mm for 100% glass and 700 mm for 8% synthetic fibre loaded AGM). The results show that the two separators are very similar in absorption and stratification.

We can interpret this similar behaviour between the two products by the fact that 8% synthetic fibre represent a very small part of the separator surface which is in contact with the acid. An influencing difference appears between 100% glass and synthetic fibre loaded product after around 10–15% of synthetic fibre present in the separator.

2.3.2. Pore size distribution

In order to see if global internal structure of the separator is really changed by adding synthetic fibres, we have measured pore size distribution using a coulter porometer II (BCI-V34-1b).

This apparatus uses a liquid displacement technique to measure the pore size distribution of a sample. The wetted sample is subjected to increasing pressure, applied by a gas source, this liquid is pushed out, by following the pressure applied and the flow going through and comparing that to dry state flow, pore size distribution is calculated.

Fig. 9 shows pore size distribution of 100% glass AGM compared to its equivalent containing 8% synthetic fibres. The pore size distributions are very similar and the presence of 8% of synthetic fibres does not change the pore structure.

3. Battery manufacture and electrical testing

3.1. Prototype build and electrical performance evaluation

Prototype batteries (also called monoblocs) were manufactured with 100% glass AGM and 8% synthetic loaded AGM separator paper. All the build details except the separator paper, were identical in the trial build. Samples

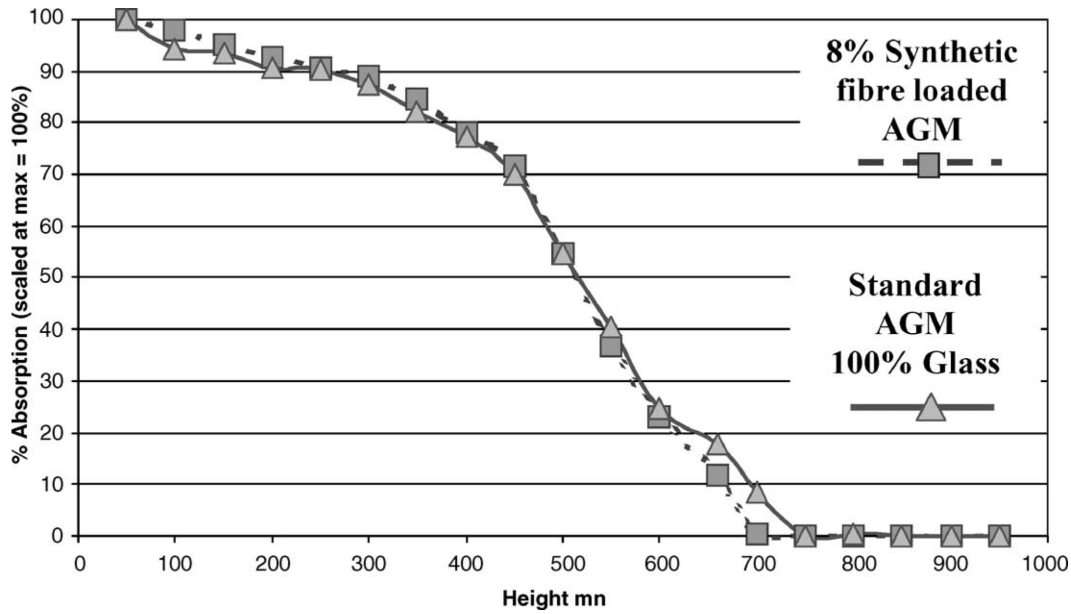

Fig. 8. Capillarity rise 24 h acid 1.30.

were put through electrical testing. Capacity test results obtained are similar for AGM and synthetic loaded AGM batteries. Battery cycling and accelerated float life (AFL) results are described in the following sections.

3.1.1. Cycling

One of the criterion for qualification of the new separator is battery cycling.

In order to evaluate the performance of the 8% synthetic fibre separator paper during extensive cycling, a 65 A h front terminated (FT) prototype sample was subjected to cycling using an optimised regime (Fig. 10). The plates in this monobloc were the tallest in this capacity range. The regime used in this trial was as follows.

Discharge to 75% DoD, immediate charge for only 3 h at 2.4 V per cycle and continue cycling for 50 cycles. After 50 cycles, residual capacity check was carried out by discharging to an end point voltage of 1.7 V per cycle, after which the monobloc is recharged for 24 h. Cycling is continued as before. In Fig. 9, the residual capacity is plotted against the cycle number. Altogether at 75% DoD, 1350 cycles were obtained with additional 27 C3 capacity cycling (cumulative 48600 A h for a nominal 65 A h monobloc) with C3 capacity close to 100% after 1350 cycles. The data has been particularly impressive given the fact that the only 3 h are allowed for charging. Acid stratification has been minimal and the endurance of the separator paper to extensive cycling has been excellent. Very similar results were obtained

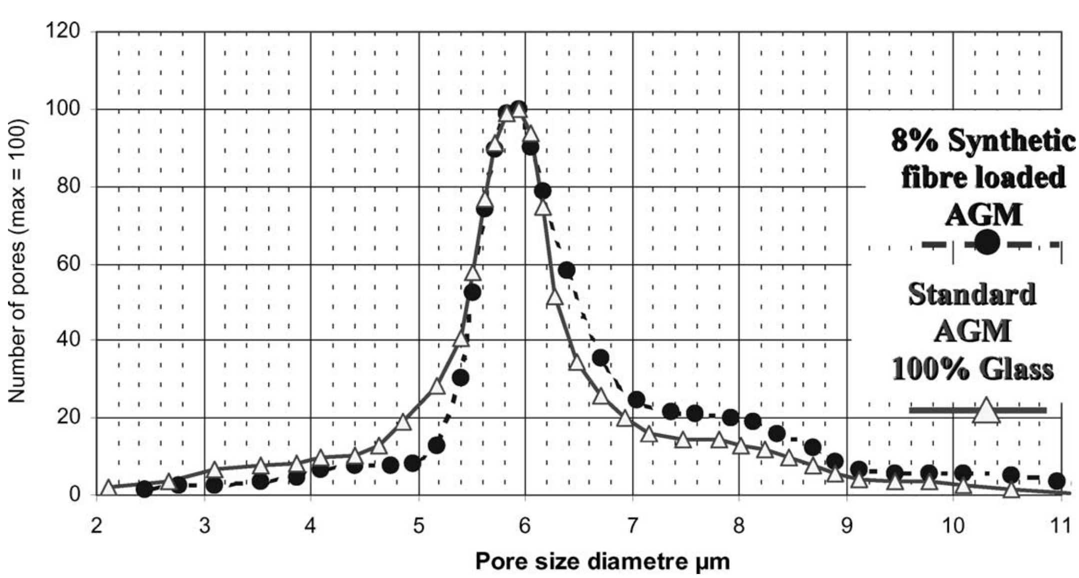

Fig. 9. Pore size distribution coulter porometer II 200 g/m^2.

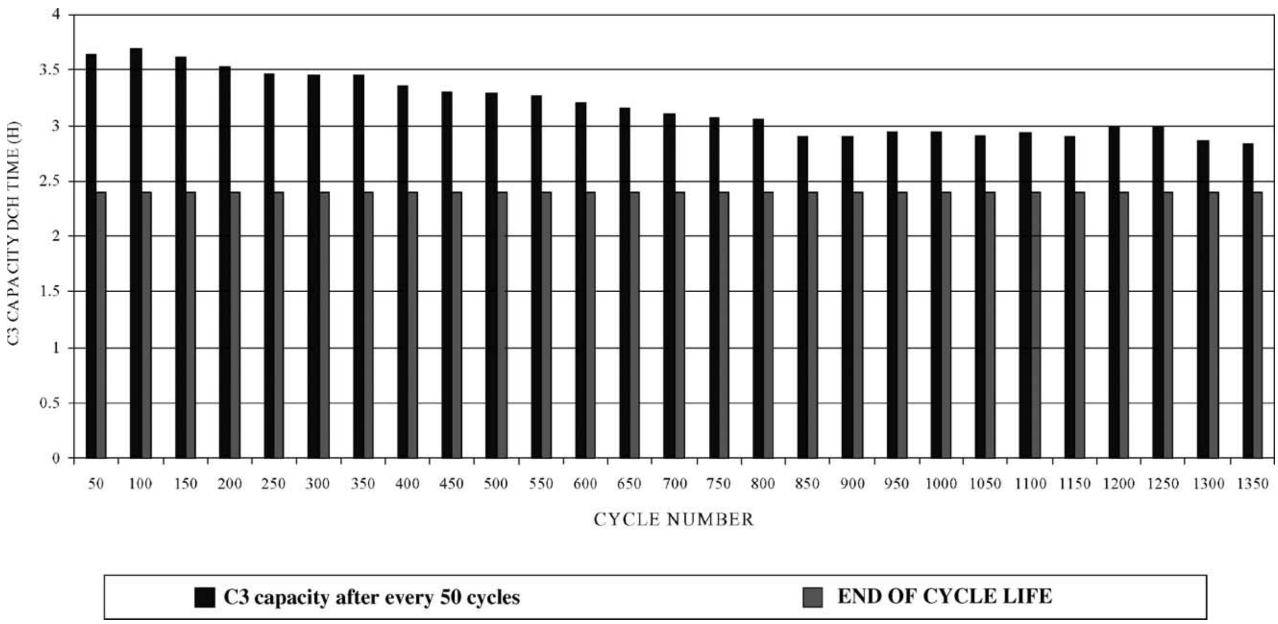

Fig. 10. Seventy-five percent DoD C3 cycling (recharge only for 3 h) with capacity check every 50 cycles (12 V, 65 A h, front terminating), 8% synthetic fibre.

with the AGM counterpart. Cycle tests conducted using float voltage recharge have given very favourable results as well.

3.1.2. *Accelerated float life test*

Various manufacturers routinely use AFL test at elevated temperature to evaluate the float life of VRLA batteries. We have followed BS6290 part 4 standard for this evaluation. The test is based on the assumption that float life is halved for every 10 °C rise in temperature. In this trial, monoblocs were continuously float charged at 55 °C using 2.27 V per cycle float voltage. After 42 days at 55 °C, monoblocs were cooled to 20 °C under float charging. C8 capacity test was carried out to determine the residual capacity of the monobloc. Testing continued until the capacity fell below 80% of the nominal value. Fig. 11 compares the prototype test results. Both 100% AGM and 8% synthetic loaded separator paper gave 15 years

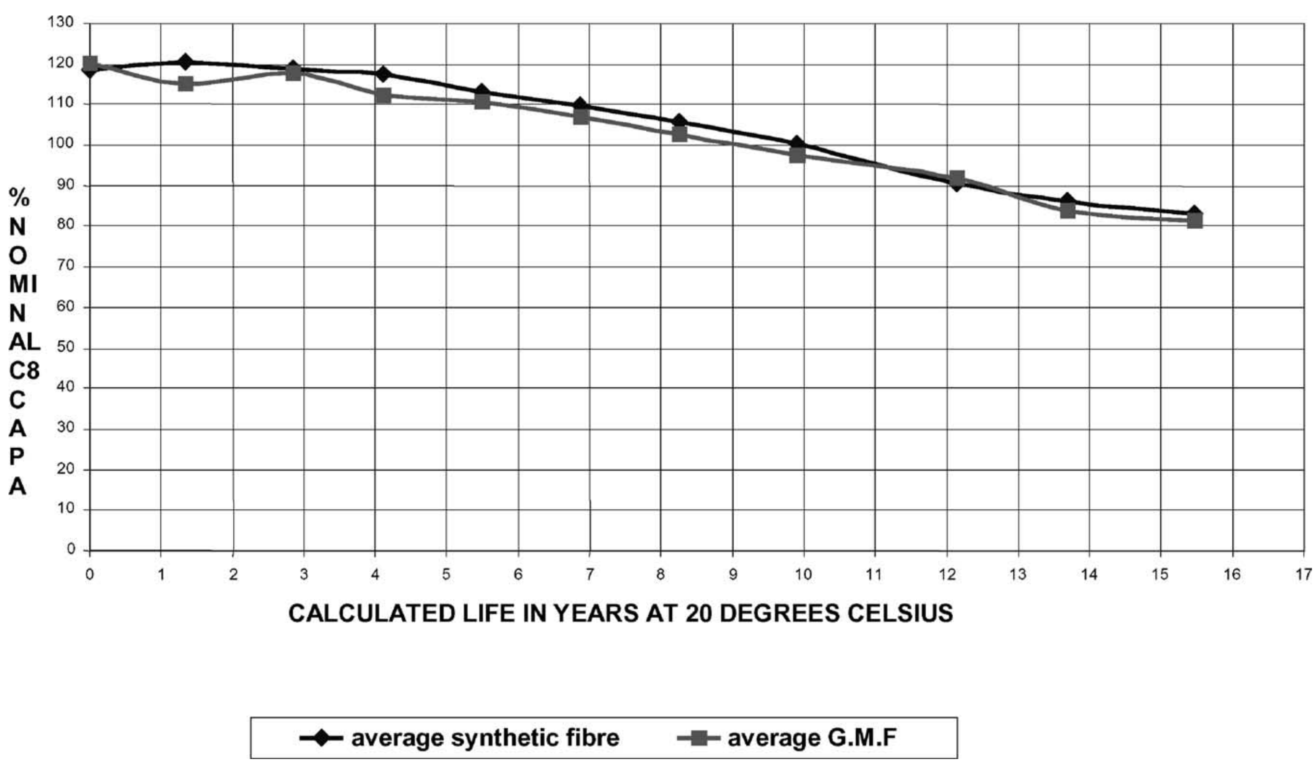

Fig. 11. Comparison of AFL results—100% GMF vs. 8% synthetic loaded separator paper (12 V, 52 A h prismatic design).

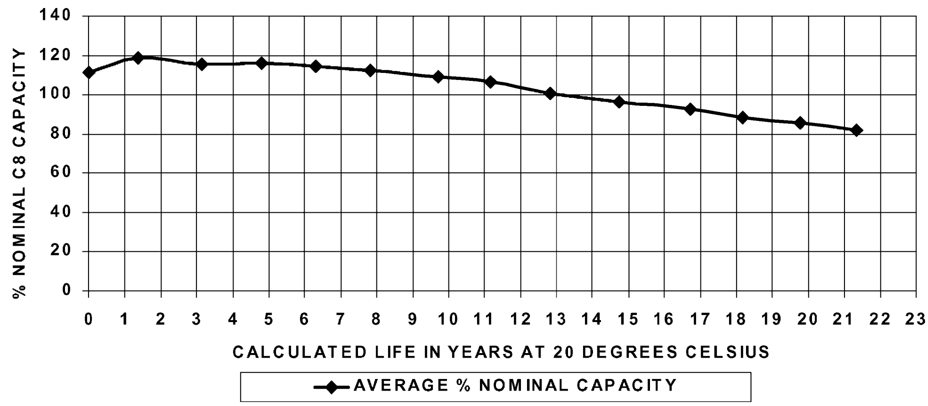

Fig. 12. AFL test data obtained recently on a 6 V/110 A h monobloc manufactured with 8% synthetic loaded separator paper.

float life at 20 °C. indicating that synthetic loading does not deteriorate the long term performance of the battery even after continuous float testing at elevated temperature.

Recent trial on a 6 V/110 A h prismatic design manufactured with 8% synthetic loaded separator paper delivered over 21 years float life (Fig. 12).

3.2. Process improvement

Following the electrical test qualification, a large scale production run was carried out to evaluate the processability of the separator paper under normal production conditions. Both 100% AGM and 8% synthetic loaded separator papers were put through identical processing conditions. The work was carried out as part of the '6 Sigma' process improvement and control program started within the Enersys group. The team, led by a 6 Sigma "black belt", was able to clearly demonstrate the benefits brought about by using 8% synthetic fibre separator paper. Metrics and evaluation tools and techniques used within the "6 Sigma" work clearly quantified the benefits associated with 8% synthetic fibre separator.

4. Conclusions

Bernard Dumas and Enersys, Newport, worked together to develop a new AGM separator for VRLA batteries with the addition of 8% synthetic bicomponent fibres. The synthetic fibres have the property to bind glass fibres together and reinforce the AGM.

As a consequence to this synthetic fibre reinforcement, puncture resistance has been considerably increased, preventing plate shorting through the separator paper during battery assembly and service life of the product. Moreover, addition of synthetic fibres did not have any adverse effect on the acid absorption behaviour and pore structure of the AGM. As a consequence to this, electrical properties of the batteries made with synthetic separator are as good as or even better than those manufactured using 100% glass AGM. The use of this separator type increases factory throughput and moreover enhances the quality and reliability of VRLA batteries.

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Reference

[1] Battery Council International—Test Method 214-3b-032.