A multi-layered approach for absorptive glass-mat separators

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Abstract

The traditional method of manufacturing absorptive glass mats (AGMs) for valve-regulated lead–acid (VRLA) batteries is to blend two or more types of fibres together in an aqueous acidic solution and deposit this blend on to either a moving endless wire or a roto-former (another version of an endless wire). The sheet acquires consistency as the water is withdrawn; it is then pressed and dried against heated drums. The methods of fibre dispersion and deposition can be changed so that the different constituent fibre types of an AGM separator are processed separately in distinct and separate layers. This fibre segregation results in the enhancement of some key characteristics of the separator and thus brings some very definite advantages to the performance of VRLA batteries, e.g., the ability to deliver higher currents at higher discharge rates. Also, important AGM characteristics, such as wicking, porosity/pore-size and stratification, are radically modified by adoption of the multi-layered AGM design. As a consequence, the high-rate and cycling performances of VRLA batteries are equally affected. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Absorptive glass mat (AGM) separators which are used to immobilize the acid in valve-regulated lead–acid (VRLA) batteries are composed of a blend of two or more different types of fibre. Most of the desirable characteristics of these separators come from the presence of fine glass microfibres. Therefore, should the ideal AGM separator be made exclusively of fine fibres? The answer is 'no'! The coarser fibres also play a role in the ability of the AGM separator to fulfil its many functions.

The classic technique of producing an AGM separator calls for the deposition, as a single sheet, of a mixture of fibres dispersed in an aqueous acid solution. This fibre mixture has a desired ratio of fine fibres to coarse fibres. Considerations used in establishing this ratio include the desired separator characteristics and cost. What would happen if the fibres were segregated and deposited in two or more distinct layers with each layer containing up to 100% of one type of fibre? In other words, what if the AGM separator was orientated in much the same way as separators have been oriented for years in traditional flooded lead–acid batteries?

Over the years, battery designers have learned that the distinct needs of each electrode polarity require special designs of separator. For example, better performance is obtained when ribbed separators have their ribs facing the workhorse positive plates to provide an adequate volume of acid. Later, with the advent of gelled-electrolyte VRLA batteries, new separator designs were required in which ribs facing the negative plates gained in importance. By arranging distinct and different fibre structures against the different electrodes, the function of the AGM separator can be optimized and made to suit the specific needs of each electrode type.

2. Glass microfibres

Glass microfibres all have cylindrical cross-sections, but depending on the process by which they are made, they can exhibit a wide range of diameters and lengths. Of interest in the making of AGM are fine and coarse glass microfibres, as well as chopped glass fibre.

Two methods exist to produce glass microfibres: the rotary and flame-blown processes. The different equipment and energy requirements of these two methods explain the large difference in the cost of the two types of fibres. In the rotary method, molten glass is dispensed from a rotat-

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ing metal bowl which is perforated with many tiny holes. The cooled glass fragments are then collected and are in the shape of discrete glass fibres with a wide range of diameters in excess of 1 μm and with lengths of nearly 1 mm. The internal BET surface-area of these fibres is between 0.5 and 0.6 m^2 g^{-1}.

The flame-blown production of glass microfibres is more complex. Molten glass is drawn into fine filaments which are sheared off by hot air at high velocity. The sheared glass fibres are very small and highly contorted. They are gathered on a moving collector. The diameters achieved with this process are generally below 1 μm, typically 0.6 to 0.8 μm, and the lengths are around 0.3 mm. The BET surface area of these finer fibres is about 2.0 m^2 g^{-1}.

The first important characteristic of glass microfibres is their stability in the highly oxidative environment which exists within the lead–acid battery. Other fibre characteristics which are affected by the process parameters of fibre production include: surface chemical composition, fibre diameter, fibre length, fibre shape.

So-called 'chopped' fibres are much larger than the microfibres; these glass fibres can have diameters which range from 8 to 13 μm and are several millimetres in length. As the name suggests, the fibres are produced by chopping bundles of glass fibres. Such fibres play a significant role in the production of most AGM separators since they provide structural integrity and reinforce the fibrous structure of the AGM separator (much as steel rods reinforce concrete). They also impart a smooth surface and a good finish to the material.

One easy method of measuring the average diameter of glass microfibres is to determine the pressure drop across a sheet made of such fibres. This is based on Darcy's Law for laminar flow of a fluid through a porous structure [1]. When two sheets are deposited one on top of the other, the total pressure drop is the summation of the pressure drop in each of the constituent sheets. For practical purposes, the 'fibre number' is used and is defined as: one-tenth of the value of the pressure drop (in Pa) across a sheet of 90 g m^{-2} when the applied air current is 0.0167 m s^{-1}. The sheet being measured is created in the laboratory from a water suspension of fibres.

The following empirical relationship relates the fibre number (FN) directly to the fibre diameter (d):

$$\text{Fibre number} = 5.5/d^2 \quad \text{or} \quad d = \sqrt{5.5/\text{FN}} \qquad (1)$$

Thus, the use of the fibre number is a fast and fairly accurate measurement of the internal make-up of a fibrous structure. It does not replace the need for BET measurements, but it is a complimentary assessment technique.

3. Fibre deposition and mat creation

The first step in the production of AGM is the dissolution of the glass fibres in a large amount of acidified water. The mixture of fibres and water is then deposited on a surface where vacuum is applied and most of the water is removed. The formed mat is then slightly pressed and dried by means of heated rolls. At the end of the drying section, the water content of the mat is below 1 wt.%.

There are three commonly used devices to form and de-water an AGM; these are sketched in Fig. 1. The first is the traditional paper-making technique. The fibre–water mixture is deposited directly as a slurry on to a moving endless wire. In the second case, an inclined wire picks up part of the fibres from the fibre–water suspension; this method is especially recommended for the creation of wet-laid, non-woven materials in which the fibres are rather long. The third device is the roto-former in which a moving drum picks up the fibres from the mixture and
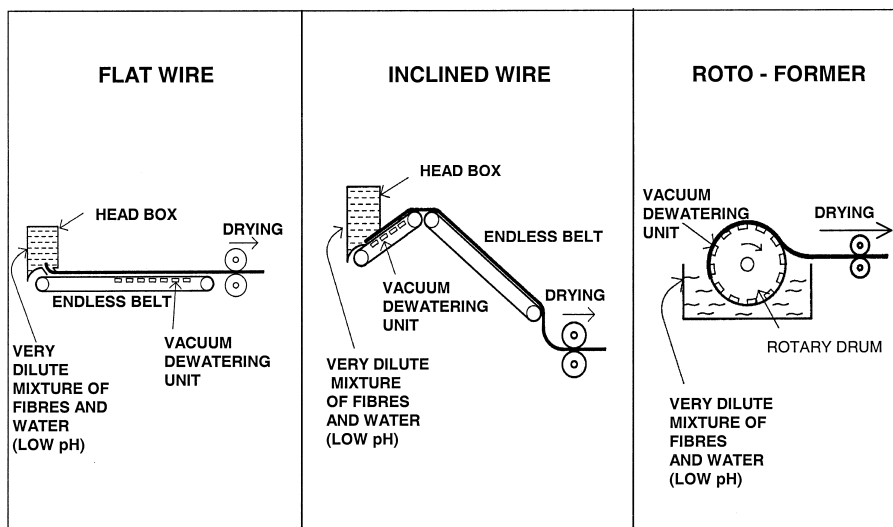

Fig. 1. Sketch of three methods of depositing glass microfibres to produce AGM.

sheet formation is achieved by de-watering. In all cases, the strength of the AGM is created at the stages of fibre dispersion, deposition and de-watering.

In the presence of acidified water, the tetrahedral molecules of SiO_2 present on the fibre surfaces can form hydroxyl groups. Due to the partial charges on the molecules, this leads to the establishment of hydrogen bonds with the water molecules which are present between the fibre surfaces. Such bonds contribute greatly to the cohesion of the mat during the initial formation phase. A similar situation occurs when a cellulosic fibre mat is created [3].

The strength of the glass-fibre mat is also dependent on the amount of water. The relationship is not constant, however, and this suggests that there is an optimum water content which favours the creation of the largest number of hydrogen bonds between the fibres. Measurements performed samples taken from the production line indicate that maximum strength is achieved when the material has a water content of about 35 wt.%.

Some evacuation techniques can result in uneven de-watering. This is the cause of the 'orange peel' effect seen with some AGM separators, particularly the thicker ones. Such a characteristic should be avoided since an uneven surface will give rise to uneven fibre compression and probably to poor contact with the plate surface. Ideally, even the thicker AGM separators should have perfectly smooth surfaces.

4. Characteristics of multi-layered AGM

4.1. Reduced pore size and improved tensile strength

In the range of 20 to 40% fine fibres, the reduction in measured Coulter pore sizes is considerable. For example, from the mono- to the multi-layer construction, there is a 50, 40 and 25% reduction in maximum, average and minimum pores, respectively (see Fig. 2). These data refer to extremes of fibre separation performed under laboratory
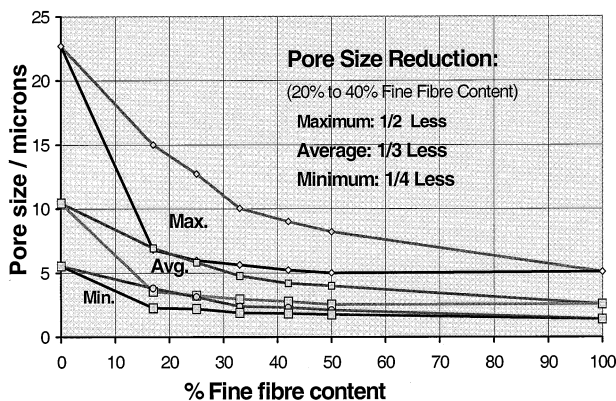

Fig. 2. Effect of fibre segregation on Coulter pore-size distribution.

conditions. Subsequent measurements performed on AGM material produced under production conditions confirm these results. The existence of a closer fibrous structure in one of the layers explains the difference in the Coulter pore-size measurements between the two types of mats.

The next characteristic to be considered is tensile strength. Measurements of sheets made from glass fibres with different diameters clearly show that finer fibres are much stronger than coarser ones [2]. For example, a 10-fold increase in tensile strength is observed with fibres whose diameters ranged from 0.1 to about 3 μm. If the fine fibres of an AGM separator are segregated and allowed to form a layer on their own, the overall structure will gain in strength. The increase in tensile strength reaches a maximum (i.e., 40% increase) at a 50% fine-fibre content. This observation has been confirmed by many studies undertaken on production materials. Naturally, many other factors influence the tensile strength of an AGM sheet, and most of these factors are related to the manufacturing process and subsequent handling of the material.

4.2. Improved speed of upward / downward wicking

Whereas the tensile-strength test tries to predict how the AGM separator will behave during the manufacture of VRLA batteries, the wicking test (also known as the capillarity test) can provide the following information on (i) how fast the AGM absorbs acid and (ii) how much acid is absorbed and the saturation profile which it creates. The speed of wicking is particularly relevant for the filling operation, where fast absorption and complete wetting are essential. Filling can also be duplicated by the downward wicking test which is mentioned below. The total amount of acid absorbed and the saturation profile give an important indication of the electrochemical role of the separator in the performance of a VRLA battery.

In an excellent paper, Culpin [4] has approached the wicking characteristics of AGM from a theoretical as well as a practical point of view. Culpin-type wicking measurements undertaken on fine and coarse fibres are presented in Fig. 3. It can be seen that single-layered AGM separators with various ratios of fine to coarse fibre have wicking speeds and maximum heights that are somewhere in the middle of the extremes for 100 and 0% fine fibres.

The same logic cannot be used for the multi-layered AGM, known as AMER-GLASS. Here, the known fibre content is in the region of 35 to 40%, but the wicking speed right from the start is higher than that of the single-layer, 100% coarse-fibre sheet. It is also known that the average pore size of this multi-layered AGM is much less than half of the average pore size of the 100% coarse-fibre sheet. The superior wicking behaviour of the multi-layered AGM is due to a synergy between the wicking characteristics of each component layer: the coarse fibre layer acts like a 'pump' for the acid, while the fine fibre takes the acid to greater heights at a fast rate.
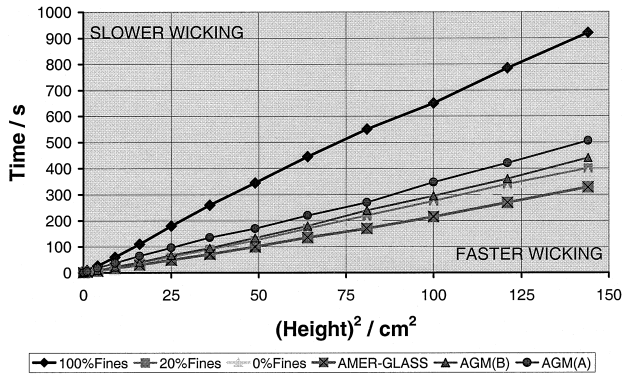
Fig. 3. Effect of fibre mix and segregation on vertical wicking speed of electrolyte by glass microfibre sheets. Strips of AGM not compressed. Note: All AGM samples are single layered except AMER-GLASS, a multi-layered AGM.

Wicking tests in which acid is allowed to be absorbed downwards shows similar trends for different AGM materials. The multi-layered material wicks faster than its fibre composition alone would permit. This test confirms that the same synergistic effect carries the acid downwards faster than in a single-layered AGM. This advantage cannot be overstated because of the importance of proper filling.

5. Multi-layered AGM and battery performance

The impact of the AGM separator on VRLA battery performance is beyond dispute. Although it is somewhat of an overstatement to suggest that it is a 'third electrode' [5], by its ability to influence how the acid behaves, the AGM separator is very much the key player in determining how well or how poorly a VRLA battery performs.

The following considers the impact of the multi-layered design on the performance of VRLA batteries—starting with the filling process, and then examining at the electrical performance.

5.1. Electrolyte filling

Experts in the field of VRLA design and manufacture have recognized that correct filling is critical. It is highly dependent on the plate height, the spacing, and the degree to which the separator is compressed.

The ratio of plate height to plate spacing can be used as a rough measure of the difficulties encountered in filling [6]. If this ratio is equal to or less than 50, then easy filling results. If it is between 50 and 100, care should be taken to avoid potential problems. Filling becomes more difficult when the ratio is between 100 and 200, and is almost impossible at ratios above 200. The fast wicking properties of multi-layered AGM are of great advantage in the 'grey zone' of filling where the ratio of plate height to plate spacing is between 50 and 200.

Equally significant is the fact that as compressions are increased within the VRLA battery to reduce the effect of premature capacity loss, the pores in the z plane are affected but not those in the x–y plane. The former is the filling plane and increase in compression causes a gradual reduction in these pores. Thus, it is advantageous to use an AGM which has in its structure a layer of high porosity with large pores, i.e., the type given by the fibrous structure created by the coarse fibres in the multi-layered AGM.

5.2. High-rate discharge performance

When a lead–acid battery undergoes fast discharge at a high rate, the end of the discharge is determined by the performance of either the positive or the negative electrodes.

The type of battery that is most universally known for its high-rate capability, particularly at low temperatures, is of course the ubiquitous automotive (SLI) battery. In this design, it is usually the negative electrodes which limit the high-rate output of the battery. The acid present inside the electrodes is quickly consumed and it must be replaced immediately by fresh acid from the immediate vicinity of the electrode. The electrochemical discharge reaction will continue for as long as it can be sustained by the structure and chemical composition of the active material.

In the case where acid is immobilized in an AGM separator, various patents [7,8] have claimed that there are advantages to be gained in high-rate discharge performance when there are special arrangements in the fibrous structure of the AGM. Some researchers express these special arrangements in terms of the internal surface area of the AGM. In other words, a high surface-area vs. a low surface area AGM. Various measurements have confirmed that the BET surface area of an AGM made with 100% commercially available fine fibres is close to 2 m^2 g^{-1}, whereas the coarse fibres yield a value of around 0.6 m^2 g^{-1}. Thus, various combinations of high and low surface area fibrous structures have been suggested to achieve enhanced high-rate discharge performance (see Fig. 4).
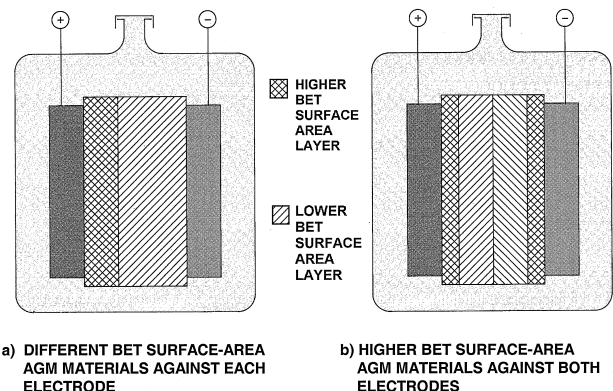

Fig. 4. Possible arrangements of multi-layered AGM separators to favour high-rate discharge performance.

It should be noted, however, that most VRLA batteries have rather generous ratios of negative to positive active material and, therefore, it is in fact the positive electrode which tends to limit high-rate discharge. This being the most prevalent situation, it then becomes very important to minimize stratification effects at this electrode. Accordingly, it is proposed that a low-stratification, 100% fine-fibre layer should always be placed against the positive electrode. Electrolyte stratification is the 'number one enemy' of VRLA battery electrical output, especially at high rates when the entire system has to deliver its best performance.

5.3. Cycling performance

Electrolyte stratification is also the enemy of good cycling performance. Stratification results in different zones of activity in the positive electrode and thus reduces the ability of a VRLA battery to function effectively. The orientation of the AGM can be a distinct advantage in terms of cycling performance. In particular, the fine pore structure created by the finer fibres allows greater retention of acid and offers a denser fibrous structure. This denser structure is probably insufficient to stop dendritic growth, but it can offer more protection than mixed-fibre, more open AGMs.

A very promising construction for cycling is the positioning against both electrodes of fine-fibre layers with a microporous polymer membrane in between. The membrane must have a sufficiently high volume porosity ($>$ 80%) and an optimum pore size (3 to 5 μm). Transport of oxygen gas across the separator system is essential for the proper functioning of the VRLA battery. Thus, it is critical that any polymer type of separator used in this application does not hinder this transfer. In summary, the average pore size must be sufficiently large to match as closely as possible the large openings which exist in AGM, and yet be sufficiently small and tortuous to offer greater resistance to lead deposits and growths.

6. Conclusions

Correct orientation brings another dimension to the characteristics of the AGM separator. The resulting advantages are reflected in improvement in the performance of VRLA batteries.

A finer overall pore structure is the first consequence of including within the multi-layered AGM separator a denser

layer with smaller pores which are created by finer glass fibres. Thus, maximum pores are reduced by a half and the average pores are also nearly halved.

The impact on the minimum pores is a reduction by one quarter.

The synergy which exists between fine and coarse glass fibres is detected in all the wicking characteristics of the multi-layered AGM. The coarse fibre layer will wick very quickly but to a limited height, whereas the finer side will carry the acid to greater heights. Thus, the individual advantages of the two types of fibre are combined. By virtue of the enhanced wicking properties, the critical process of filling VRLA batteries is improved and the particular problem of filling tall plates with tight plate spacing are lessened.

The advantages of orienting the AGM separator on the performance of the VRLA battery are manifested in terms of improvement in both high-rate performance and cycling ability. The technique involves placing different fibrous structures preferentially against each electrode. The open, high porosity, coarse-fibre structure creates an ideal reservoir to allow the free access of acid to the negative plates. This is a requirement for good high-rate discharge performance. By contrast, acid is more closely bound in the tight structure of the fine fibre layer and is suitable for the longer time delivery of acid that is needed during cycling. In addition, the denser nature of the fine-fibre layer offers some protection against lead deposits and growths.

In the special case of automotive batteries, the multi-layered AGM can be modified to provide an all-glass-fibre separator which can be sealed as a pocket and offer resistance to perforation at the plate edges.

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