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# AGM separator for 36 V batteries

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**Abstract**

The requirements of the environment, saving resources, and comfortableness for automobiles are constantly increasing year after year. There is a trend to reduce the fuel cost and exhaust gas by changing the power source to high voltage, shutting the engine off during stopping and replacing the hydraulics parts and compressor, etc. which are driven by the out-put of the engine, with electrically actuated parts. A valve-regulated lead-acid battery is considered to be promising as a power supply suitable for this 42 V electrical power system from the viewpoint of reliability and price, and is being actively studied. The 36 V-VRLA battery applied to the 42 V power supply system of the automobile demands higher out-put characteristics and longer life than a conventional automobile battery. Distances between electrodes are less than in a conventional battery and the pressure to assemble the electrodes will be higher than in the conventional battery. Mechanical short-circuit caused by physical force and chemical short-circuits caused by dendrite growth in this design of the battery could cause problems. We solved the problems by adding organic fibers for preventing the mechanical short-circuit and inorganic filler to restrain the chemical short-circuit to the AGM separator. This new AGM separator has twice the performance preventing mechanical short-circuits and five times for preventing chemical short-circuits in comparison with the separator in the past mixed with the fine glass fibers and coarse glass fibers. This AGM separator can restrain mechanical short-circuits and chemical short-circuits even if the thickness of the separator is decreased. This developed AGM separator should be of wide application because it can be applied to the VRLA battery demanded for the high out-put performance.


*Keywords:* 36 V-VRLA; Mechanical short-circuit; Organic fiber; Chemical short-circuit; Dendrite-short-circuit; Inorganic filler

## 1. Introduction

Most cars are equipped with a 12 V flooded lead-acid battery. Initially, the main purposes of using these batteries were for starting the engine, lighting the headlights and igniting the spark plugs. However, the number of electrical devices in the car has been steadily increasing, and dealing with the increasing electrical power consumption only using the 12 V power source is becoming difficult. Moreover, loads to the environment, such as the large consumption of oil, which is a limited resource, and global warming by the voluminously exhausted $CO_2$, etc. are increasing due to the rapid popularization of the car. Based on this information, the development of the hybrid vehicle, which is equipped with a 42 V power source, is now occurring as a means to achieve a car with low fuel consumption and a small exhaust gas volume. There is a trend to reduce the fuel cost and exhaust gas by changing the power source to high voltage, shutting the engine off during stopping and replacing the hydraulics parts and compressor, etc. which are driven by the out-put of the engine, with electrically actuated parts. A valve-regulated lead-acid battery is considered to be promising as a power supply suitable for this 42 V electrical power system from the viewpoint of reliability and price, and is being actively studied. The performances demanded for this battery are expected to be a higher out-put and longer lifetime compared with the conventional 12 V flooded lead-acid battery, because it will be used for assisting the engine power during the starting of the car, and running the air conditioner during stopping of the car, etc. In order to satisfy these required performances, it is obvious in view of the cell design that the electrode will be thinner, and the space between the electrodes will be reduced. Furthermore, it can be expected that the pressure required during placing of the electrode stack into the battery case will be increased compared to that of the conventional valve-regulated lead-acid battery in order to prolong battery life.

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## 2. Experimental

When a lead-acid battery is discharged by a high current, the reaction of the active material on the surface of the electrode takes priority over other areas, and the active material on the surface is primarily consumed. Moreover, it is reported that the consumption of the electrolyte, which is held on the surface of the electrode and in the surface layer of the separator, take priority over other areas [1].

Consequently, it is common to increase the reaction area by reducing the thickness of the electrode and increasing the number of electrodes per cell in order to improve the high rate discharge performance. In this case, because the internal resistance decreases and the distance between the electrode decreases, a further improvement in the discharge performance can be expected. Moreover, various methods for extending the battery cycle life can be enumerated such as: the technique relating to the electrode design (for instance, the optimization of the particle size and density of the positive electrode, and the selection of the active material additives), the technique relating to the grid designs (for instance, the optimization of the grid alloy composition) and the battery assembly conditions (for instance, increasing the assembly pressure), etc.

In the development of the separator for the 36 V valve-regulated lead-acid battery, we anticipated its design as follows compared with the conventional cell design:

(1) The space between the electrodes will become smaller, i.e. the separator will become thinner.
(2) The battery assembly pressure will be higher.

Based on these two points, we started our development to satisfy the following requirements:

(a) Mechanical strength equivalent to the conventional AGM (absorptive glass mat) level should be maintained.
(b) The function to inhibit the short-circuiting caused by dendrites that occurs when the space between the electrodes decreases should be maintained.
(c) The volume of the electrolyte retained in the separator should not be significantly decreased.
(d) A sufficient gas permeability to smoothly allow the recombination reaction should be maintained.
(e) The decrease in the pressure of the electrode stack caused by filling of the electrolyte should be small.
(f) The wicking rate for the electrolyte should not be remarkably slow.

### 2.1. Improvement in mechanical strength

As for the separator of the valve-regulated lead-acid battery, the following mechanical strength factors are required:

(1) Tensile strength.
  - It is required when unwinding the separator which is wound in the form of a roll.

(2) Puncture resistance (strength against local compressive stress).
  - In order to prevent minute projections from penetrating the separator.
  - In order to prevent the separator from compressive failure between the grids of the negative and positive electrodes.

When the thickness of the separator decreases, these strengths obviously decrease. In particular, the electrode stack is assembled at a high pressure in order to make the battery long-life, and it causes any projections on the surface of the electrode act to come under local compressive stress on the separator and cause a short-circuit by penetration. Consequently, it is required that the puncture resistance does not decrease even when the thickness of the separator decreases.

In this study, we investigated improving the puncture resistance by blending with organic fibers.

The apparatus shown in Fig. 1 was used to evaluate the puncture resistance. The maximum load when the needle penetrated the separator was measured. As shown in Fig. 2, the developed separator with a thickness of 1 mm, in which the organic fibers were blended, exhibited a puncture resistance equivalent to that of conventional type separator having a thickness of 1.7 mm.

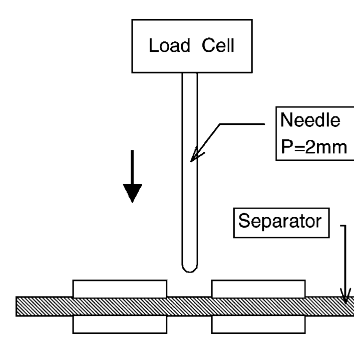


Fig. 1. Testing apparatus for evaluating puncture resistance.

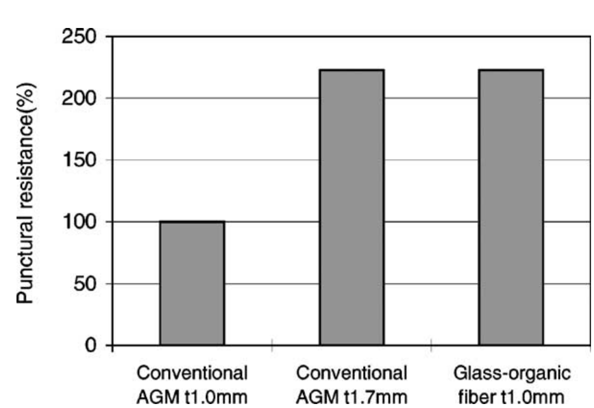


Fig. 2. Puncture resistance (needle penetration).

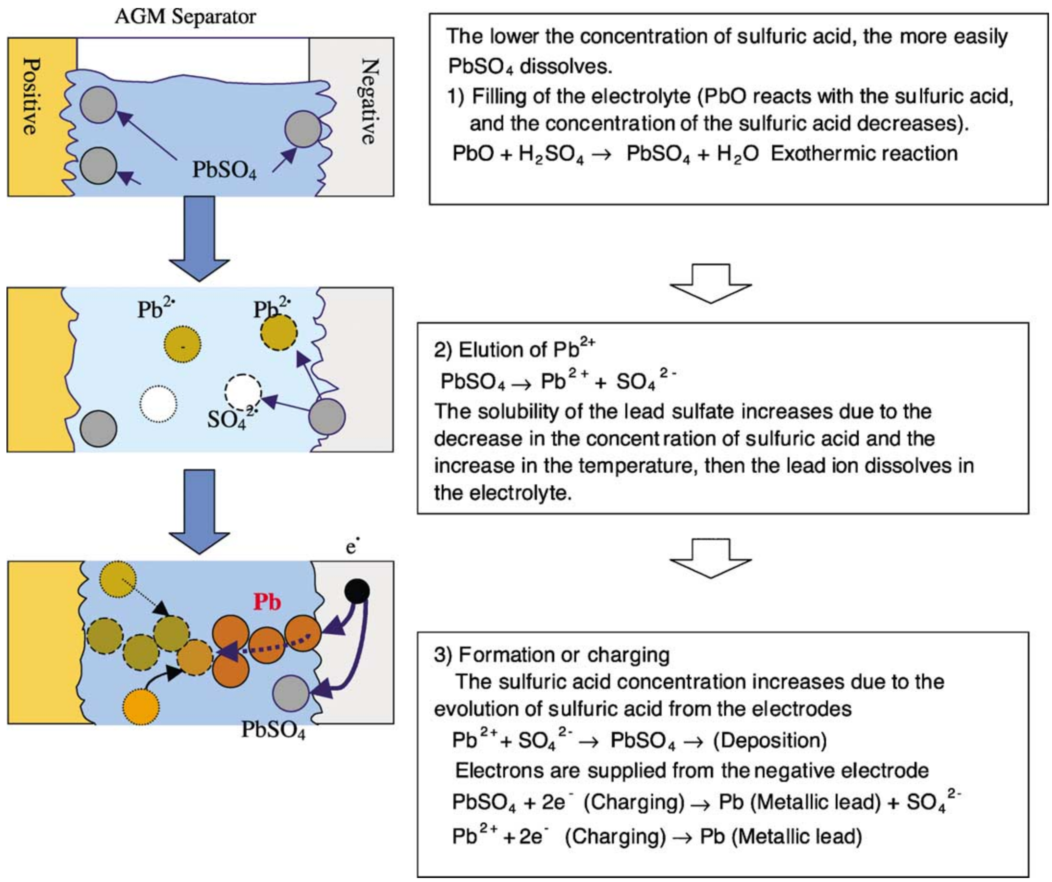


Fig. 3. Schematic illustration explaining the mechanism of generating dendrite-short-circuit.

### *2.2. Improvement in the performance to inhibit the occurrence of short-circuits caused by dendrites*

The high rate discharge performance is improved by decreasing the space between the electrodes. However, it increases the risk in which short-circuits easily occur during the forming process, and during charging after leaving it in over-discharge, which is called a ‘‘hydration short’’. The mechanism of these short-circuits is considered to be the one indicated in Fig. 3.

Because the occurrence of this short-circuit phenomenon is attributed to the fact that the solubility of lead sulfate is affected by the concentration of sulfuric acid, it is impossible to completely prevent it as long as the electrolyte is retained in the voids of the AGM separator. However, it is considered that the time required for growing metallic lead from the negative electrode to the positive electrode can be prolonged by finely partitioning the space where the electrolyte is retained and dispersing the place where the dissolution and deposition of lead sulfate occur. Concerning the method for evaluating the short-circuit inhibiting performance of the separator, a test method of passing an electrical current to the lead electrode in the saturated lead sulfate solution was reported by Tsuboi et al. [2]. This method measures the time until short-circuit by carrying out a mimetic electrolysis under the condition that excessive lead ions exist in the separator, thus precipitating metallic lead. In this experiment, the time until short-circuit was measured according to the thickness using two kinds of AGM separators with a different proportion of fine glass fiber. The results are shown in Fig. 4.

The following information has been understood from these results:

(1) The short-circuit time could be prolonged by increasing the proportion of fine glass fibers.
   - There is a possibility that the short-circuit time can be prolonged by using glass fibers with a smaller fiber diameter.

(2) The short-circuit time could be prolonged by increasing the thickness of the separator, that is, the space between the electrodes.
   - This conflicts with the improvement of the high rate discharge performance, which is the intended purpose.

(3) Almost no difference was observed in the slope of the graph of the separator thickness versus the short-circuit time for conventional type and the high-performance type.
   - When the short-circuit performance of a separator material is to be evaluated, it is possible to evaluate it by measuring the sample with a specific thickness.

It can be expected that it is possible to prolong the short-circuit time more than that of the high-performance type AGM separator, which consists of 100% fine glass fibers,

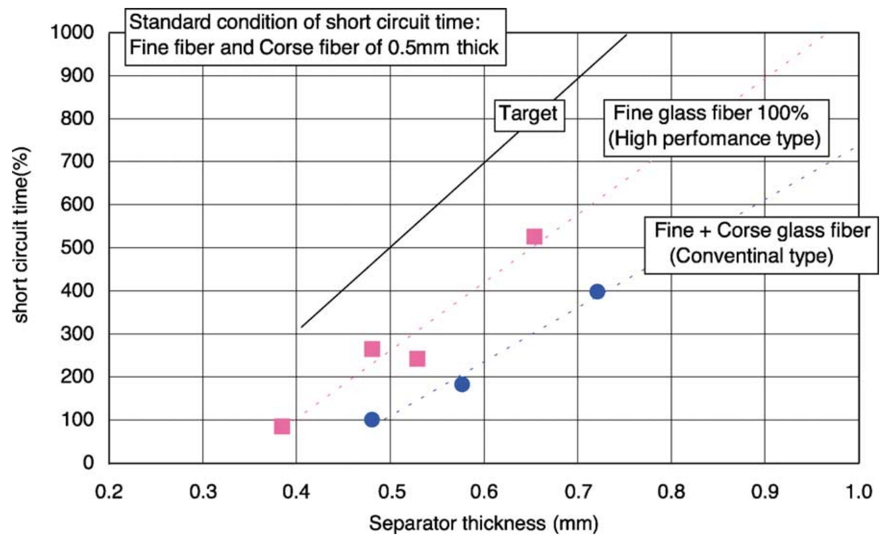


Fig. 4. Relation between thickness of separator and short-circuit time.

by blending the glass fibers with small diameter fibers. However, decreasing the fiber diameter is not a realistic method because it causes a remarkable increase in the manufacturing cost of the glass fiber, and remarkably decreases the manufacturing productivity of the AGM separator. Therefore, a different approach was required. Prolonging the short-circuit time was examined by blending a minute inorganic filler, which has an acid resistance property and oxidation durability equivalent to the glass fiber. Before starting the examination to prolong the short-circuit time, the targeted value of the short-circuit time was set to about five times conventional type or about twice the high-performance type with a separator thickness of 0.5 mm. This targeted value is indicated as the "targeted level" line in Fig. 4.

The relation between the inorganic filler content and the time until short-circuit is shown in Figs. 5 and 6. The following results have been determined:

(1) The time until short-circuit can be prolonged if the content of the inorganic filler is increased.
(2) The inorganic filler content which satisfies the targeted value of the short-circuit time can be achieved at level B.

Based on the results of this experiment, composition B was adopted as the inorganic filler content.

(1) After discharging, lead sulfate in the electrode dissolves while on open circuit.

$$PbSO_4 \rightarrow Pb^{2+} + SO_4{}^{2-}$$

(2) Lead sulfate is deposited on the surface of the separator component material.

$$Pb^{2+} + SO_4{}^{2-} \rightarrow PbSO_4$$

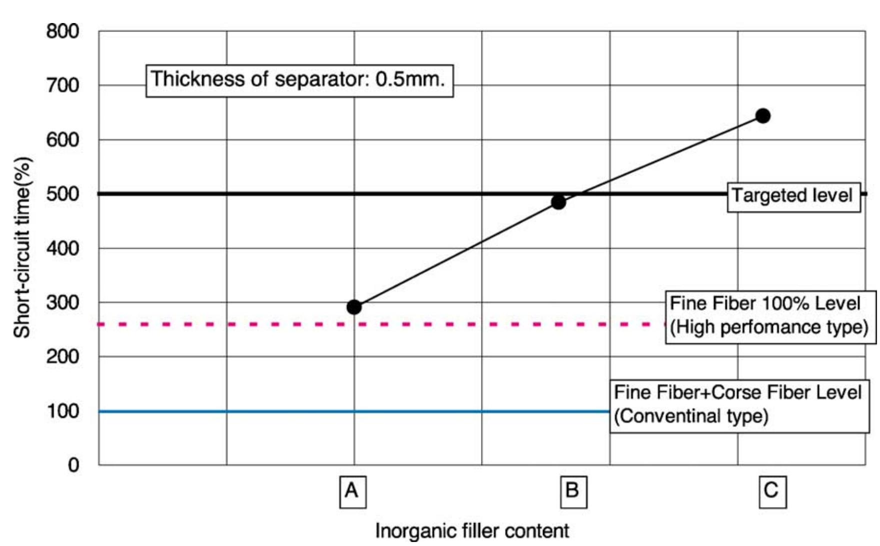


Fig. 5. Relation between inorganic filler content and short-circuit time.

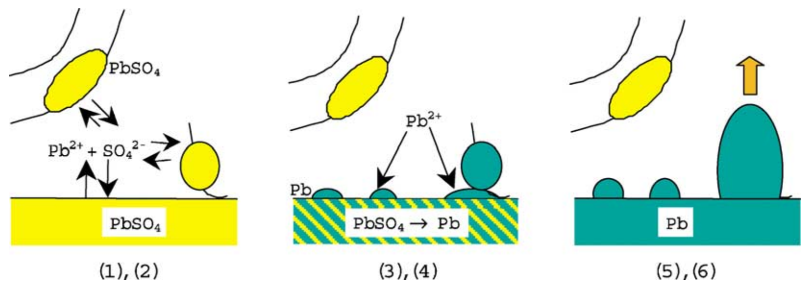


Fig. 6. Assumed mechanism for improvement in short-circuit time by blending inorganic filler.

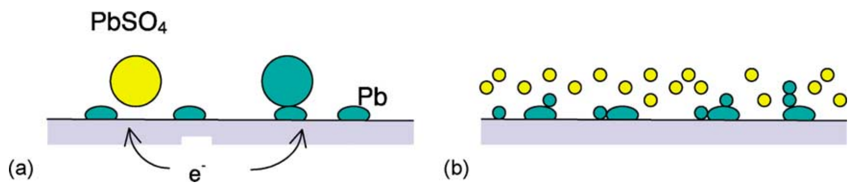


Fig. 7. Schematic illustration of metallic lead deposition on the conventional glass fiber separator and developed separator. (a) Conventional glass fiber separator; (b) developed separator (inorganic filler blended).

(3) When a current is applied, lead is deposited on the surface of the negative electrode.

$$Pb^{2+} + 2e^- \rightarrow Pb$$

(4) Lead sulfate, which precipitated near the negative electrode, is reduced and becomes lead.

$$PbSO_4 + 2e^- \rightarrow Pb + SO_4{}^{2-}$$

(5) A lot of minute dispersed crystals gradually grow during the initial stage [formation of crystalline nucleus].
(6) When a crystal more than a certain size is formed, it begins to selectively grow [crystal growth].
   ○ Starting of the dendrite growth.

Fig. 7 shows the comparison of the deposition processes of metallic lead between the conventional separator (7a) and the newly developed separator (7b).

When the inorganic filler is blended, the electrolyte retained in the separator is subdivided, and the finely dispersed lead sulfate precipitates uniformly. Therefore, it is considered that the time until reaching the counter electrode (i.e. short-circuit time) was prolonged because the metallic lead grows in a dispersed form on the surface of the electrode.

### 2.3. Gas permeability and wicking rate

Because the reaction in the valve-regulated lead-acid battery is accompanied by the oxygen recombination reaction, gas permeability is required for the separator. When the inorganic filler is blended in order to extend the short-circuit time, the gas permeability decreases, and also the wicking time decreases. These properties are significantly affected by the pore size distribution of the separator. In order to improve these problems, the diameter of the glass fiber was optimized, and the above listed properties were adjusted to the level of a conventional type separator.

### 2.4. Wet-pressure

The electrode stack is normally built into the battery case using high pressure in order to make the lead-acid battery long-life. Therefore, a stiff separator is desirable. On the other hand, it is known that the pressure decreases when the electrolyte is absorbed after the AGM is pressed under a certain pressurizing force. It is reported that this effect increases as the diameter of the glass fiber increases [3]. In order to extend the battery life, it is effective to make the separator stiff in order to easily press it with high pressure, and to make the pressure drop due to the absorption of sulfuric acid small. The diameter requirement of the glass fiber is in conflict with these two variables as shown in Table 1. By blending the inorganic filler, the wet-pressure of the developed separator was maintained at the conventional level while increasing the stiffness of the separator.

Table 1
Relations among glass fiber diameter of separator, wet-pressure, compression property and tensile strength

| | | | |
|---|---|---|---|
| Fiber diameter | Fine | ←→ | Coares |
| Wet-pressure | Low | ←→ | High |
| Compression | High | ←→ | Low |
| Tensile strength | High | ←→ | Low |

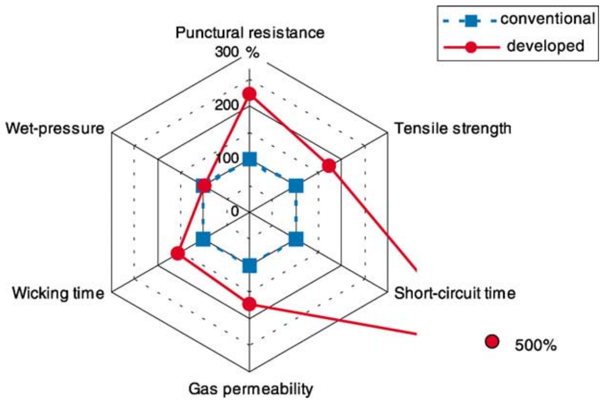


Fig. 8. Comparison between developed separator and conventional separator.

## 3. Results

The performances of the developed separator and conventional type separator are compared in Fig. 8. As shown in Fig. 8, we have solved the problems expected for the development of the separator by decreasing the thickness of the separator. The mechanical strength required for assembling the battery was doubled. Furthermore, the gas permeability and the liquid absorbing time were equivalent to the conventional separator while the short-circuit time increased by about five times.

## 4. Discussion

The properties of the developed separator are summarized as follows in comparison with the conventional type separator, which is a mixed product of fine glass fiber and coarse glass fiber:

- The puncture resistance and the tensile strength are about twice those of the conventional one, and the mechanical (physical) short-circuit during the assembly process of the electrode stack can be reduced. Moreover, the thickness of the separator can be reduced because the mechanical strength is doubled.
- Because the short-circuit time is improved by about five times (about twice that of a high-performance separator), the possibility of a chemical short-circuit occurring during the container formation is low even when applied to a battery which has a small space between the electrodes. Moreover, the possibility of a minute short-circuit occurring during the charge and discharge cycle testing becomes low, and there is a possibility that the battery life can be prolonged.
- The gas permeability, the wicking time, and the wet-pressure are equivalent to the conventional levels.

Currently, these developed products were used in cells and they are being tested by multiple battery manufacturers. Moreover, it is considered that the separator based on the concept of this development is also applicable to cylindrical lead-acid batteries because it has a high strength even if the thickness is small. Furthermore, this separator is considered to also be applicable to not only the valve-regulated lead-acid battery for cyclic use, but also to the valve-regulated lead-acid battery as a UPS power source where the high rate discharge performance is important.

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