

Effect of antimony on premature capacity loss of lead/acid batteries

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Abstract

Lead/acid batteries with antimony-free positive grids have a tendency to lose discharge capacity early in deep-discharge cycling. In this study, the effect of antimony in positive active-material (PAM) on the performance of batteries with Pb–Ca–Sn alloy grids is investigated. The corrosion layer of Pb–Ca–Sn positive grids with conventional leady oxide discharges before the PAM discharges. With Pb–1wt.%Sb leady oxide, however, the corrosion layer of positive grids of the same composition does not discharge so much, and antimony is observed in the corrosion layer. These results suggest that the antimony-containing corrosion layer discharges with difficulty and, thus, the active material discharges more readily than the corrosion layer and a passivation layer does not form at the grid/active-material interface. This suggestion is also supported by parallel discharge tests of anodic corrosion layers on lead and Pb–Sb alloys in dilute sulfuric acid. The corrosion layer of the Pb–Sb alloy has a tendency to discharge after that of pure leads in a parallel circuit. © 1997 Published by Elsevier Science S.A.

Keywords: Lead/acid batteries; Leady oxide; Passivation; Corrosion layers; Antimony; Premature capacity loss

1. Introduction

In recent years, there has been an increased use of lead/acid batteries that do not require topping up while in use. Generally, the positive grids of such lead/acid batteries employ lead–calcium (Pb–Ca) alloys that contain virtually no antimony (Sb). Lead/acid batteries using these Pb–Ca alloys are superior to conventional lead/acid batteries using Pb–Sb alloys from the viewpoint of no requirement of maintenance, which is due to factors that include a small amount of self-discharge or loss of electrolyte. On the other hand, lead/acid batteries using these Pb–Ca alloys in their positive grids sometimes lose capacity sooner than their Pb–Sb alloy counterparts during deep-discharge cycling [1,2].

This premature capacity loss (PCL) is said to be caused by the formation of a passivation layer (barrier layer) at the interface between a positive grid and its active material. The passivation layer is sometimes said to be a closely structured PbSO₄ layer (high-resistance layer) formed at the grid active-material interface [3], or lower oxides of lead, such as PbO, that are generated in a high-pH environment [4–8].

The reason why PCL hardly occurs in lead/acid batteries with Pb–Sb alloys seems to be that the antimony in the

positive grids somehow affects the interface between the grid and active material, as well as the active material itself [9–11]. There is a report that even when Pb–Ca alloys are used in positive grids, the addition of antimony compounds to the positive active-material is effective in improving cycle-life performance [12]. Thus, it appears that adding antimony to active material effectively retards PCL.

One way to add antimony to the active material involves the addition of antimony compounds to paste as mentioned above. It seems, however, that using leady oxide made from a Pb–Sb alloy makes it possible to distribute more evenly the antimony throughout the active material.

This report discusses the effects of antimony on cycle-life performance, with pasted plates manufactured using leady oxides made from Pb–Sb alloys instead of manufactured by adding an antimony compound to the active material, as well as the mechanism by which antimony improves cycle-life performance.

2. Experimental

2.1. Batteries

Five types of positive plate were prepared (Table 1) in order to study the effects of antimony on cycle-life perfor-

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Table 1
Positive plates

No.	Leady oxides	Grid alloys
1	Pure lead	Pb–0.10wt.%Ca–1.0wt.%Sn
2	Pb–0.01wt.%Sb	Pb–0.10wt.%Ca–1.0wt.%Sn
3	Pb–0.1wt.%Sb	Pb–0.10wt.%Ca–1.0wt.%Sn
4	Pb–1wt.%Sb	Pb–0.10wt.%Ca–1.0wt.%Sn
5	Pure lead	Pb–2.2wt.%Sb–0.25wt.%As

mance. The leady oxides were made from 100% lead (pure lead), a Pb–0.01wt.%Sb alloy, a Pb–0.1wt.%Sb alloy, and a Pb–1wt.%Sb alloy. All the oxides were produced in a ball mill. The amount of antimony in each leady oxide was the same as in the corresponding Pb–Sb alloy, and particle-size distributions were also nearly the same in all cases.

The four leady oxides were used to prepare pastes with densities of about 3.8 g cm^{-3} . These were applied to grids made from Pb–0.10wt.%Ca–1.0wt.%Sn alloy and with dimensions: 110 mm high, 108 mm wide, and 1.5 mm thick. The paste made with pure leady oxide was also applied to grids made from Pb–2.2wt.%Sb–0.25wt.%As alloy for the purpose of comparison. The plates were cured for 72 h at 35 °C.

Six positive plates were used, along with seven negative plates with ordinary grids of Pb–Ca alloy, to assemble single-cell batteries with 36 Ah (5 h rate) capacity. The batteries were flooded-type batteries made by container formation and adjustment of the electrolyte to a specific gravity of 1.28 (at 20 °C).

2.2. Tests

The following tests were conducted in accordance with the method prescribed in *JIS D 5301* (Lead/Acid Batteries for Automobiles).

1. *Initial capacity test*. 5 h rate discharge: (i) discharge current: 7.2 A, final voltage: 1.75 V, temperature: 25 °C; (ii) high-rate discharge: discharge current: 150 A, final voltage: 1.00 V, temperature: –15 °C.

Table 2
Initial capacity ^a

No.	Positive plates		7.2 A rate capacity at 25 °C (Ah)	150 A rate capacity at –15 °C (Ah)
	Leady oxides	Grid alloys		
1	Pure lead	Pb–Ca–Sn	38.4	12.1
2	Pb–0.01wt.%Sb	Pb–Ca–Sn	38.8	12.0
3	Pb–0.1wt.%Sb	Pb–Ca–Sn	39.5	12.4
4	Pb–1wt.%Sb	Pb–Ca–Sn	37.3	11.6
5	Pure lead	Pb–Sb–As	38.1	11.7

^a Test cell: flooded type, 36 Ah (5 h), and test method: *JIS D 5301*.

2. *Water consumption test* (measuring rate of the weight loss during constant-voltage charging). Charging voltage: 2.40 V, charging period: 28 days, and temperature: 40 °C.
3. *Self-discharge characteristics test* (measuring rate of decrease in high-rate discharge capacity when battery is left standing). Time left standing: 28 days, and temperature: 40 °C.
4. *Heavy load cycle-life test*. (i) Charge/discharge conditions: discharging: 20 A for 1 h, charging: 5 A for 5 h, temperature: 40–45 °C. (ii) Capacity test during cycle life test (performed every 25 cycles): discharge current: 20 A, final voltage: 1.70 V, temperature: 43 °C. (iii) Cycle-life determination criterion: under 50% of initial capacity.

3. Results

3.1. Initial capacity

Table 2 shows the initial capacities of the batteries with different amounts of antimony in the leady oxides used to make their positive plates. There were only minor differences among the low-rate and high-rate discharge capacities of the batteries. This indicates that the presence of antimony in the positive-plate leady oxides exerts little effect on the initial capacity.

3.2. Maintenance-free characteristics

The results of the water consumption and self-discharge tests are presented in Table 3. Up to an antimony content of 0.1 wt.% in the positive-plate leady oxide, there was little effect on the self-discharge characteristics. As a consequence, these batteries would require less maintenance than batteries using Pb–Sb–As alloys. When the antimony content reached 1 wt.%, there was a significant worsening of the water consumption and self-discharge characteristics of the batteries. This makes the batteries

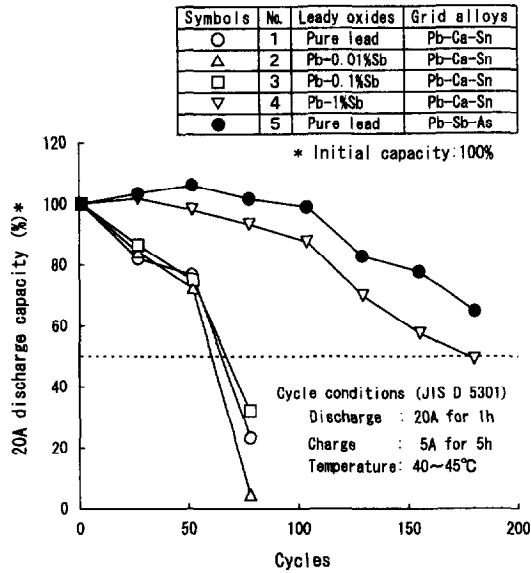


Fig. 1. Effect of antimony in leady oxide on cycle life.

inferior in maintenance-free characteristics to those using Pb-Sb-As alloys.

3.3. Cycle-life performance

The results of the JIS heavy-load cycle-life test are given in Fig. 1. Although the battery using Pb-Sb-As alloy in its positive grids retained 65% of its initial capacity even after 175 cycles, when Pb-Ca-Sn alloy was used, the battery with no antimony in positive leady oxide, as well as those with 0.01 wt.% and 0.1 wt.% antimony, was spent after 70 cycles (they had under 50% of their initial capacity). By contrast, batteries with 1 wt.% antimony content kept over 50% of their initial capacity up to 175 cycles. Thus, they had over twice the cycle-life performance of batteries with no antimony.

Therefore, even if Pb-Ca-Sn alloys are used in positive grids, batteries with leady oxide containing about 1 wt.% antimony will offer cycle-life performance equivalent to that of batteries using Pb-Sb-As alloys.

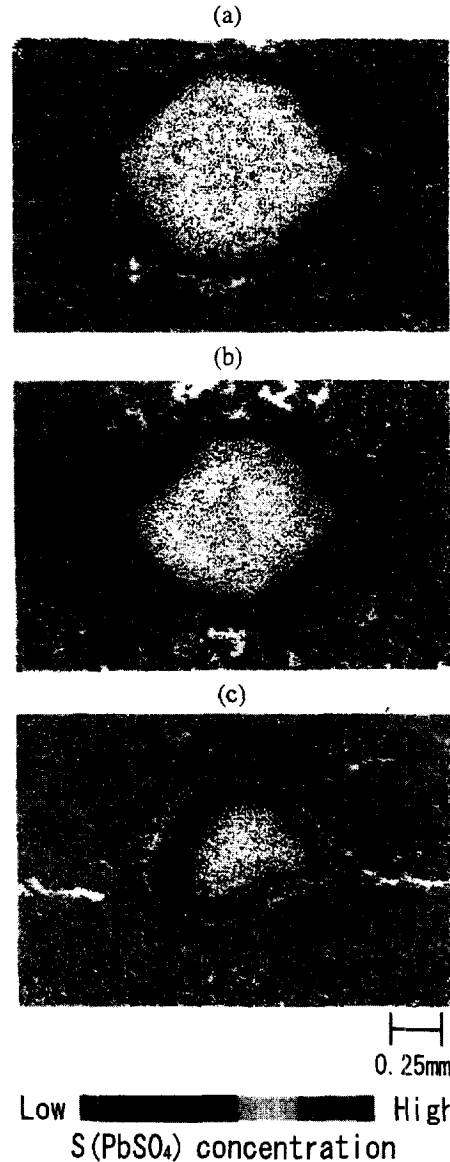


Fig. 2. Lead sulfate distribution of discharged positive plates after cycling test: (a) No. 1: pure lead oxide, Pb-Ca grid, after 75 cycles; (b) No. 4: Pb-1wt.%Sb oxide, Pb-Ca grid, after 175 cycles, and (c) No. 5: pure lead oxide, Pb-Sb grid, after 175 cycles.

Table 3
 Maintenance-free characteristics ^a

No.	Positive plates		Water consumption during charge at 40 °C (g/(cell day))	Self-discharge rate at 40 °C ^b (%/day)
	Leady oxides	Grid alloys		
1	Pure lead	Pb-Ca-Sn	0.25	0.75
2	Pb-0.01wt.%Sb	Pb-Ca-Sn	0.26	0.79
3	Pb-0.1wt.%Sb	Pb-Ca-Sn	0.33	0.82
4	Pb-1wt.%Sb	Pb-Ca-Sn	1.91	1.98
5	Pure lead	Pb-Sb-As	1.48	0.92

^a Test method: JIS D 5301.

^b Decrease of 150 A rate capacity.

4. Discussion

4.1. Examination of positive plates after cycle-life tests

The positive plates were discharged after the cycle-life test and the distribution of lead sulfate (S) was determined in order to examine the mechanism by which antimony contained in positive leady oxide improves the cycle-life performance of batteries that use Pb–Ca–Sn alloys in their positive grids. The observation was carried out with a Model EPMA-C1 Electron Beam Microanalyzer and a high-speed mapping device (H II) made by Shimadzu Corporation.

The distribution of lead sulfate in the cross sections of

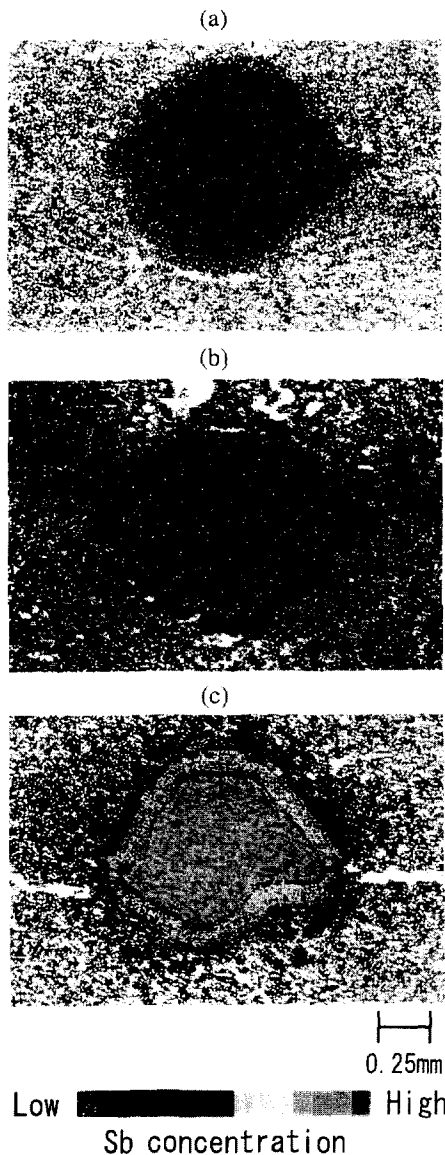


Fig. 3. Antimony distribution of discharged positive plates after cycling test. (a) No. 1: pure lead oxide, Pb–Ca grid, after 75 cycles; (b) No. 4: Pb–1wt.%Sb oxide, Pb–Ca grid, after 175 cycles, and (c) No. 5: pure lead oxide, Pb–Sb grid, after 175 cycles.

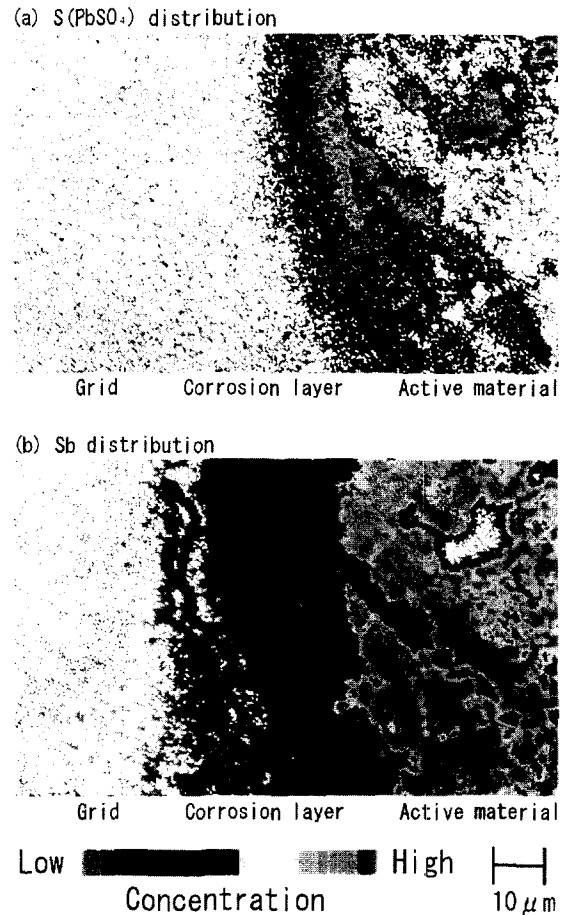


Fig. 4. Lead sulfate and antimony distribution of discharged positive plates after cycling test, after 175 cycles: No.4: Pb–1wt.%Sb oxide, Pb–Ca grid.

discharged positive plates is shown in Fig. 2. When a Pb–Ca–Sn alloy was used for the positive grid, plates made from leady oxide that did not contain antimony underwent localized discharging at the interface between the grid and active material, while the active material itself was hardly discharged at all. This indicates that because the grid/active-material interface discharges before any other part and formed a passivation layer (barrier layer), the active material itself is unable to discharge, and the battery is unable to provide adequate discharge capacity.

By contrast, plates with leady oxide that contained 1 wt.% antimony discharged less at the grid/active-material interface than in the active material itself, so that all the active material was discharged. Moreover, positive plates with Pb–Sb–As alloy grids exhibited similar behaviour. These experiments show that antimony, either in active material or in grids, limits discharge at the grid/active-material interface.

Antimony distribution in cross sections of positive plates was shown in Fig. 3. The locations are the same as in Fig. 2. It is found that in plates with leady oxide that contained 1 wt.% antimony, the antimony was preferentially concen-

trated at the grid/active-material interface. In addition, the corrosion layer on Pb–Sb–As alloy grids was thicker than that in Pb–Ca–Sn alloy grids, and there was considerable antimony in the corrosion layer.

Next, the relationship between the antimony distribution and the discharge state of the corrosion layer was analyzed. This involved examining the grid/active-material interface at higher magnification and determining the distributions of antimony and lead sulfate in positive plates made from leady oxide with 1 wt.% antimony. The lead sulfate distribution in Fig. 4(a) and the antimony distribution in Fig. 4(b) show that antimony is distributed in a disproportionately large quantity in the corrosion layer of the Pb–Ca–Sn alloy grid, which was not supposed to have contained any antimony, and that the location in which antimony is disproportionately present is hardly discharged at all.

Even though antimony was evenly distributed in the positive active-material when the plates were made, the element was disproportionately distributed at the grid/active-material interface (corrosion layer) after the cycle-life test. This is because antimony migrates to the interface during charge/discharge cycling in the form of anions such as $[\text{SbOSO}_4]^-$ and $[\text{Sb}_3\text{O}_9]^{3-}$, as discussed by Dawson et al. [13]. Corrosion layers containing antimony discharge only with difficulty. Therefore, it appears that this characteristic limits the formation of a barrier layer at the grid/active-material interface and, thereby, improves cycle-life performance.

4.2. Characteristics of corrosion layers containing antimony

Analysis of positive plates after the cycle-life test suggests that the presence of antimony in the corrosion layer limits the discharge of the layer. Therefore, the following experiments were performed on the discharge characteristics of corrosion layers containing antimony. A schematic diagram of the cell used in the experiment is shown in Fig. 5. The test electrodes consisted of a Pb plate and a Pb–2.2%Sb alloy plate, both of which were 25 mm high, 20 mm wide, and 2 mm thick. The counter electrodes were

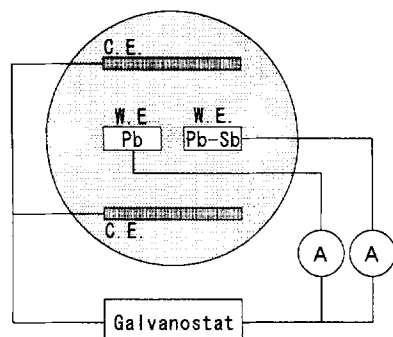


Fig. 5. Schematic diagram of test cell.

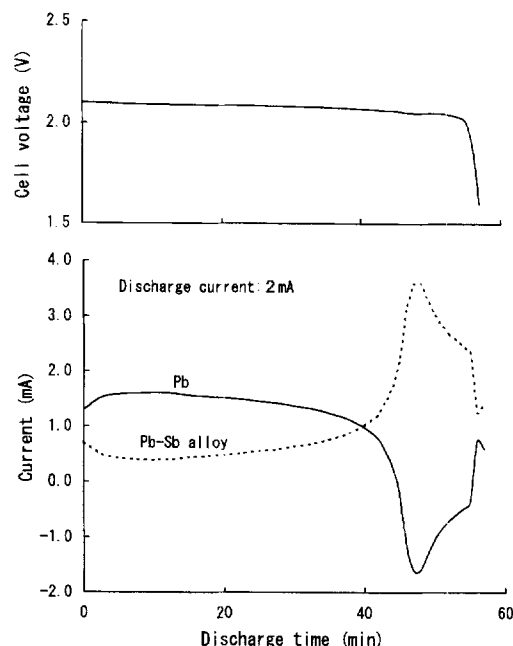


Fig. 6. Current distribution during parallel discharge of corrosion layers on Pb and Pb–Sb alloy electrodes.

negative plates with a much larger capacity than the test electrodes. The electrolyte was 5 M (sp. gr. 1.285 at 20 °C) dilute sulfuric acid.

Pre-treatment of the test electrodes comprised smoothing their surfaces with emery paper (#220, #500, and then #1000), and reducing the electrodes' surfaces in the electrolyte (–1.0 V versus Pb/PbSO₄, 10 min). The Pb electrode and the Pb–Sb electrode were then subjected to anodic oxidation for 25 and 60 min, respectively, at a current density of 0.05 A cm^{–2}. The reason for treating the two electrodes to different anodic oxidation times is to give their corrosion layers the same discharge capacity. As shown in Fig. 5, after anodic oxidation, the two test electrodes were connected in parallel, discharged at a constant current (2 mA at 25 °C), and then the discharge current from each electrode was measured with zero resistance ammeters.

The current from each electrode and the cell voltage are shown in Fig. 6. During the initial discharge phase, the discharge current of the Pb electrode was larger than that of the Pb–Sb alloy electrode, and this continued until the Pb electrode was nearly completely discharged. When the Pb electrode finished discharging, however, the discharge current of the Pb–Sb alloy electrode became rapidly larger. These experimental results show that a corrosion layer containing antimony discharges with greater difficulty than a corrosion layer without antimony. The reason for the negative current value after the Pb electrode finishes discharging is thought to be that the oxidation of metallic lead under PbSO₄ layer occurs, resulting in the formation of lead monoxide. In summary, adding antimony to active

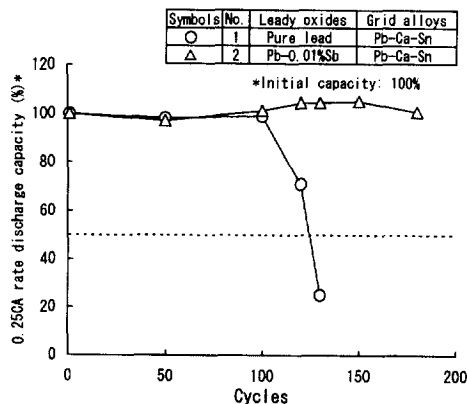


Fig. 7. Effect of antimony in positive active-material on cycle life of VRLA batteries with absorptive microglassfiber mat. Batteries: 2 V, 7 Ah. Cycle conditions: discharge: 0.25 C to 1.0 V; charge: 0.25 C/2.5 V for 10 h, and temperature: 25 °C.

material improves the cycle-life performance of batteries that use positive grids made of Pb–Ca–Sn alloy.

Antimony in positive active-material is initially distributed throughout an entire plate, but after repeated charging and discharging, the antimony migrates to the vicinity of the grid and is captured in the corrosion layer at the grid/active-material interface. The antimony-containing corrosion layer by nature discharges with difficulty. Thus, the active material discharges more readily than the corrosion layer, and a passivation layer does not form at the grid/active-material interface. The reason why the antimony-containing corrosion layer is discharged with difficulty is thought to be that its discharge potential is less noble than that of a layer with no antimony [14,15].

When Pb–Sb–As alloy grids are used for positive plates, the presence of much antimony in the corrosion layer keeps that layer from discharging, which is the reason for excellent cycle-life performance.

5. Conclusions

The effects of antimony on cycle-life performance are studied for positive plates with alloy grids and pastes with leady oxides that contain a small quantity of antimony. Results show that if the amount of antimony is about 1 wt.%, PCL will not occur, and that such a battery offers the same excellent cycle-life performance as those of

batteries that employ Pb–Sb–As alloys. To determine the reason for this, the distribution of both antimony and lead sulfate has been investigated, along with the discharge behaviour of the corrosion layer. The studies show that there is little lead sulfate in locations with much antimony, and that antimony-containing corrosion layers discharge with difficulty.

With flooded-type batteries, experiments demonstrate that using a Pb–Sb alloy for the positive leady oxide material is an effective way to improve the cycle-life performance of positive plates that employ grids made with a Pb–Ca alloy. While 1 wt.% of antimony is effective, it also considerably increases the need for maintenance. Another test with valve-regulated lead/acid batteries, however, has shown that only 0.01 wt.% of antimony is effective on cycle-life performance as shown in Fig. 7. The differences between the results given in Figs. 1 and 7 appears to originate not only from a different battery construction but also from different test conditions. Further studies are required to determine the optimum amount of antimony in valve-regulated lead/acid batteries under various conditions.

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