

# TIN-SILVER-CALCIUM ALLOYS FOR LOW CORRODING VRLA POSITIVE PLATES

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**Abstract:**

In this work we present the life test procedures and results of our search for a lead alloy grid having a substantially lower corrosion rate than that we presently employ. Our interest was in investigating the alloying elements of tin and silver. The factorial design matrix employed required nine alloy compositions to be tested. The alloy element concentrations varied within the following limits,

- Calcium 0.075%
- Silver 0.005 to 0.033%
- Tin 0.30 to 2.0%

The life tests were performed at 60°C and at a positive plate polarization at this temperature of 130 millivolts. The results of the tests showed a decrease in the plate growth rate of 3 to 4 times for alloys containing 2% tin compared to that for 0.30% tin. The alloying of silver with tin and calcium had little if any effect on the plate growth rate.

Optical microscopic examination of the various gravity cast alloys found them to be similar in lead crystal size and orientation. Also, the PbO<sub>2</sub> corrosion layer at the higher tin concentrations showed less inter-granular penetration and a thinner corrosion layer for the same time on test.

Tafel measurements were made to determine the relative alloy electrochemical characteristics. In addition to the plate growth tests each cell was discharged and the correlation of capacity to plate growth established. As expected the capacity loss rate was greatest for those faster corroding grid alloys.

This program included the testing of actual VRLA production batteries to determine battery life with 2% tin in the grids. Agreement between the plate test cells and actual batteries was not good and requires further investigation.

**Introduction**

The search for a slower corroding alloy was directed toward determining the effect of silver and tin on the rate of positive plate grid growth.

Silver has been claimed to decrease the rate of lead corrosion<sup>1</sup> but literature was not found that quantified this result. In the United States this element is a component of the lead alloy purchased from some lead suppliers. Silver at 50ppm is an impurity in the lead that would be too

costly to totally remove. It has also been stated that elevated concentrations of silver will embrittle lead to cause its fracture at relatively low stress levels.

The benefits of tin have been investigated and presented in other works<sup>ii</sup>. The thrust of this work was to determine if a specific combination of tin and silver existed that would provide a more corrosion resistant lead alloy.

**Test Cells**

**Experimental**

Employing a three by three matrix yielded nine grid alloy compositions, all containing 0.075% Calcium. The lead alloys were supplied by NOVA Pb Inc. of Quebec, Canada, as shown in the following table.

TABLE 1

Tin & Silver Contents, %		
GRID 1 0.30 Sn  0.005Ag	GRID 2 1.0 Sn  0.005 Ag	GRID 3 2.0 Sn  0.005 Ag
GRID 4 0.30 Sn  0.015 Ag	GRID 5 1.0 Sn  0.015 Ag	GRID 6 2.0 Sn  0.015 Ag
GRID 7 0.30 Sn  0.033 Ag	GRID 8 1.0 Sn  0.033 Ag	GRID 9 2.0 Sn  0.033 Ag

The 15x15 centimeter grids were 2.6 mm thick, cast, pasted and cured as in our normal manufacturing processes. The plates on average weighed 347.5 +/-3.4 grams. Each test cell was composed of three positive and four negative plates. A micro porous rubber separator was placed between the plates to prevent shorting. The construction was such that the test cell could readily be taken apart for plate growth measurements and reassembled.

To insure uniform plate voltage distribution each cell was flooded with 1.30 specific gravity sulfuric acid. The

test temperature was 60°C and positive plate polarization was maintained at 130 mV.

The cells were removed from heat approximately every twenty days, cooled and discharge at the 5-hour rate. Upon recharge each positive plate was measured in the vertical and horizontal growth directions. The growth measurements in each direction were averaged and are reported in the following discussion and results section.

In addition to the above, sections of the new and aged grids were placed under metallurgical examination for crystal morphology and oxide corrosion character.

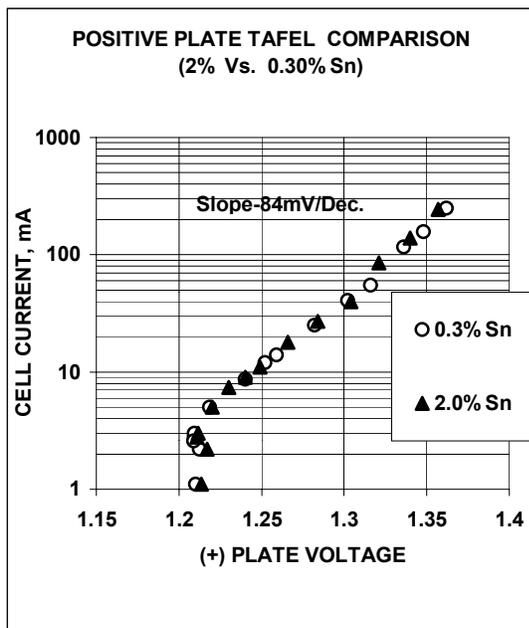


Figure 1

**Results and Discussion**

Sections of the newly cast grids were mounted in epoxy, polished and etched for microscopic analysis. From these test samples it was observed that there was no difference in the crystal size or orientation for the various alloys under study. The as formed and after float charge capacity of the nine cells was determined at the 5-hour rate of discharge to 1.75VPC with the average capacity at 5.5+/-0.10 hours.

A second set of cells was built to compare the positive plate Tafel characteristics of the various alloys. The data was taken after one discharge and a comparison is shown

in Figure 1 for the plates of the most extreme alloy compositions (Grids 1&9). Although the Tafel slopes and intercept or exchange currents are the same no information could be gained as to the corrosion currents or their relationships. The negative plate state of charge is dependent on the positive plate corrosion current. Therefore, a change to a lower corroding alloy should always be made with knowledge of its affect on the negative plate state of charge.

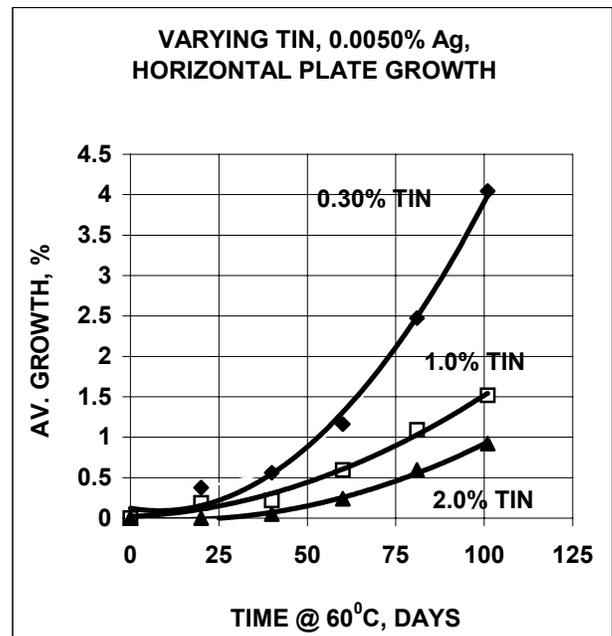


Figure 2

The growth of the various alloyed grids at the above test parameters is shown in Figures 2, 3, 4. The plots in these figures depict the effect of tin and silver additions on plate growth.

In figure 2 the effect of tin on horizontal plate growth is shown. Figure 3 depicts the vertical growth of the same plates. Both charts show the growth of tin alloys containing 0.005% Ag and 0.075%.

The horizontal growth rates in Figure 2 are seen to dramatically decrease with increasing tin content. An increase in tin from 0.30% to 2.0 percent is shown to decrease the growth by approximately 4 times.

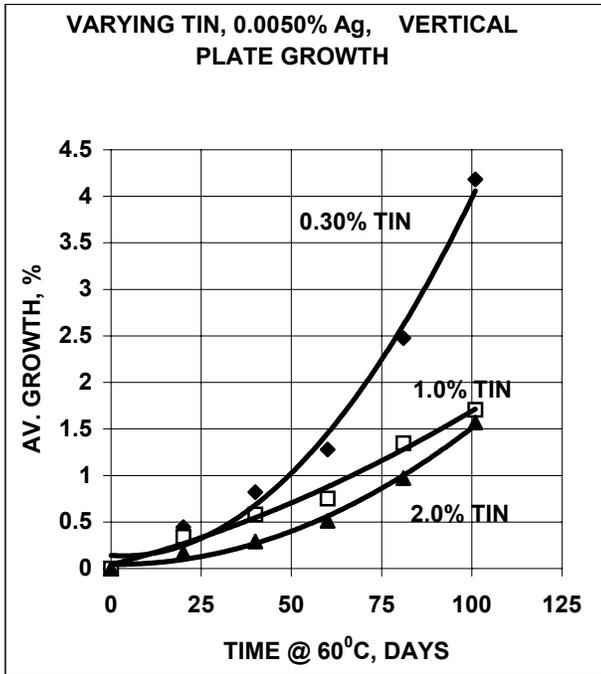


Figure 3

Figure 3 is for plate growth in the vertical direction. Growth in this direction also shows significant reductions in rate with increasing tin content. Although not shown the other alloy combinations also depict the beneficial effects of tin.

Plate instead of grid growth was studied because of the result of our previous experiments. In these works it was found that plate growth was three times faster than that of the grid.

In figures 4 and 5 the effect of silver on the rate of plate growth is shown. The growth data is for the alloys containing 0.30 and 1.0% tin. The graphs in both figures show the contribution of silver in lowering plate growth to be minimal if at all. Similar results were obtained for silver in alloys with 2% tin.

Prior to the plate growth measurements the cells were cooled to room temperature, charged and discharged at the 5-hour rate to 1.75 volts. With each cell having one more negative than positive plate the resultant cell capacity should be limited by the positive plate. Reference electrode readings during discharge verified the expected result. The cell capacity shown is the percent loss of the aged cell capacity from that when new.

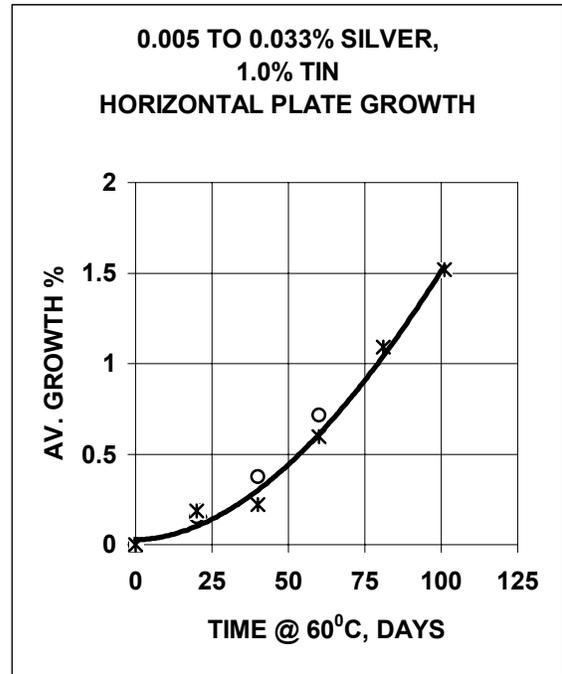


Figure 4

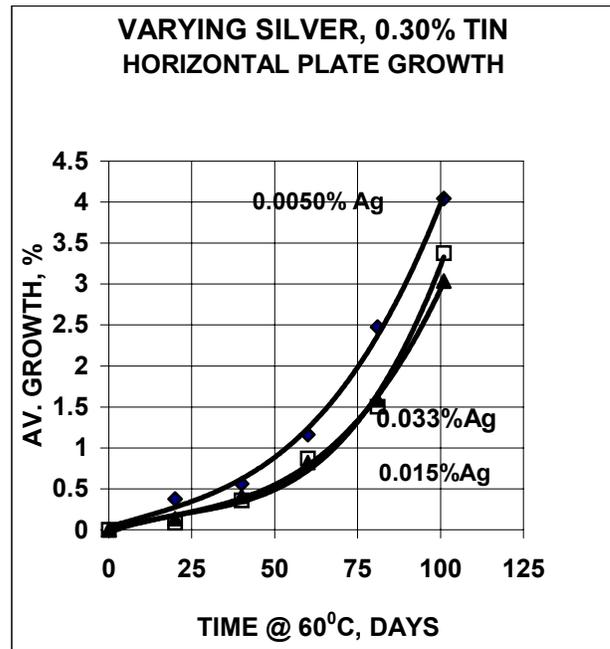


Figure 5

The graph in Figure 6 depicts the loss of capacity with aging at 60°C for tin alloys containing 0.005% silver. In this figure the rate of capacity fall off is obviously a function of the tin concentration. This correlation is not unexpected when it is viewed with the plate growth data

shown in figure 2. Figures 2 and 6 indicate that after 2 to 4% plate growth capacity life is ended.

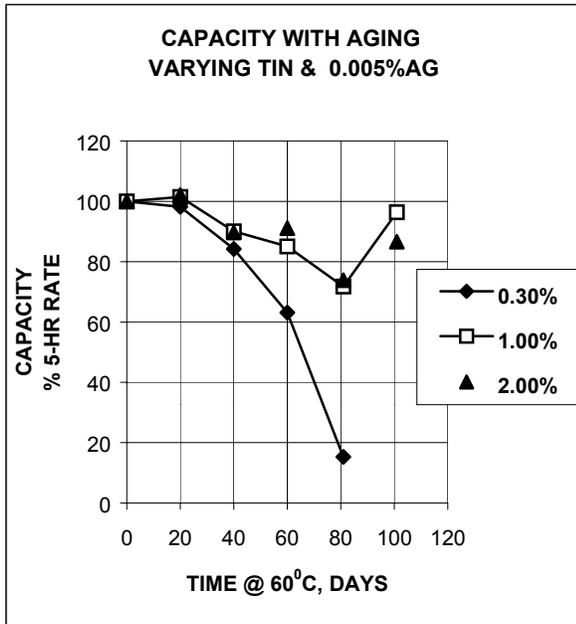


Figure 6

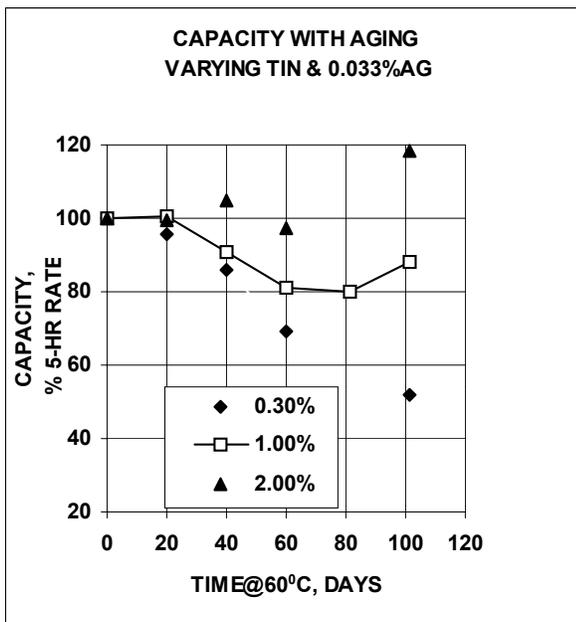


Figure 7

In Figure 7 is the plot for the highest silver concentration of 0.033% and it is similar to that of 6. It is apparent that the tin concentration determines grid life, not silver.

The rise in the capacity of the two higher tin content alloys cannot be explained at this time. It is significant that the lowest tin alloy grid continued to fall in capacity.

Explanation of these phenomena will require more time at temperature and additional growth and capacity measurements.

The results obtained for the alloys containing 0.005% silver are similar to that seen in the previous two figures. Further effort was made to determine the effect of thickness on the growth of the positive plate. The thickness of the grid employed in our UPS batteries is 2.7 mm; to increase grid life the thickness was increase to 3.6 mm. The life test compared the two plates each alloyed with 0.005% silver and 0.30% tin.

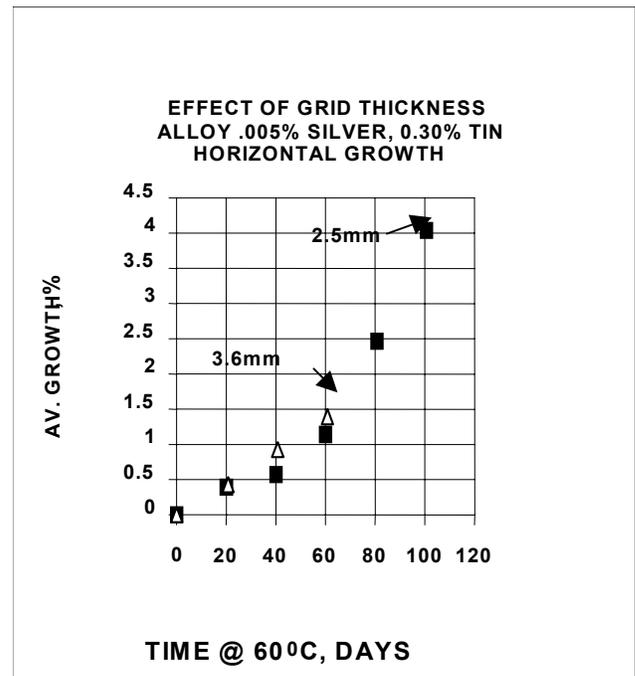


Figure 8

In Figure 8 is a graph depicting the effect of thickness on the growth of the positive plate. The results show that the growth rates are the same for the difference in thickness of approximately one millimeter.

### Conclusion

It is concluded from this work that, at the concentrations employed, silver when alloyed with tin has little effect on slowing the growth of the positive plate. It has been further demonstrated that any increase in plate life due to slowing of the lead corrosion rate was the result of tin additions.

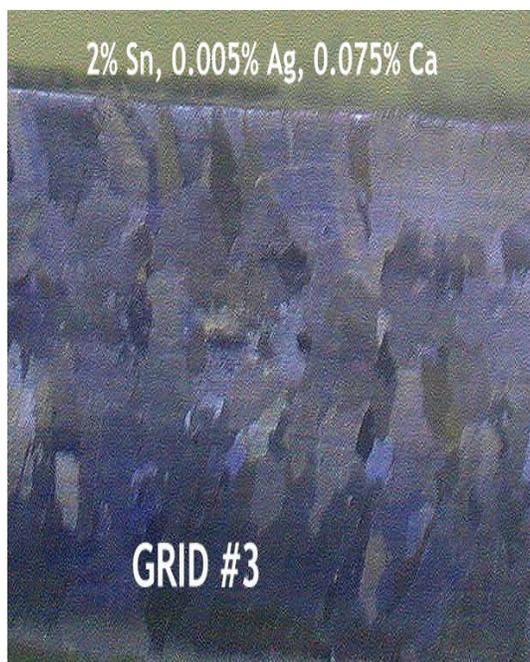


Figure 9

To determine why the lead corrosion rate was decreased by tin, photographs of the magnified crystalline and corrosion patterns of the alloys were studied. In Figure 9 is a picture of the as cast lead alloy of Grid 3 of Table 1. The lead crystal size is moderate and vertical orientation of relatively larger crystals is seen toward the surface of the grid. All of the alloy compositions viewed were quite similar to that in Figure 9. This commonality does not explain the beneficial effect of alloying tin with lead.

To obtain insight into the mechanism of tin's ability to lower the lead grid corrosion rate, sections of the aged grid were next examined. The figure below is of grid sections corroded at 60°C for 81 days at 130 mV of polarization.

The alloys examined contained 0.005% silver, 0.075% calcium and either 0.30% or 2.0% tin. After polishing the grid sections they were etched with a 2:1 acetic acid-hydrogen peroxide solution at room temperature.

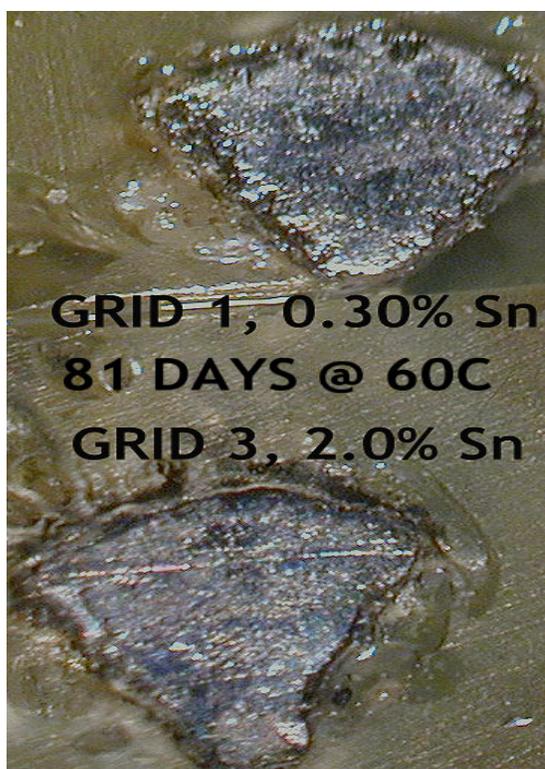


Figure 10

It is obvious from this picture that the grid with the lower tin content exhibits penetrating inter-granular corrosion. That of the grid with 2% tin shows a relatively even corrosion layer with little if any oxide penetration into the grain boundaries. Based on these observations a plausible explanation for the beneficial affect of tin is found in its precipitating into the grain boundaries<sup>iii</sup>. Such tin deposits prevent inter-granular intrusions of corrosion product and extent plate life.

#### **Battery Tests Experimental**

In this sequence of tests 100A-hour batteries were build and tested at 60°C in float service at 2.27 VPC. Batteries with positive plate grids containing 2% tin were compared to control batteries with 0.3% tin. Battery life and performance was determined for product with a relatively new enhanced puncture resistance. This separator was provided by Hollingsworth & Vose under the trade name of "Energyguard"<sup>TM</sup>.

As in the cell test sequence battery aging was monitored by capacity measurements complemented by weight loss, internal resistance and charge current measurements.

## Results

Previous testing of the “Energyguard”™ found the capacity of batteries built with it to be low as a result of its higher ionic resistance. In figure 11 is graphed the capacity of batteries containing the above separator and 2% tin along with control batteries. From the initial discharge test, before aging, it is seen that capacity losses caused by the higher resistant separator are negated by employing 2% tin.

Figure 11 also shows that although the 2% tin positive plate batteries demonstrated better performance initially this advantage is lost after 40 days of testing at 60°C. In fact no improvement in life, and perhaps a loss, was apparent with this level of tin addition to the positive plate grid.

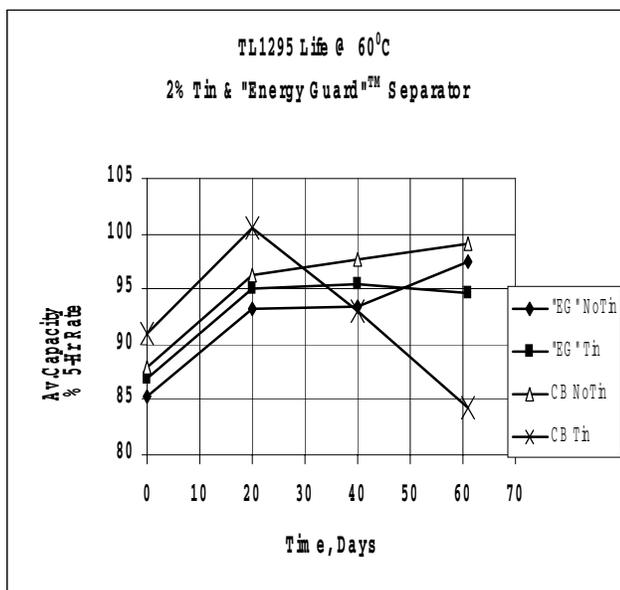


Figure 11

Obviously one is required to understand the above contradictions before tin is alloyed with lead in the positive grid of the VRLA battery.

## Acknowledgement

The authors thank the management of Power Battery for providing the support necessary to make this study possible.

<sup>i</sup> D. Scott, et al, INTELEC'96, pp. 327.

<sup>i</sup> Y. Oneda, et al, INTELEC'98, pp.85.

<sup>ii</sup> W. Hofmann, Lead and Lead Alloys, 1970, pp 99.