# ANTIMONY POSITIVE GRIDS:

# The Answer to High-Temperature Endurance and Premature Capacity Loss in Maintenance-Free Lead Acid Batteries

*By Thomas J. Clough*

The following is based on a presentation given at the 116th BCI Convention and Trade Show.

It is well known that antimony positive grids offer substantial performance advantages in lead acid batteries. Recent studies by major battery companies have shown the advantage of 0.5-1.7 wt% antimony positive grids for higher underhood temperatures and hot climate environments, longer cycle life, recovery from deep discharge and the substantial elimination of premature capacity loss caused by an increase in the resistance of the corrosion layer, its passivation and the discharge of the corrosion layer before the active material discharges. There is a significant trend in the design and manufacture of OEM automotive, heavy duty truck and marine batteries to use absorbent glass mat (AGM) battery separators. In addition, flooded-maintenance free automotive lead acid batteries are being designed for high temperature endurance using J240 testing at 75° C as well as the modified J240 at deeper depths of discharge. The only outstanding limitation on the use of antimony positive grids in maintenance free and valve regulated lead acid batteries (VRLA) is the effect of antimony ion plating out on the negative plate which increases hydrogen evolution, water loss, self discharge and the inhibiting of full recharge of the negative plate.

Ensci has approached this one major deficiency of antimony positive grids through the use of a new, patented battery separator which acts as an antimony binding reactive filter. The separator has incorporated the metal control additive ES-A-4 which irreversibly binds antimony at ambient temperature and at 75° C. Ensci has demonstrated that the ES-A-4 additive has substantial activity and capacity for irreversibly binding antimony at 75° C and at all acid molarities. The designs for AGM, polyethylene and polyvinyl chloride separators use a high particle count powdered selective ion exchange additive which achieves a fully electrolyte accessible, uniform distribution and association with the separator. The additives are porous organic polymers with both surface and interior functionality that selectively binds antimony. The additives contain both micron and submicron particles for higher reactivity and capacity. The additives are associated with the battery separator directly or through coupling with a unique cylindrical porosity additive. The use of the porosity additive allows for rapid contact efficiency between the additive and antimony ion. The selective additive typically has 50 percent of the number of particles on a particle number count basis less than two microns. Ensci has manufactured the additive in commercial production equipment at Sturtevant Inc., Hanover, Mass., using starting selective ion exchange resin reactants furnished by Bayer Chemical Corporation.

It is well known that lead/antimony alloys used in positive grids offer a substantial performance advantage in many different types of lead acid batteries. The primary areas of performance advantages have been in capacity and cycle life of the lead-acid battery. Traditionally antimony lead alloy positive grids have been used in SLI batteries having antimony contents up to about 2 percent and in deep cycle lead acid batteries such as golf car and motive power. With the advent of maintenance-free SLI batteries, antimony lead alloy positive grids have been displaced by the use of calcium lead alloy positive grids. In deep cycle applications such as golf car and motive power, antimony positive grids with antimony contents up to 8 percent continue to be used extensively in deep cycle traction type applications. One of the outstanding properties of positive antimony lead alloy grids is the conductivity of the corrosion layer that allows electrical contact between the grid and the positive active material. It is believed that the presence of antimony establishes electronic semiconductor conductivity which provides for the continued interface between the antimony grid and the positive active material.

Numerous studies have investigated this phenomenon with mechanisms being advanced that the antimony containing corrosion layer undergoes discharge with difficulty that minimizes the formation of a passivation layer between the grid/active material interface[1]. In addition it has been proposed that antimony accelerates the conversion of lead oxide to conductive lead dioxide thus preserving the grid positive active material electroconductivity interface[2]. Lastly, it has been proposed that the presence of antimony improves the electronic conductivity of a gel zone which forms between the antimony positive grid and the positive active material[3].

A number of studies have shown the substantial increase in cycle life for lead antimony grids when compared to lead calcium tin grids[1]. In this same study an antimony effect was also shown by incorporating a lead antimony alloy directly into the lead oxide.

Other studies have shown the substantial performance advantage of antimony grids in photovoltaic battery applications[4]. In various evaluations, the antimony positive grids showed electronic conductivity between the grid and the positive active material and the ability to convert a substoichiometric lead oxide back to conductive lead oxide. These studies compared the performance of the positive antimony lead alloy grid with traditional calcium tin grids.

## Table 1 Antimony Positive Grids

**Advantages-**

- **Long Cycle Life**
- **High Electrical Conductivity Grid/PAM**
- **Improved High-temperature Performance**
- **Extensive Manufacturing Technology Base**

The battery environment today includes higher operating temperatures for the battery particularly in automotive and heavy duty truck. In addition to an increase in operating temperature, the operating environment increases the duty cycle for the battery, i.e., more electrical energy required and increased depth of discharge for the battery.

As the operating environment demands of higher temperature and deeper depths of discharge increase, companies have designed maintenance-free batteries with hybrid technology, i.e. positive antimony grid plates and lead calcium negative grid plates. The higher temperature environments have been the result of the requirement for more electrical energy, a smaller available space and the automotive design changes that produce these electrical load requirements. To simulate these design changes, the automotive SLI battery testing regime includes high temperature endurance using J240 testing at 75°C and the modified J240 testing under deeper depths of discharge.

The higher under-hood temperatures in current and future automotive designs and the smaller space requirement for the battery provides an opportunity for the use of antimony lead alloy positive grids containing from 1-1.7 wt% antimony. In a study presented at the 115th BCI Convention, a report was given on

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## Antimony Positive Grids

continued from page 17

battery technology for tropical countries[5]. The environment defined for tropical countries is the increase in actual temperature that the battery experiences during the life of the battery. In the paper, various plots were given which related under-hood temperature, electrolyte temperature and battery size to battery capacity and life. A statement was made that there is sufficient evidence that the life of lead-acid batteries in tropical zones is appreciably lower than that obtained in the cold temperature climates. Further, the trend in higher under-hood temperatures in less tropical climates also presents a similar high temperature environment to the lead-acid battery. Of particular interest in the study was the use of hybrid positive grids containing from 0.5-1.65 wt% antimony with further alloying agents being arsenic, selenium and tin in flooded lead acid automotive batteries. The data presented showed a substantial advantage of antimony positive grids in cycle life over a control using a calcium positive with tin alloying agent. The only deficiency presented with the use of a hybrid antimony positive/lead calcium negative was the total water loss compared to the calcium positive grid. The water loss for this flooded battery was significantly higher for the antimony lead positive grid than the calcium positive grid. Evidence of shorter life of lead-acid batteries at high operating temperatures is also substantiated by the BCI surveys of failed batteries removed from service.

In recent studies a number of market trends have been identified for passenger cars and light duty vehicles. For example, original equipment battery sales are projected to increase through 2007 and one of the major trends in replacement batteries is an increase in Group 65 and 78 size batteries due to more SUVs and heavy duty applications. The design trends for automotive batteries included an increase in size, higher capacity requirements and higher temperature battery environments.

**Table 2 Batteries – Automotive/Heavy Duty Market/Design Trends**

- **Higher Temperature Battery Environments**
- **Higher Capacity Requirements**
- **Limited Space Requirements**

As described in many studies, the limitation on the use of antimony positive grids is in battery applications where water is not routinely added to the battery over the life of the battery, such as maintenance-free flooded lead acid batteries and VRLA batteries using an AGM separator. The mechanism for the loss of water involves the corrosion of the antimony positive grid and the liberation of antimony as an antimony ion.

The antimony corrosion products only become partly soluble in the electrolyte with a significant majority of the antimony being deposited in the positive active material as an insoluble oxide.

The antimony from the positive grid can eventually deposit on the negative active material. Once deposited on the negative plate, antimony can have the undesirable effect of increased self-discharge, hydrogen evolution, diminished recharging efficiency and water loss.

## Antimony Control Additive Design Factors

The lead-acid battery presents a challenging environment for controlling adverse effects of antimony deposition. One of the major environmental design factors, which has to be taken into consideration, is the varying sulfuric acid concentration and battery potentials (voltages) that occur during the charge and discharge of a lead-acid battery. For example, the sulfuric acid concentration in deep discharge applications can

## Antimony Positive Grids

continued from page 18

change from 38wt% sulfuric acid on charge to 8wt% sulfuric acid on discharge. Further, the electrochemical potential of both plates will change as the battery is discharged.

Table 3 sets forth the battery environment in which soluble contaminant antimony is released to the electrolyte.

### Table 3 Battery Environment During Charge/Discharge

- **Acid Concentration Changes (Moderate to Substantial)**
- **High Hydrogen Ion Concentration**
- **Voltage Changes**
- **Intermediate Soluble Lead Ions**

From an additive design standpoint the additive must bind antimony ions at the varying acid concentration and voltage conditions during the charge/discharge cycles of the battery and such binding of antimony must be irreversible. The additive design for irreversibly binding of antimony is particularly difficult as the hydrogen ion concentration increases during the charge sequence of a battery where the hydrogen ion favors release of antimony.

In the battery environment the additive has to selectively and permanently bind ionic forms of antimony in order to minimize its detrimental effect. The battery environment also provides an environment where an intermediate soluble lead ion may be formed during the conversion of solid lead to insoluble lead sulfate. In this environment the additive design requires a stronger binding affinity to antimony ion than to any intermediate soluble lead ion and if any binding does occur the lead ion must be quickly released.

Table 4 sets forth the design criteria for an antimony control additive.

### Table 4 Additive Design Factors

- **Irreversible Binding**
- **No Antimony Release During Cycle**
- **High Selectivity for Antimony Contaminant**
- **High Capacity for Antimony Contaminant**
- **Low Selectivity for Lead Ion**
- **Release of any Lead Ion During Cycle**
- **High and Rapid Accessibility to Electrolyte**

### Additive Description

The antimony inhibiting additive ES-A-4 is a porous organic particle having an elongated geometry and antimony binding functional groups. The additive has both surface and interior functionality that irreversibly binds antimony ion. A substantial portion of the functionality is in the internal pore structure as opposed to the surface. The moisture content of the additive is approximately 40 percent by weight as manufactured. The additive has a density of 0.98 g/cc at 40 weight percent moisture, is hydrophilic and is easily wet by sulfuric acid electrolyte.

### Additive/Separator Design Overview

In order to be cost effective for antimony contaminant control, Ensci has approached the separator design using a high particle count additive per unit separator volume and achieving a uniform distribution of the additive in the separator. The design approach is to have additive particles associated with a substantial portion of the silica used in the manufacture of polyethylene and polyvinyl chloride separators and glass fiber in AGM separators. The additive is combined with silica initially followed by conventional extrusion, extraction and drying to form the finished separa- ➤

## Antimony Positive Grids

continued from page 20

tor. The pore size distribution in a PVC separator is bimodal with pores at 0.06 and 1-2 microns. The results to date show that there does not appear to be interfacial bonding or smothering of the silica/additive powders by the polymer and that the electrolyte is accessible through the pores and channels created in the separator. A further additive design includes the manufacture of a high particle count antimony control additive associated with a silica-based porous carrier. The silica based porous carriers are open cell, having a generally cylindrical and fiber like geometry and a void volume of about 85 percent. The carriers are manufactured by Eagle Picher Inc. The carrier can provide excellent contact efficiency between the antimony contaminant in the electrolyte and the additive, much like a reactive surface coating on a filter. The additive on a silica based porous carrier material has been evaluated in the manufacture of AGM separators. Current data shows that the particle size can be reduced while maintaining capacity and increasing rate. At the present time ES-A-4 is manufactured at a particle size distribution of from 0.5 to 15 microns with an average (volume percent) of from 7 to 10 microns. On a number count basis, 50 percent of the particles are less than 2 microns. The preferred design is to form a surface coating such as a monolayer of a very high particle count antimony control additive, preferably less than a 5 micron average, on the silica of the polyethylene or polyvinyl chloride separator or the glass fiber of an AGM separator. This allows for very high contact efficiency of the additive with the antimony contaminated electrolyte. The amount of additive on a weight percent basis can vary from 0.25-4 wt% of the total weight of the separator with the actual weight percent of the additive being dependent on the amount of contaminant antimony that enters the electrolyte. Once the antimony is bound to the additive it is not released at the varying acid molarities in the lead-acid battery.

- **Results and Discussion**
- **Irreversible Binding**
- **Ambient Temperature**

In an evaluation protocol to determine the overall capacity of the ES-A-4 additive, 230 ppm of antimony was added to an 8 weight percent sulfuric acid solution and 830 ppm of antimony was added to a 38-weight percent sulfuric acid solution, each solution containing 4 weight percent of the ES-A-4 additive, 25 ppm of ferric ion and 2 ppm of lead ion The additive from the 8 percent sulfuric acid solution after determining antimony binding capacity, was filtered and reslurried in 38 percent sulfuric acid solution containing no metals to determine if any bound metals were released.

The ES-A4 metal control additive evaluated in this protocol produced greater than 99 percent uptake of both antimony, 228 ppm uptake, and iron, 24.5 ppm uptake at the 8 percent concentration and greater than 99.5 percent uptake of both antimony, 828 ppm uptake, and iron, 25 ppm uptake at the 38 percent concentration. When the ES-A-4 additive with bound metals that was used for the capacity determination at 8 percent sulfuric acid was reslurried in 38 percent metal free sulfuric acid, no antimony or iron release was observed. The data demonstrated the high irreversible metal binding of the ES-A-4 additive. Furthermore, the additive showed a low binding efficiency for trace amounts of soluble lead ion and had no binding of lead ion at 38 percent sulfuric acid.

## High Temperature 75°C

The testing methodology investigated the effectiveness of the antimony control additive ES-A4 for irreversible binding antimony at ambient temperature and at 75° C for from 24 hours to seven days. The experimental design evaluated ES-A-4 by itself, with a carrier and associated with an AGM separator. Twelve individual tests were conducted including 24 hours at ambient temperature and 75° C and seven days at ambient temperature and at 75° C. Antimony irreversible binding was determined at ambient. temperature, at 75° C. and at 75° C for an additional time which allowed for electrolyte cool down. The methodology allowed for the determination of the irreversible binding efficiency for antimony, the effect of temperature and time on the overall capacity and the overall stability and effectiveness of the antimony control additive.

Observations: The data showed that the ES-A-4 additive, alone, associated with the Ensci porosity forming separator additive and associated with a separator, had a metal binding capacity of from 260 to 279 mg of antimony per gram of dry ES-A-4 additive at ambient temperature and was at least 80 percent effective at 75° C for irreversible binding of antimony when compared to ambient temperature and approached 90 percent effectiveness when the electrolyte solution was allowed to cool down from 75° C. The data on irreversible binding for the ES-A-4 separator showed near 100 percent irreversible binding of antimony upon cool down from 75° C when compared to ambient temperature.

The capacity and activity for the ES-A-4 additive at 24 hours and seven days for both ambient and 75° C were approximately the same, +- 5%.

The conclusions drawn from the evaluation was that the ES-A-4 additive has a high degree of irreversible antimony binding activity at high temperature for example 75° C and that the ES-A-4 additive is stable and does not lose activity/capacity at high temperature over reasonable periods of use.

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Antimony Positive Grids continued from page 23

## Battery Separator

A number of different AGM, polyethylene and polyvinyl chloride separators were evaluated. The manufacture of the AGM separator included the combining of the ES-A-4 additive having an average particle size distribution of 7 microns in a very dilute mixture of fibers and water at a low acidic pH. The ES-A-4 additive was processed through a vacuum dewatering unit and dried to the final separator. The ES-A-4 additive alone and associated with a porous silica carrier, average particle size distribution of 15 microns, were manufactured. The polymeric separators, both polyethylene and polyvinyl chloride, were manufactured by combining the ES-A-4 additive with a silica pore former, the polymer and extractant followed by extrusion of the finished separator.

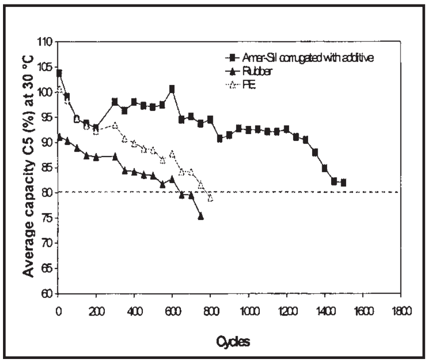
The evaluation of the three separators in the antimony protocol test showed that the amount of antimony irreversibly bound to the additive separator correlated with the control using ES-A-4 only. The data showed that each separator achieved a binding capacity of from 200 to 265 milligrams of antimony per gram of additive.

The conclusions that can be drawn are that the ES-A-4 additive is highly efficient for irreversible binding of antimony when incorporated into AGM and polymeric separators and that the separator manufacturing procedure provides a very uniform distribution of the additive. Furthermore the additive is highly accessible to the electrolyte. It was also found that a reduced particle size and increased surface area improves overall ES-A-4 rate and capacity.

## Traction Cells – PVC Separator

A cell test was made comparing a corrugated Amer-Sil separator with ES-A-4 with PE and rubber separators. Figure 1 shows the number of cycles for each separator. The test was performed on tubular traction cells using an accelerated testing cycle: Temperature: 47°C. Depth of Discharge: 60 percent. Loading factor: 1.2. Three cycles per day. The corrugated Amer-Sil with the ES-A-4 additive gave an outstanding result concerning cycle life and a similar slope on the negative plate potential compared to rubber up to the failure of the polyethylene and rubber separator cells. Water loss was not recorded. Post mortem analysis is pending.

### Figure 1



*Courtesy of Amer-Sil SA*

## Table 5 Antimony Control Additives

**Advantages-**

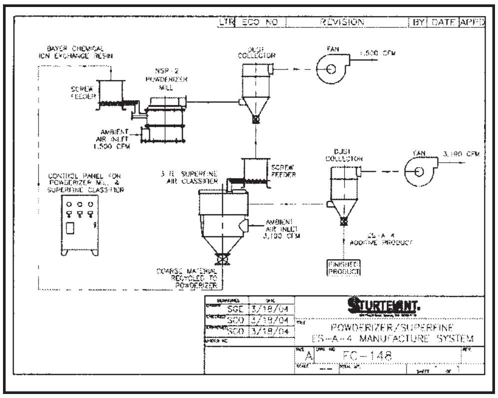
- **Control at Point Source**
  - **Minimize Effects of Antimony Plating on Negative Plate**
  - **Protect Expander From Metal Ion Catalytic Effects**
- **Cost Performance Alternative for Antimony Positve Grids in Maintenance Free Flooded and VRLA Batteries**
- **Flexibility to Use Only Concentration of Additive Required for Amount of Antimony Present**
- **No Capital Investment Required**

## ES-A-4 Manufacturing Process

ES-A-4 is manufactured from an antimony/iron selective macroporous ion exchange resin in bead form. The ion exchange resin has antimony selective functionality on a divinyl benzene cross linked polystyrene resin. The ion exchange resin beads are manufactured commercially by Bayer Chemical Corporation.

Ensci has undertaken four commercial trials at Sturtevant Inc. for the production of the ES-A-4 metal control additive and to establish a commercial design base for the manufacture of the additive. The process developed at Sturtevant has sufficient flexibility to be used for all current ES-A-4 type high number count additives based upon initial starting resin feed. Sturtevant Inc. is a manufacturer of Milling and Size classification equipment. In the process the starting selective ion exchange resin bead is reduced in size in a mill having internal classification to a certain particle size distribution. The resulting powder is then processed through a super fine classifier to recover a product powder (finer material). The coarse fraction is recycled to milling for further size reduction.

### Figure 2



Ensci presently has 13 issued United States patents and five pending United States patent applications directed at metal control additives, their use in various products including recombinant AGM, polyethylene and PVC separators and two European patent applications directed at such additives and products.

## Conclusions

Studies have shown that the ES-A-4 antimony control additive can irreversibly bind antimony metal ion at the acid concentration and voltage potentials that occur during the charge and discharge reactions in a lead-acid battery to minimize the adverse effect of water loss through deposition of antimony metal on the negative plates.

The additives have shown an increase in capacity as a function of both single cycle discharge and energy delivered over the life of the battery. The additives offer the potential for increased battery capacity, power and life in maintenance free flooded and VRLA batteries. Improved cycle life in traction batteries has been demonstrated. The additives were successfully incorporated into three different types of commercial separators at high uniformity and total accessibility to the electrolyte.

The additives have been successfully manufactured on commercial equipment and can be associated with a porous silica carrier for further improvements in additive distribution in a separator.

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