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The Lead Selenium Cell, Fact or Fiction?

Abstract:

It is highly misleading to the users of lead acid batteries to see a new classification called Lead-Selenium cells, as if they are new types of cells. A more accurate description of the "Lead-Selenium cell" is to call it what it is: "a low-antimony cell".

The low-antimony describes any cell which contains less than 4% Sb in the positive grid. This is an old technology that has been used for many years to provide good cycle life when compared to Pb-Ca products of similar design.

Selenium has been used in lead-antimony grid alloys by many of the Lead Acid battery manufacturers, including Enersys, for many years. The selenium is a grain refiner which, when used in combination with other elements, such as arsenic, also helps to increase the alloy rigidity and correspondingly eases plant handling of the materials. In this area of additives, there are also many other elements that are used such as sulfur, tin, or copper. Use of any one alone or combination of them improves plant processing such as casting rates, dross generated in the molten lead pots, as well as added benefits inside the final cell such as increasing the grids resistance to corrosion.

Enersys offers this type of alloy primarily in our Traction battery lines, however we do also provide a limited line of flooded stationary products with a Pb-Sb-Se alloy.

When utilizing a Pb-Sb-Se product, users should be aware of depolarization problems that can be caused by the plating of the antimony onto the negative plate. This can lead to early failures due to undercharged negative electrodes or, at best, result in increased watering intervals.

EnerSys is the leader in stored energy solutions and offers one of the largest product portfolios in the world. Based on this, it is critical to understand a user's application prior to making any blind recommendations and/or statements selecting one product or competitor over another. Every product has it strengths and weaknesses and it is only by clearly understanding all factors in an application that a robust and long-term solution can be implemented for the user.

Introduction:

A misconception is being promulgated in the lead-acid battery marketplace, by the promotion of a supposedly different line of lead acid cells called "lead-selenium" cells. The literature states that this type of cell uses a lead-selenium lead alloy in the positive grids that is resistant to corrosion and provides longer life than the lead-calcium grid alloys.

It is the purpose of this paper to explain that what is being called a lead-selenium grid alloy is nothing else than a standard low-antimony alloy, which is normally not recommended for use in the same applications as the lead-calcium, or lead-calcium-tin alloys.

Lead-Antimony-Selenium Alloys:

Prior to the 1960's the use of high antimony lead alloys (10-11% Sb) was very common. This alloy was easy to cast and was ready to process almost as soon as the grid castings were ejected from the mold. The batteries produced with this alloy provided excellent deep-discharge cycle performance.

During the 1960's the battery manufacturers started lowering the antimony content to take advantage of the cost reduction and also to minimize the phenomenon known as "poisoning", or depolarization, of the negative electrodes during operation of the lead acid cell. This manifests itself in increased gassing, even at low voltages, and more frequent watering intervals to prevent dry-out and oxidation of the top portion of the active materials.

As the trend towards lower antimony continued more was learned on the techniques required to produce castings below the 6% Sb barrier, and even to levels below 1% Sb.

It was found that, as the antimony content was decreased, the strength of the castings also decreased, due to the tendency of developing coarse dendritic structures which made the grids easily susceptible to cracking in the manufacturing process.

It was also discovered that the addition of a small amount of selenium (0.005% to 0.05%) to the binary Pb-Sb alloy produced grids that are stronger and less prone to anodic corrosion.

During that time, the manufacturers also determined that other elements, such as arsenic, tin, copper, and sulfur were beneficial for improved production. The addition of arsenic allowed the grids to harden faster, and essentially decreased the time that a grid had to be stored after casting before it could be processed further in the plant. The tin additive made the molten lead-antimony alloy more fluid and easier to cast.

Although the other elements also helped to refine the grain size, selenium appeared to be the most effective and the most widely used.
Through metallographic analysis and repeated casting trials the manufacturers have optimized the composition of the low antimony alloys and its production parameters.

Today there is a wide selection of lead-antimony alloys for mostly any use, including low-maintenance lead acid batteries. But their use in low maintenance cells is limited and continuously challenged by antimony-free alloys because, even at the lowest antimony levels, the “poisoning” of the negative electrode is only slowed down but not eliminated.

Lead-Calcium alloys:

Starting as early as the 1940’s the battery manufacturers were aware of the antimony “poisoning” problem and during the 1950’s started extensive research into alternative alloys. Out of all the experimentation arose a favorite alternative: the binary Pb-Ca alloy.

Ideally the use of pure lead provides the lowest maintenance batteries, but the ductility of pure lead makes it difficult to process in the manufacturing operations. The Pb-Ca alloy seemed to take care of this problem while providing the same electrochemical performance as the pure lead electrode.

Due to a rapidly growing demand for batteries that did not need frequent water additions, the battery manufacturers dedicated considerable resources towards the research and development of antimony-free grid alloys. Most of the work was conducted from the 1960’s through the 1990’s, in parallel with the research on low antimony alloys. Throughout this period the lead-calcium alloy underwent a great degree of optimization.

The benefits of using the antimony-free alloys were not limited to low gassing rates relative to conventional antimonial alloys. The shelf- life of Pb-Ca batteries was much better than those with antimony alloys and, since Pb-Ca has better conductivity, the cold-cranking performance was also substantially improved.

Overall the binary Pb-Ca alloys achieved the intended objectives of producing batteries with the lowest watering intervals. Unfortunately this came at the great cost of reduced cycle life for deep discharge applications, or premature capacity loss.
It became evident that one alloy could not serve all the requirements of the market place.

During the 1970’s the manufacturers were experiencing problems in controlling the calcium content in the casting pot, and found that the addition of aluminum would help reduce the loss of calcium from the molten lead. The aluminum also improved the grain structure, and facilitated the next quantum leap in optimization of Pb-Ca-Sn ternary alloys with balanced components of low calcium (<0.7%) and high tin (0.5% to 2%).

With the advent of the Valve Regulated Lead Acid (VRLA) batteries the new lead-calcium-tin alloys became the alloys of choice because they provided good deep-discharge capabilities while retaining all the advantages of the binary Pb-Ca alloys.

Recommended Applications:

EnerSys offers products which utilize the latest developments in lead alloys and today there are many variations of those alloys but, at the risk of oversimplifying the situation, we can assume that the majority of the industry uses almost exclusively the following two types:

- Lead-Antimony alloys
- Lead-Calcium alloys

The Lead-Antimony alloys include what's being advertised as Lead-Selenium.
The selenium is only a minor component of the alloy (< 0.05%), while antimony is normally > 1%, therefore EnerSys does not use the lead-selenium denomination but prefers the more standard industry practice of classifying Lead-Antimony alloys by the amount of its antimony content. The selenium is an additive that is utilized prevalently in most of the antimony alloys.

The Lead–Calcium alloys include the corrosion resistant Pb-Ca-Sn alloys, which normally utilize minor additions of aluminum and other elements.

The traditional application for the above two types of alloys have been to use Lead-Antimony for Cycling (Traction, Marine, etc.) and Lead-Calcium for Float applications (Stationary, UPS, Switchgear, etc.), but the selections can overlap each other when one needs to compromise to obtain a product which can function in all applications, as shown in the following table. The table provides a relative measure on a scale of 1 to 10, with 10 being the best fit:

Lead-Alloy	Cycling	Float	VRLA
High Antimony (> 6%)	10	1	1
Medium Antimony (4% - 6%)	8	1	1
Low Antimony (2% - 4%)	6	3	1
Very Low Antimony (< 2%)	3	5	5
Calcium	1	10	5
Calcium-Tin	6	10	10

Most of the above antimony alloys contain selenium as a minor component.

Conclusions:

- The Lead-Selenium product-name is somewhat misleading and can create confusion in the Lead Acid battery marketplace, since it is nothing more than a conventional cell using conventional lead-antimony alloy grids.
- The lead-selenium denomination appears to be an attempt to market a standard industry product under the semblance of a unique technology.
- Enersys offers the same alloy selection among its numerous products and cautions our customers to be skeptical when a product is promoted as the cure-all for all ills. The low antimony products have slowed the process of “poisoning” of the negative electrode but have not eliminated it. During product selection a user must understand all factors (advantages/disadvantages) in order for the best long-term solution to be chosen.