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Evaluation of hybrid rubber-polyethylene industrial battery separators

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Abstract

Antimonial lead alloys continue to play a key role in the overall success of the lead-acid battery in deep cycle applications. In markets such as motive power and golf car, these alloys have long been known to assist the performance of the positive plate by promoting a healthy, grid-active material interface. Antimony, on the other hand, is a well-established poison to the negative plate and ultimately leads to gassing, water-loss and cell failure. Reports in the literature indicate that specific battery separator materials may be used to delay the onset of gassing by suppressing the effects of antimony. Literature findings also suggest that the suppression effect may be due to a combination of the chemical make-up of the separator and its physical attributes. It is the intention of this paper to introduce a novel method for evaluating battery separator materials in terms of their ability to suppress the deleterious effects of antimony. Results presented here indicate that the chemical composition of the separator is a controlling factor in suppressing the influence of antimony in the lead-acid battery. Initial information on the characteristics of a new hybrid rubber-polyethylene battery separator is also presented. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lead-acid battery; Separator design; Traction battery

1. Introduction

The ultimate deep cycle battery must offer the user: (1) high discharge capacity, (2) superior power, (3) very low maintenance and (4) excellent cycle-life. In applications such as motive power, scrubber and golf car, cycle-life is the most important factor, since the user typically wants to minimize the cost per cycle.

The need for maximum cycle-life, therefore, dictates that the battery manufacturer must use antimonial lead alloys. In the deep cycle market, the importance of cycle-life is confirmed by the fact that nearly all motive power batteries sold today still feature antimonial lead alloys in the positive plate (and the negative plate).

Despite the positive attributes of antimonial alloys, their use does have its downside. The antimony used in the positive grid eventually leaves the grid as the battery ages and the grid corrodes. The antimony (in the form of Sb^{+3}) then makes its way to the negative plate where it immediately "plates out" [1]. Finally, the metallic antimony, now widely distributed over the high surface area negative, causes a dramatic increase in gassing and water-loss during charging (antimony has a very low hydrogen over-potential compared to lead). The increase in gassing at the negative plate causes a marked increase in the end of charge current and a subsequent decrease in charge efficiency. The ineffective charging of the negative, quickly leads to cycle after cycle of capacity loss, and ultimate battery failure caused by the vicious circle depicted in Fig. 1.

Over the last several decades battery manufacturers have determined from both laboratory and field results that natural rubber battery separators can be effectively used to forestall the onset of this failure mechanism as is shown below in Figs. 2–4.

Fig. 2 shows the capacity performance improvement in identical cells except for the separator type. The enhanced cycle-life induced by the rubber separator is directly related to the low end-of-charge current (Fig. 3) and the reduced water loss (Fig. 4). Despite the observed improvement in battery cycle-life, the mechanism related to the ability of natural rubber to suppress the effects of antimony are still not well understood [2,3]. Previous tests, such as the antimony transfer test [4–6] have been devised to quantify the ability of the separator to inhibit antimony transfer. This test assumes that the separator is a physical barrier to antimony transport. In the antimony transfer test the separator is mounted in a liquid tight frame and positioned so as to physically separate two distinct solutions of sulfuric acid. Each solution contains a lead grid (one grid is antimonial lead) and a type of overcharge test is performed. As the

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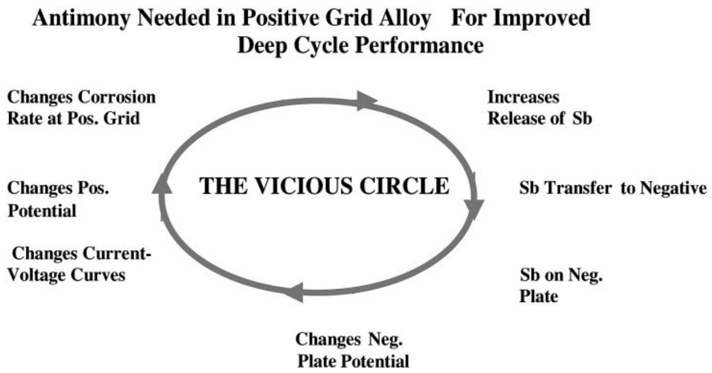

Fig. 1. Antimony poisoning effect on cycling behavior.

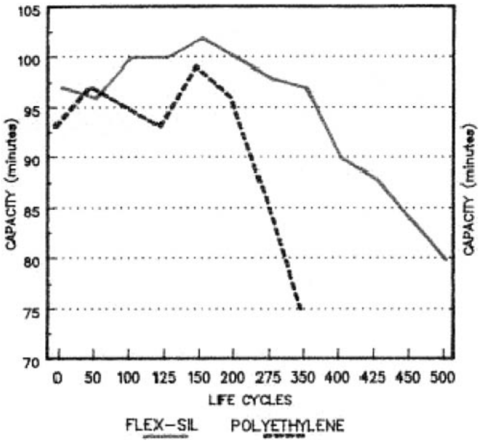

Fig. 2. Battery capacity vs. cycle-life.

positive grid (the one containing antimony) corrodes, the separator is evaluated for its ability to inhibit antimony transport as measured by the presence of antimony in the opposite solution and on the negative grid. This test has proven that natural rubber separators do indeed inhibit ‘‘antimony transfer’’, but does not address the fact that the effect may be ‘‘chemical’’ rather than ‘‘physical’’. It is our hypothesis that the suppression of the effect of antimony is not a ‘‘physical’’ effect but a ‘‘chemical’’ effect, one that is related to leachable compounds in the natural rubber itself.

2. Experimental

Antimony suppression analysis is based on the basic technique of cyclic voltammetry. This methodology has a rich history within the battery industry and continues to be used for evaluations of such diverse areas as expander activity as well as other related chemical contaminant characteristics [7–10]. All experiments were conducted with the use of an EG&G potentiostat/galvanostat. And were performed in a 300 ml test cell in order to minimize the effects of antimony consumption. The working electrode was a 6 mm diameter pure lead rod (99.999% Alfa Aesar, Inc.) fitted with heat shrink tubing so as to expose only about 13 mm of the rod in the 1.265 S.G. sulfuric acid electrolyte. The reference electrode was of the Hg/Hg_2SO_4 type (Koslow Scientific).

The antimony suppression analysis (ASA) test procedure begins with a 72 h pre-conditioning step, whereby the exposed end of the new lead rods are placed in the

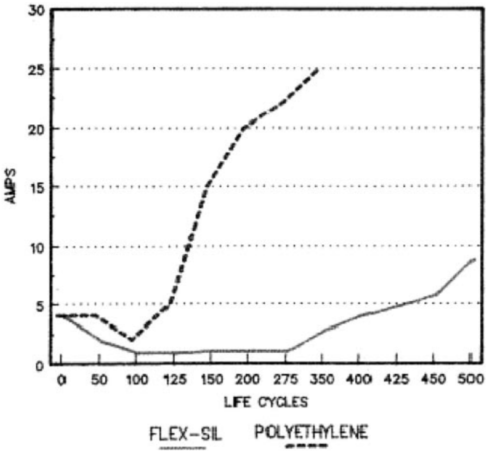

Fig. 3. Battery top of charge current acceptance vs. cycle-life.

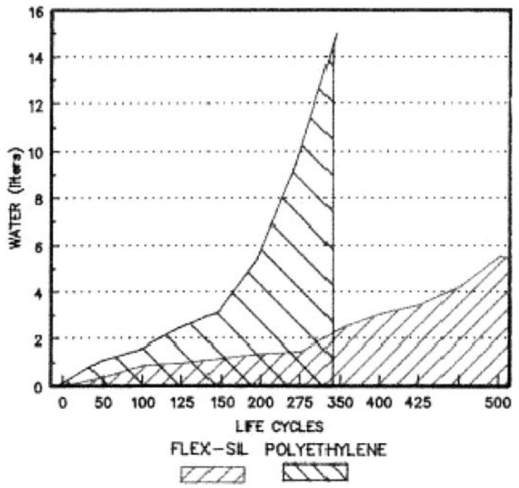

Fig. 4. Cumulative battery water loss vs. cycle-life.

voltammetry cell and repetitively cycled between the potentials of −820 and −1140 mV vs. Hg/Hg_2SO_4 at a scan rate of 1 mV/s. This cycling procedure is performed in order to increase the surface area of this monolithic electrode and in essence create a miniature plante' negative. This procedure is used to prepare multiple ASA test electrodes in parallel, typically six at a time.

Separator samples for the ASA test are refluxed for 72 h in sulfuric acid solution to leach (extract) possible chemically active components. This portion of the ASA procedure begins by cutting the prescribed battery separator sample size (185 mm × 170 mm) into 25 mm × 25 mm squares (approximate). The squares are placed in 250 ml of 1.265 S.G. sulfuric acid, covered with a watch glass and heated at 150°F for 72 h. The separator samples are then removed from the acid and the solution (now referred to as the ''leachate'') is stored for later use.

The next step in the ASA procedure involves selecting a pre-conditioned lead electrode and subjecting the electrode to more voltammetric cycling under the aforementioned conditions with a continuous nitrogen gas purge. The pre-conditioned electrode is cycled for an additional 24 h and the charge/discharge efficiency is calculated for the last cycle (by integrating the area under the charge and discharge current–voltage curves). The coulombic efficiency of the charge/discharge cycle is typically 95% or more. Efficiencies less than 95% indicate the presence of an impurity such as trace metals, oxygen or other unknown moieties.

At this point in the procedure, 25 ml of the leachate is then added to the test solution followed by a 15 min increased nitrogen gas purge. The charge/discharge cycling is continued for another 8 h. The coulombic efficiency is recorded and is typically still >90%. After the 8 h period, the solution is ''spiked'' with an antimony standard (Fisher Scientific, 1000 ppm Sb standard) to produce 5, 10 or 20 ppm antimony concentrations in the sulfuric acid electrolyte. The charge/discharge cycling is continued for an additional 16 h that serves to contaminate the lead electrode by ''plating-out'' the antimony. At the end of the 16 h ''plate-out'' period, the coulombic efficiency is recorded one final time. The antimony contamination results in a poisoning effect and a decrease of the coulombic efficiency. This procedure is repeated for three levels of antimony (5, 10 and 20 ppm) as well as for each type of separator to be tested. A ''blank'' (no separator leachate of any kind) is recorded at each level of antimony poisoning to establish a baseline effect.

3. Discussion

Figs. 5 and 6 show the cyclic voltammetry of the lead electrode and the effect of adding various amounts of

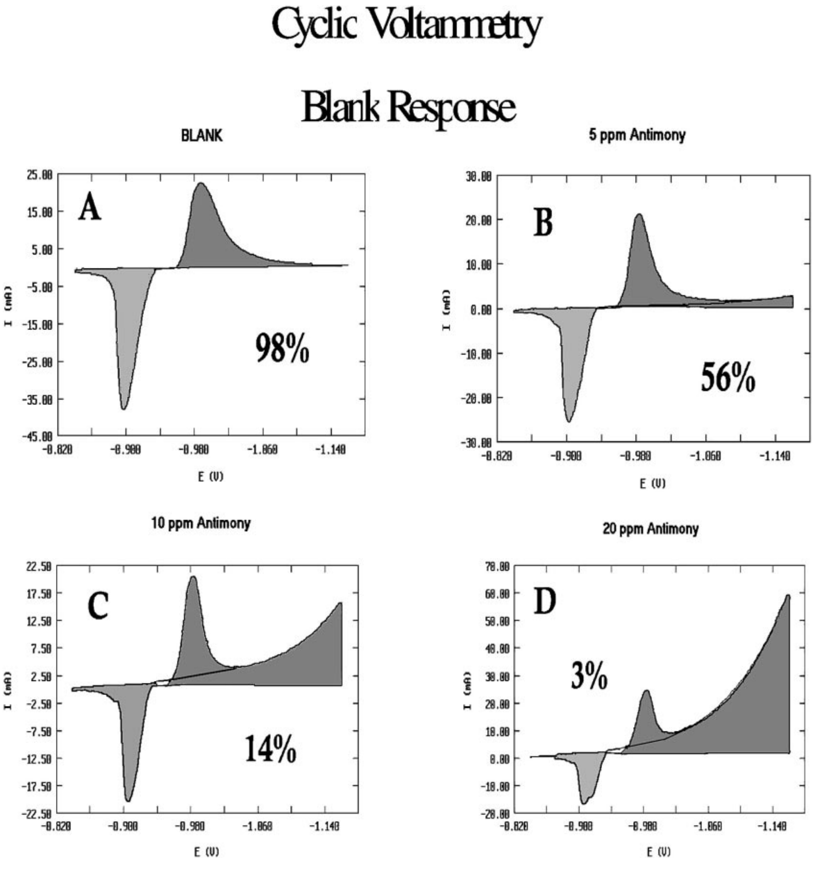

Fig. 5. ASA testing-blank response to antimony additions.

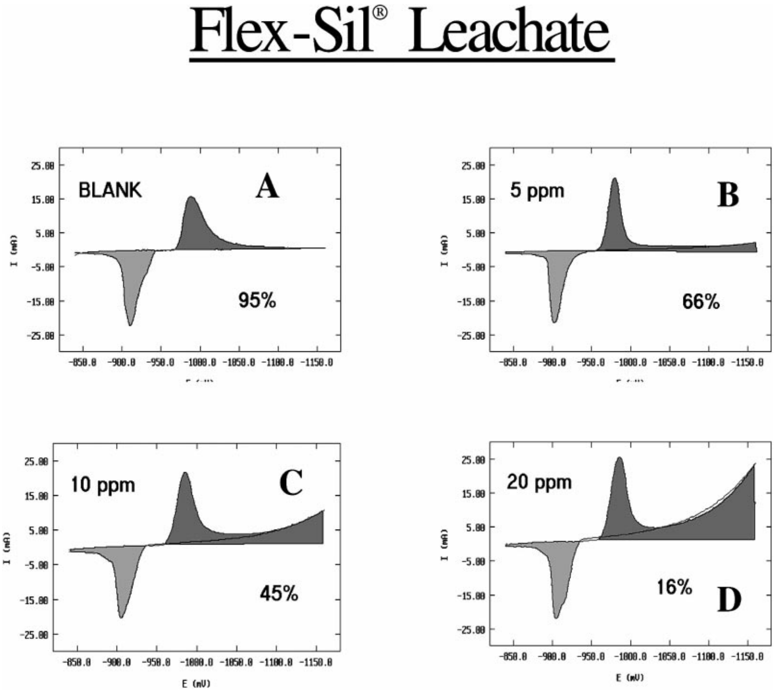

Fig. 6. ASA testing-rubber separator leachate effects.

antimony to a solution containing only 1.265 S.G. sulfuric acid. Fig. 5A represents the voltammetric behavior of the ‘‘blank’’ which is the lead electrode itself (no antimony and no separator leachate). The charge peak at −0.99 V vs. Hg/Hg_2SO_4 is indicative of the conversion of lead sulfate to metallic lead. The peak area (coulombs) relates to the amount of material converted in the charging process. The lead itself is very pure and therefore, no gassing currents are observed as indicated by the fact that the charging current returns to the baseline at potentials more negative than the lead charging peak.

On reversing the voltage scan, a discharge peak is observed at −0.90 V vs. Hg/Hg_2SO_4 representing the conversion of metallic lead back to lead sulfate. The charge/discharge process is very efficient as indicated by the ratio of the areas under each peak. In the specific case shown below the coulombic efficiency is very high (i.e. 98%).

Additions of 5, 10 and 20 ppm antimony reduce the coulombic efficiency (Fig. 5B–D). With 20 ppm of antimony in the test solution, more than 95% of the charging current is attributable to gassing and not to charging the lead electrode. The antimony has ‘‘plated-out’’ on the lead electrode causing a marked decrease to 3% in the charging efficiency.

The effect of adding separator leachate to the sulfuric acid electrolyte is shown in Fig. 6. In this experiment, a leachate of a natural rubber separator (Flex-Sil®) was prepared. Fig. 6A shows the behavior of the pure lead electrode in the presence of the ‘‘Flex-Sil®’’ leachate alone.

The coulombic efficiency in the presence of ‘‘Flex-Sil®’’ leachate is still 95% and is very comparable to the ‘‘blank’’ shown in Fig. 5A.

Fig. 6B–D show the effect of the incremental additions of antimony to the Flex-Sil® leachate solution when followed by 16 h of cycling. When the antimony is added to the solution, the coulombic efficiency is reduced, but not to the extent as observed in the ‘‘blank’’ (Fig. 5B–D). The coulombic efficiency in the presence of the ‘‘Flex-Sil®’’ leachate is higher in all instances. Fig. 7 shows a point-by-point comparison of the voltammetry data for the ‘‘blank’’ and ‘‘Flex-Sil®’’ leachate. This data again confirms the improvement in coulombic efficiency through the use of a separator leachate, and clearly indicates the nature of the antimony suppression effect is chemical rather than physical.

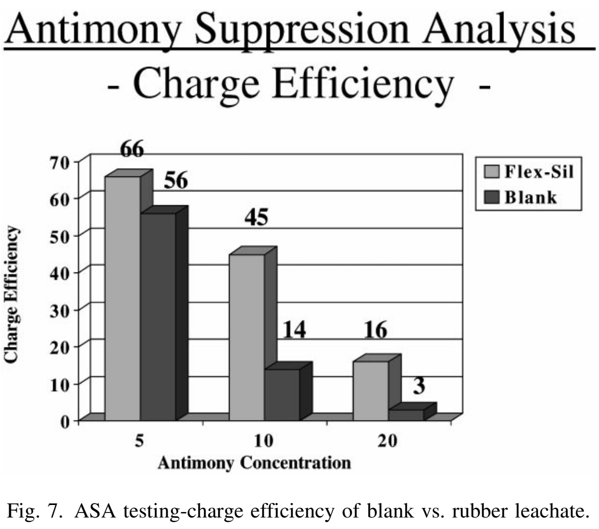

Fig. 7. ASA testing-charge efficiency of blank vs. rubber leachate.

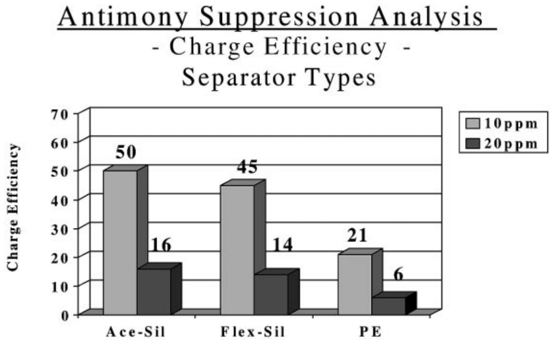

Fig. 8. ASA testing-charge efficiency of different separator types.

Similar ASA tests were performed with three different separator types. Two were based on natural rubber (Ace-Sil® and Flex-Sil®) and one was manufactured from petroleum-based polymers (polyethylene). Fig. 8 shows the ASA behavior of these separators at two levels of antimony contamination. At the 10 ppm antimony level, the coulombic efficiencies were 50, 45 and 21%, respectively for Ace-Sil®, Flex-Sil® and PE. Upon increasing the level of antimony contamination two-fold, the efficiencies drop to 16, 14 and 6%, respectively. Again indicating the rubber separator's ability to suppress gassing.

A final series of tests were performed in an attempt to establish the nature of the antimony suppression effect. In this test, a microporous polyethylene separator was manufactured to include a small percentage of natural rubber (approximately 20%). This material was extruded and calendered into a standard golf car battery separator and leached in sulfuric acid as described in Section 2. The ASA test results are shown in Fig. 9. At an antimony level of 20 ppm, the hybrid rubber/PE separator material showed an efficiency of 12% while the natural rubber product was 14% and the pure PE product was 6%.

To conclude, we believe that a viable test for evaluating the ability of a battery separator to suppress the deleterious effects of antimony has been developed. This test, appropriately named, ASA, is based on the assumption that the separators contain leachable components that suppress the effects of antimony. Results obtained through the application of the ASA test have demonstrated that the chemical composition of the separator is the controlling factor in suppressing the influence of antimony in the lead-acid battery. We have also shown that the ability of a separator to suppress the deleterious effects of antimony is primarily a chemical process and not a physical effect. We have used the ASA test to evaluate the ability of a separator to impact the charging efficiency of the negative electrode of a lead-acid battery.

The fact that natural rubber can have a positive effect on the charging efficiency was also demonstrated in combination with polyethylene separator material. Historically several methods which have included additions of chemical additives (VCR's, VCA's, etc.) or special coatings have been attempted to mimic this natural rubber effect [11,12]. These

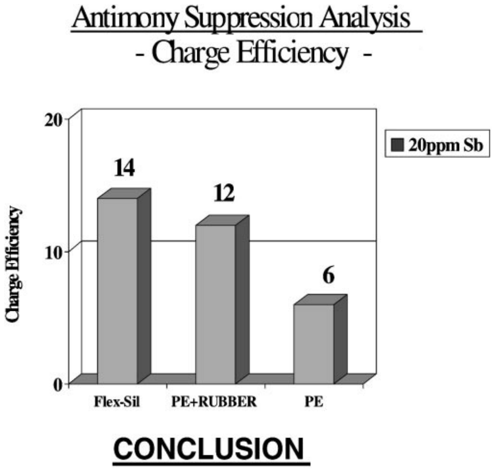

Fig. 9. ASA testing-charge efficiency results of rubber-polyethylene separator.

CellForce™

Suppression of Antimony Poisoning

Lowered Battery Maintenance

Enhance Deep Cycle Performance

Longer Battery Life

Compatible with Automated Battery Assembly

Can Be Sleeved or Enveloped

Comparable Physical Characteristics with PE

Available in Leaf or Rolls

Fig. 10. CellForce separator features.

Physical and Chemical Properties
Industrial Battery Separators
CellForce™ versus Polyethylene

	CellForce	**Typical PE**
Total Oil Content %	17 ± 3	17 ± 3
Ash Content %	50-60	55-65
ER (Ω-cm²) (0,65 mm BW)	0,35-0,45	0,30-0,40
Tensile Elongation		
Mach. Direction %	700-800	600-700
Cross Mach. %	350-450	400-500
Median Pore (μm)	0,1	0,1
Volume Porosity %	50-60	50-65
Moisture Content %	<3	<3
Trace Elements	pass ECC	pass ECC

Fig. 11. Comparison of CellForce and polyethylene separators.

attempts have resulted in short-lived activity and/or deleterious voltage effects in batteries. We have shown that by combining the chemical attributes of natural rubber with the physical attributes of polyethylene, a totally new type of hybrid separator can be offered to the industry. This new separator, now introduced to the world by AMERACE, under the trade name "CellForce$^{\text{TM}}$". Features of the new separator are presented in Fig. 10.

The physical and chemical properties of CellForce$^{\text{TM}}$ are very comparable to the presently available polyethylene-based separator materials (Fig. 11).

Battery testing is ongoing and results indicate that performance advantages related to antimony suppression have been achieved. Figs. 12 and 13 provide battery cycling data on deep discharge golf car type mono-blocks containing a 6% antimony alloy in the positive grids and a 3% antimony alloy in the negative grids. Discharge was at the C2 rate to a 1.75 V/cell cut off with a failure point of 50% of rated capacity. Recharge was accomplished using a 12 h limit with tapered constant current at 25 A maximum and 2.54 V/cell voltage limit. Failure of the PE separator cells at approximately 450 cycles can be directly related to the top of charge current acceptance as shown in Fig. 13. Because of the reduced antimony transfer and improved negative plate voltage characteristics on the CellForce$^{\text{TM}}$ batteries, the overcharge current is limited when compared to the PE separator batteries in the mid to later stages of cycle-life. As a consequence of these lower recharge currents, battery temperatures were on average lower and resulted in the need for less watering. Failure mechanisms for the PE batteries were attributed to positive grid corrosion and active material shedding. The CellForce$^{\text{TM}}$ batteries are still on test at the time of this writing with an estimated cycle-life in excess of 600 cycles.

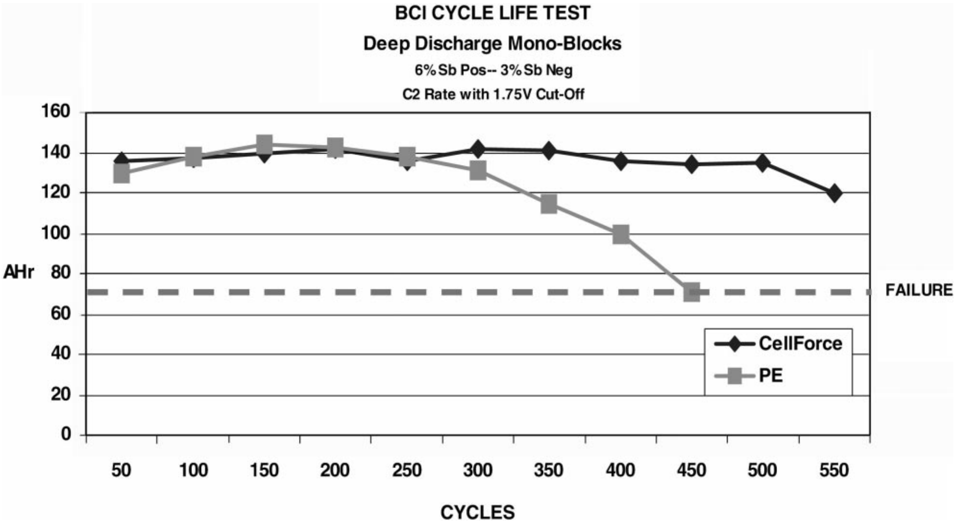

Fig. 12. Battery test comparison-life cycle capacity on CellForce vs. PE separators.

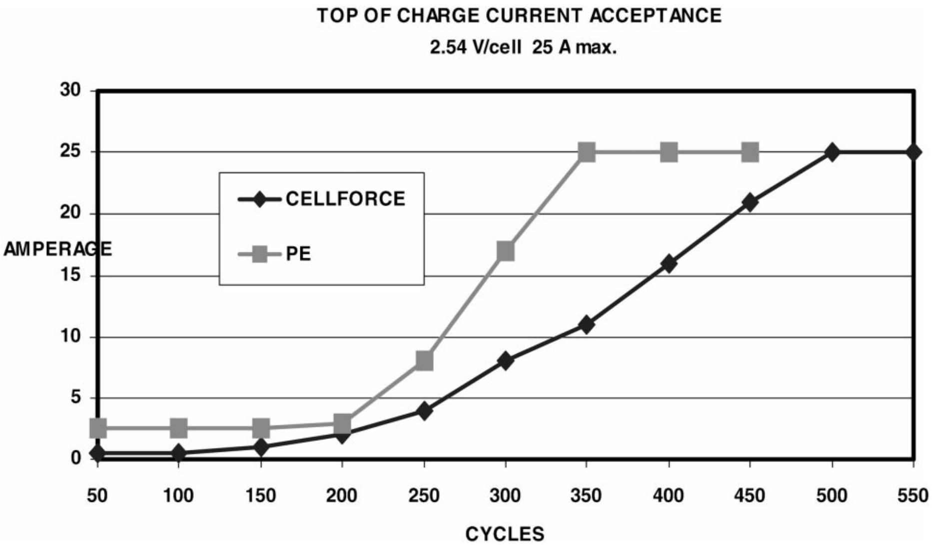

Fig. 13. Battery test comparison-life cycle top of charge current acceptance on CellForce vs. PE separators.

Future work will seek to further explain the mechanism(s) for antimony suppression as well as determine the effective life for the suppression activity. Investigations of the new hybrid rubber-polyethylene separator will also be completed to further identify the relationships between residual oil content and type versus oxidation resistance and the potential for release of oily deposits during battery field service.

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