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Highly Refined Supersoft Ultra Recycled Lead for Critical Applications

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Supersoft Ultra Secondary Lead

- → Doe Run will close their Herculaneum primary lead smelter at the end of 2013. Doe Run is the highest purity lead produced by a primary smelter.
- → The high purity refined lead from this plant will no longer be available for critical battery material
- → RSR Technologies believed that they could develop a refining process for secondary lead which could produce the same performance in VRLA batteries as the Doe Run primary lead.

Supersoft Ultra Secondary Lead

→ Pierson and Weinlein in Power Sources 5 demonstrated that certain impurities in recycled lead had more influence on gassing than others.

→ The ALABC in Project N3.1 demonstrated the effects of various impurities in lead on the float currents for VRLA batteries using Doe Run lead as a base.

→ RSR Technologies utilized the guidance of this R&D to pyro-metallurgically refine and remove the gassing elements in a high purity secondary lead to very low levels which we call Supersoft Ultra.

Production of Oxide

- → Northstar Battery agreed to perform a comparison of the Supersoft Ultra with Doe Run primary for all the lead components of their batteries.

- → RSR produced a large lot of lead and sent 100,000Kg to Omni oxide to be converted into both standard grey negative oxide and red lead positive oxide.

- → The melt pots, barton pots, and oxide systems were purged for 2 days to assure that they contained only the Supersoft Ultra lead oxides.

Comparison of Materials (ppm)

Element	Supersoft Ultra		
	Positive	Negative	Doe Run
→ Antimony	<0.1	<0.1	0.1
→ Arsenic	<0.1	<0.1	<0.1
→ Bismuth	85.0	85.0	7.0
→ Cadmium	<0.1	<0.1	0.2
→ Copper	2.0	1.8	0.2
→ Chromium	<0.1	<0.1	<0.1
→ Cobalt	<0.1	<0.1	<0.1
→ Iron	0.7	2.2	0.7
→ Manganese	<0.2	<0.2	<0.2
→ Nickel	0.6	0.8	0.2
→ Selenium	<0.2	<0.2	<0.2
→ Silver	37.0	39.0	2.0
→ Tin	<1.0	<1.0	<1.0
→ Tellurium	<0.2	<0.2	<0.2
→ Zinc	2.5	1.0	0.4

ALABC Study of Impurities: Rate of Change of Float Current From Impurities

Elements	Rate of Change (mA Ah^{-1} per ppm)		
	I *float*	I *hydrogen*	I *oxygen*
Ni	+ 0.03772	+ 0.00019	+ 0.03772
Sb	+ 0.01860	+ 0.00059	+ 0.01828
Co	+ 0.04332	+ 0.00109	+ 0.04252
Cr	+ 0.01782	+ 0.00016	+ 0.01774
Fe	+ 0.01958	+ 0.00014	+ 0.01951
Mn	+ 0.04643	+ 0.00080	+ 0.04543
Cu	+ 0.00625	+ 0.00038	+ 0.00583
Ag	+ 0.00097	+ 0.00006	+ 0.00103
Se	+ 0.10410	+ 0.00500	+ 0.09950
Te	+ 0.10167	+ 0.00933	+ 0.11233
As	+ 0.00887	+ 0.00030	+ 0.00881
Sn	+ 0.00393	+ 0.00002	+ 0.00399
Bi	- 0.00026	- 0.00001	- 0.00026
Zn	- 0.00003	- 0.00002	- 0.00001
Cd	+ 0.00027	+ 0.00001	+ 0.00026

Float Currents and Gassing

- As seen from the previous slide the major problem in gas generation on float is the effects of impurities on the positive plate.
- Oxygen generated there transfers to the negative where it depolarizes the negative.
- Too much oxygen and the battery temperature can increase, the positive grid can corrode, and water can be lost due to incomplete recombination.

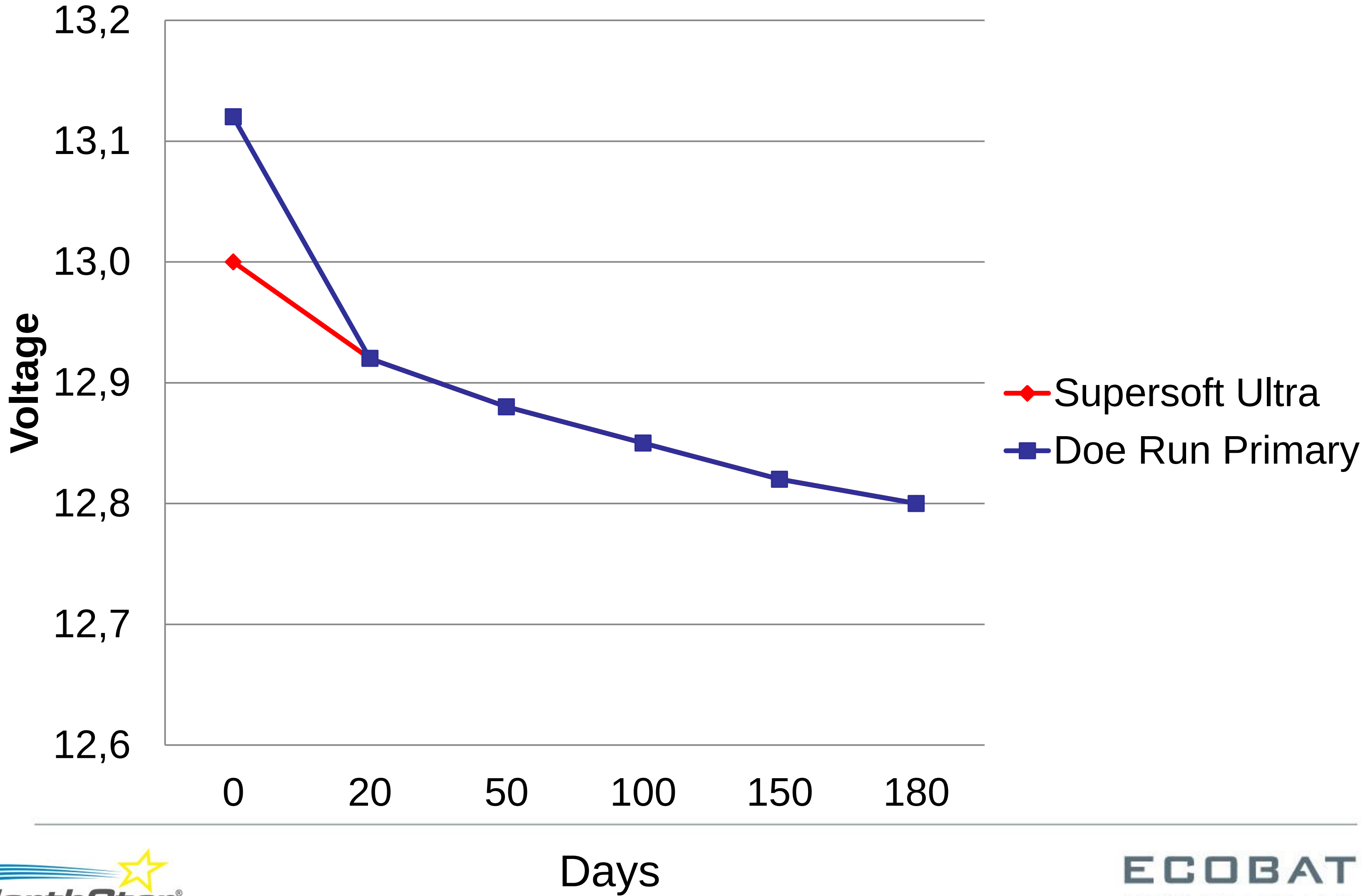
Composition of Oxides

- To match the low impurity content of the Doe Run primary lead, the Supersoft Ultra was extra refined to reduce the gassing impurities.
- Sb, As, Cd, Cr, Co, were reduced to <0.1ppm.
- Mn, Te, and Se were reduced to <0.2ppm
- Ni and Sn were reduced to <1ppm
- Cu, Zn, and Fe were reduced to 2ppm or less.
- Silver at 38ppm and Bi at 85ppm were not removed.

Initial testing

- Thirty 100 Ahr batteries were constructed each containing Doe Run Primary positive and negative oxides or Supersoft Ultra positive and negative oxides for comparative testing.
- The batteries were produced using pure lead thin plate grids and utilized the Supersoft Ultra lead for both the grids and active material.
- The initial testing showed that the starting battery performance of the two materials was similar.

Charge Retention (Self Discharge During Storage at 25°C)



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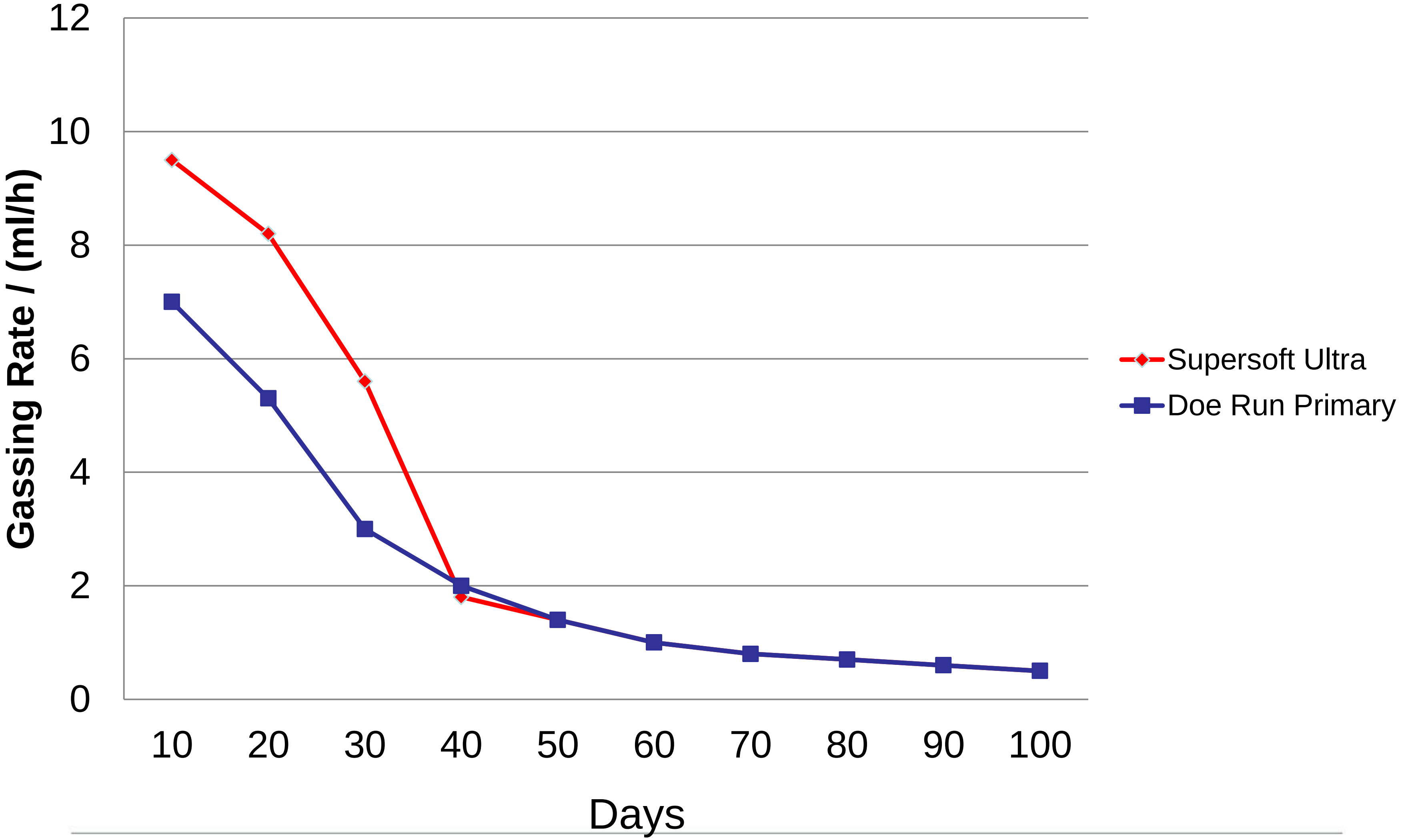
Gassing Rate (Float at 25°C and 2.27 Volts)



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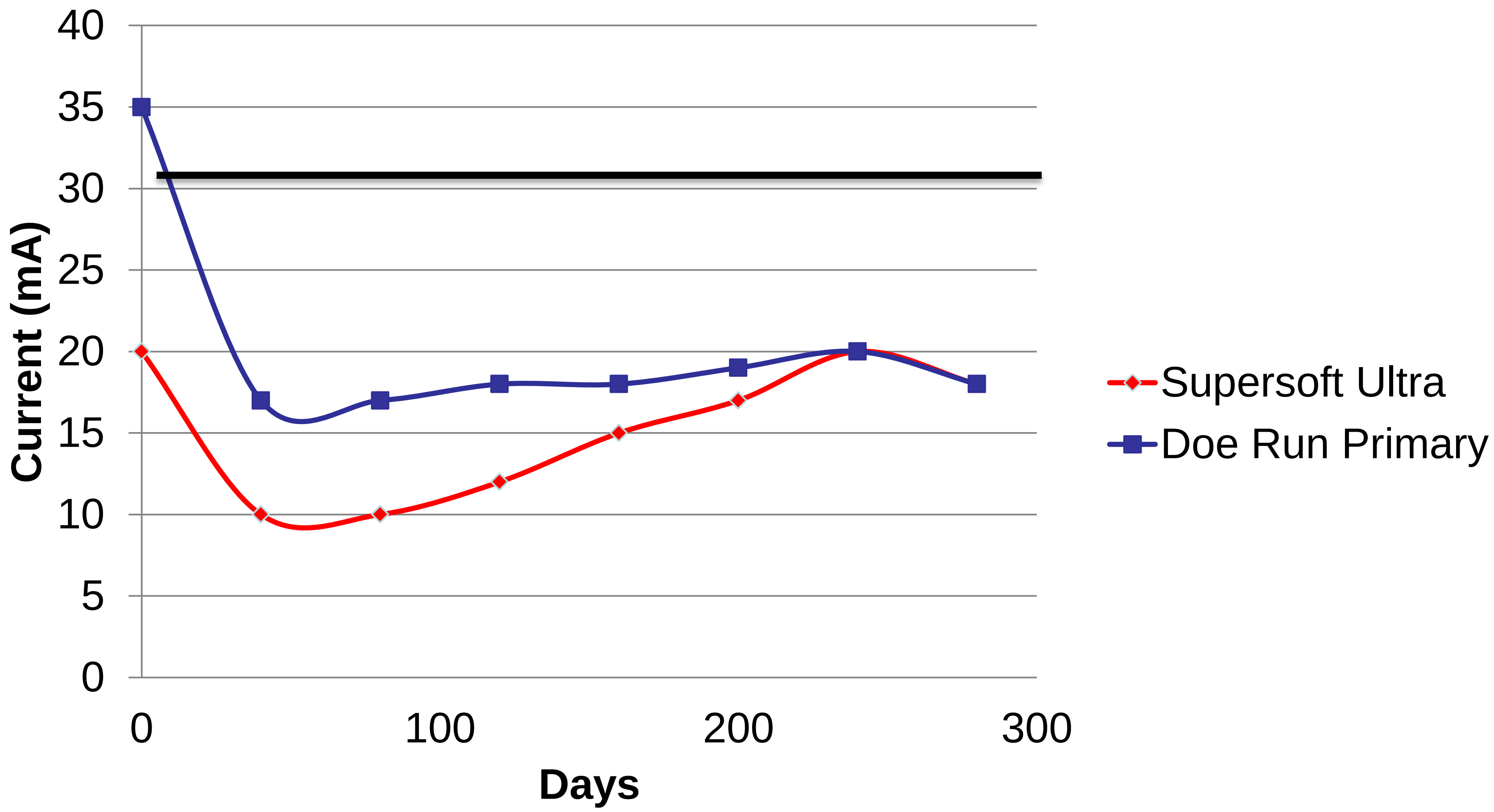
Float Current Stability (Mean Float Current at 25°C and 2.27 Volts Float Voltage)



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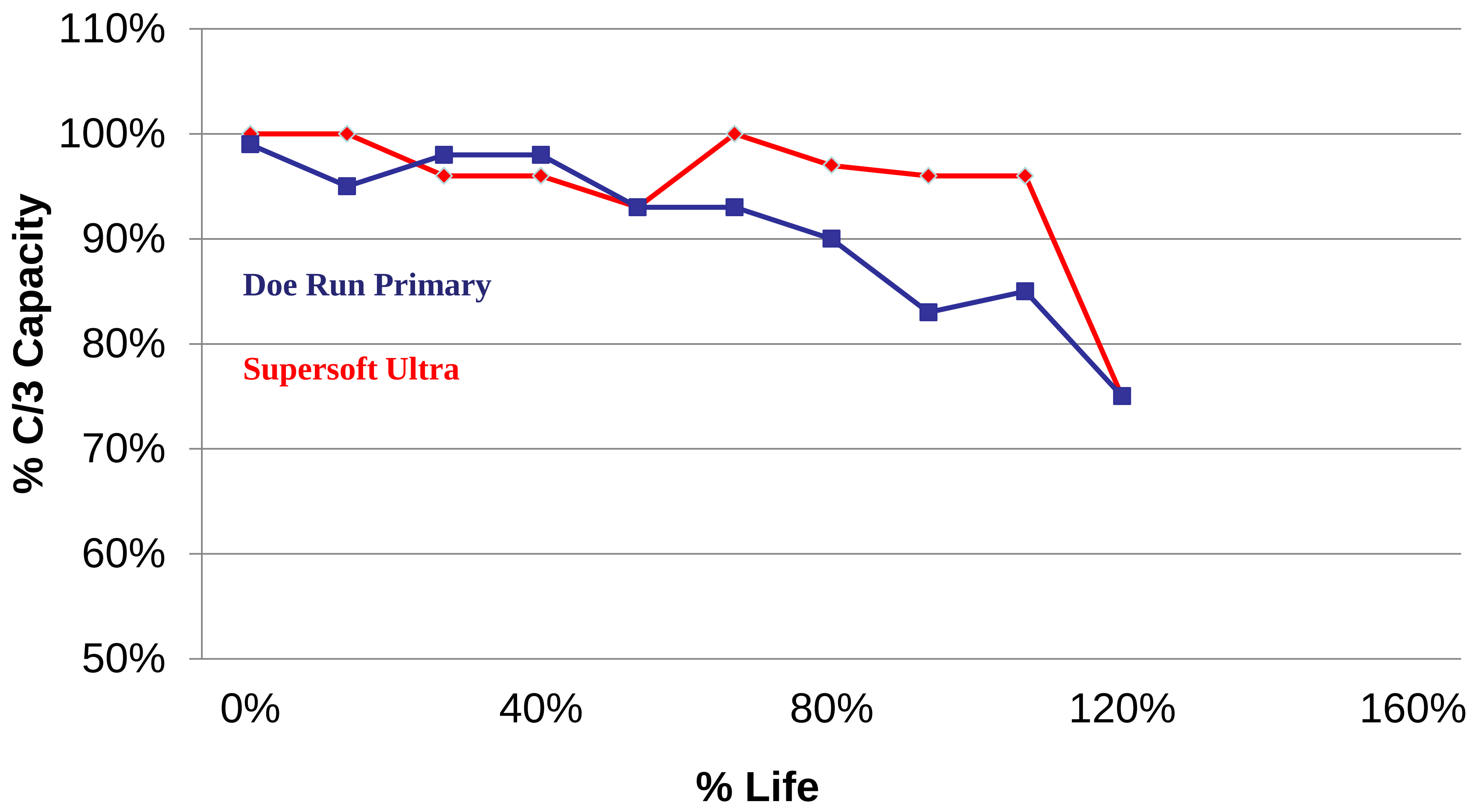
Accelerated Float Life at 65°C



Battery Sampling

- → A battery containing Supersoft Ultra positive and negative active material which had undergone battery tests was cut open and the positive and negative active material removed from the grids.
- → The material was analyzed to determine what changes may have taken place during the testing.
- → The results are seen below.

Results

- The self discharge rates were identical
- The gassing rates for both declined for the first 40 days and then were low and identical
- The float current for the Supersoft Ultra was initially lower than the doe Run primary but the two were similar and much lower than the 30mA current considered good practice.
- The cycle life of the two were virtually identical. The Supersoft Ultra may have retained higher capacity longer than the Doe Run Primary.

Composition of Cycled AM

→ Most of the silver, copper, and zinc were transferred to the negative active material from the positive active material.

→ The Sb, As, Te, Se, Mn, Co, Cr, Ni, remained in place and at the low initial levels.

→ Transfer of silver and copper to the negative results in lower float currents, lower gassing, and self discharge.

→ The information from ALABC project N3.1 allows calculation of the effects of the impurities on float currents.

Calculation of Impurity Effects

- Using the data developed by CSIRO in the ALABC project N3.1, we can calculate the effects of various impurities on the float current of a battery.
- (Ampere hour capacity of the battery) X (concentration of the impurity in ppm) X (gassing effect of the impurity) = increase or decrease in float current
- We have to calculate the effects for both the positive and the negative plate to get the total effect.

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Change in Float Current due to Transfer of Silver from Positive to Negative

Initial Silver

- → Positive Silver 38ppm
- → Increase in positive float current 3.94 mA
- → Negative silver 38ppm
- → Increase in negative float current 0.228 mA
- → Total increase in float current due to silver in active material 4.142mA

Silver after testing

- → Positive silver 3.5ppm
- → Increase in positive float current 0.360mA
- → Negative Silver 72ppm
- → Increase in negative float current 0.429mA
- → Total increase in float current due to silver (new float current 0.789mA)

Change in Float Current due to Transfer of Copper from Positive to Negative

Initial Copper

- → Positive Copper 2.0ppm
- → Increase in positive float current 1.17mA
- → Negative Copper 1.8ppm
- → Increase in negative float current 0.068mA
- → Total increase in float current due to copper in Active Material 1.23mA.

Copper after testing

- → Positive copper 0.2ppm
- → Increase in positive float current 0.117mA
- → Negative Copper 3.8ppm
- → Increase in negative float current 0.148 mA
- → Total increase in float current due to copper (new float current 0.268 mA)

Reduction of the Float Current due to Bismuth in the Active Material

Bismuth reduces gassing

- → Bismuth is only one of two impurity elements which has been shown to reduce float current and gassing on active material.
- → Bismuth is not transferred from positive to negative.

Bismuth in Active material

- → Positive bismuth is 85ppm
- → Bismuth reduces the positive float current by minus 2.210 mA.
- → Negative bismuth is 92ppm
- → Bismuth reduces the negative float current by minus 0.092mA
- → Total reduction -2.302mA

Summary

→ Recycled Supersoft Ultra lead can perform as well as even the highest purity primary lead when used in critical applications.

→ The gas causing elements such as Te, Se, Ni, Sb, As, Co, Mn, Cr, Fe, and Cu must be removed to levels about 5-10 times lower than normal secondary lead specifications.

→ Silver and Bismuth do not have to be removed and present virtually no problem in the use of this lead for VRLA and low gassing batteries.

Summary

- → The Supersoft Ultra high purity secondary lead is an acceptable replacement for the diminishing amount of primary lead soon to be produced in North America.
- → Supersoft Ultra can be used for both highly critical grid material for pure lead batteries as well as active material for all VRLA float or cycling batteries as a replacement for primary lead.

Thank you for your kind attention.

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