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SILVER-CADMIUM BATTERY PROGRAM

TECHNICAL DOCUMENTARY REPORT NO. WADD-TR-61-131, Pt II

March 1963

Directorate of Aeromechanics Aeronautical Systems Division Air Force Systems Command Wright-Patterson Air Force Base, Ohio

Project 8173, Task 817304-11

(Prepared under Contract No. AF 33(600)-42397 by The Gulton Industries, Inc., Metuchen, N.J. G. Rampel, J. Liska, R. C. Shair, authors.)

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This Final Report was prepared by Gulton Industries, Inc., for the Flight Accessories Laboratory, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio, under Contract No. AF 33(600)-42397. Mr. J. E. Cooper was task engineer for the laboratory.

The studies cover the period from 23 January 1961 to 1 October 1962.

This report is a continuation of work done earlier on the contract, and reported in WADD TR 61-131.

ABSTRACT

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This report covers the second phase of a research and development program leading to improved, long life, sealed silver-cadmium batteries for aerospace applications.

A silver electrode was utilized which yielded up to 50% of its capacity at the Ag^{II} oxide voltage plateau and the balance at the Ag^{I} oxide voltage plateau.

Several separator systems were tested with regard to obtaining maximum cycle life. The best separator combination consisted of single layers of Dynel-Polypor WA (coarse nylon base)-Fibrous sausage casing - V, each enclosing the positive electrodes in the order listed.

Sixty 7 ampere-hour cells, the AG-7HS, were life tested in a 90 minute cycle at several depths of discharge and at several temperatures, utilizing constant current and constant voltage recharge methods. Three thousand cycles were achieved at a 17% depth at $78^{\circ}F$.

Charging problems are discussed. It was found that a charge routine consisting of a combination of constant current followed by constant potential was better than constant current charging or constant potential charging alone.

The publication of this report does not constitute approval by the Air Force of the findings or conclusions herein. It is published for the exchange and stimulation of ideas.

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I. SUMMARY

The objective of the second phase of this research and development program was to fabricate and test sixty-five (65) seven ampere-hour sealed silvercadmium cells.

The highly porous sintered electrode was capable of discharge at the higher voltage plateau for about 50% of its capacity. The separator system selected

Ag - Dynel - Polypor WA - Fibrous sausage casing - V - Cd (coarse nylon base)

was a multi-layer combination of electrolyte retaining materials and silver migration barriers. The dynel and "V" are the electrolyte retaining layers while the polypor WA and fibrous sausage casing are the silver migration barriers. It was capable of extended cycling but still was the part of the system that generally failed first.

Two cells were tested and found resistant to the required levels for shock acceleration and vibration. Sixty cells were life tested as 5 cell batteries, cycling at -20° F, 78° F, and 120° F at 17% and 34% depth of discharge. The recharge was done by constant current and constant potential for both depths of discharge at each temperature.

The test work pointed out the problems to be expected at temperature extremes. At -20° F charging was inefficient, particularly with constant current charging which resulted in high pressures. At $+120^{\circ}$ F overheating, due to poor thermal coupling, resulted in accelerated separator breakdown.

Successful constant potential charging depended upon individual cell balance, and the performance of the batteries changed as they aged. Some cells received insufficient charge and eventually reversed, while others became excessively overcharged, resulting in high internal pressures. Constant current charging in some cases resulted in high end-of-charge voltages and pressures.

Notwithstanding the problems discussed above, hundreds of cycles were completed on all the batteries tested except two, one at $-20^{\circ}F$ and one at $+120^{\circ}F$. At 78°F the desired 3000 cycles was achieved.

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II. INTRODUCTION

The purpose of this program was to perform a silver-cadmium battery investigation which would lead to the development of a long life, deep cyclic, secondary silver-cadmium battery for military aerospace vehicles. Several specific areas of investigation were included in the program.

- 1. To procure or develop a more satisfactory separator, or separator combination.
- 2. To develop an improved silver electrode by impregnation or silver salt decomposition.
- 3. To provide maximum overcharge capability.
- 4. To fabricate prototype cells.
- 5. To evaluate cell and battery performance.

Specific requirements and design goals for the electrical requirements of the cells and batteries developed under this contract were:

- 1. That the battery be capable of discharge at 4.0 amperes for 35 minutes with battery voltage maintained between 29.0 and 23.0 volts.
- 2. That the battery be capable of accepting recharge for this discharge within 55 minutes.
- 3. That the battery be capable of 11,000 charge-discharge cycles while operating in a temperature range from -20°F to +120°F.
- 4. That the battery be capable of operation without maintenance throughout its entire cycle life and operate in any position.
- 5. That as a design goal, the battery be capable of operation in a vacuum of 10^{-9} mm of Hg.

III. EXPERIMENTAL

A. SEPARATOR STUDIES

The selection of the best separator system resulted from studies of prototype test cells constructed of plastic containers with removable covers as shown in Figure 1. The cells had pressure gauges attached so that pressure data could also be recorded. The cells were built using the separator or separator combinations to be tested. The testing program included manual and automatic cycling. The cycling circuit is shown in Figure 2. The main objective of the studies was to find a separator which was capable of long cycle life, a minimum of 3000 cycles. The separators were wrapped to enclose the silver electrode, and the sequence of wrapping is denoted in the following manner:

0.0025" 0.006" 0.003" 0.009" Ag - Dynel - Polypor WA - Fibrous sausage casing - V - Cd (coarse nylon base)

The dynel^{*} was first wrapped around the positive plate, followed by the Polypor WA, the fibrous sausage casing, and finally the V, which is a non-woven nylon. The number above the separator signifies the thickness of that separator in inches. In general, the separator under test was inserted between the dynel and the V separators.

1. Separator Test Cell No. 0

0.0025" 0.0015" 0.009" Ag - Dynel - Cellophane - V - Cd

The cell was open and flooded with electrolyte. The cell was cycled at room temperature in a 90 minute routine at a 25% depth. The charge and discharge voltages were at the higher plateaus associated with $Ag^{II}O$. Cycling was terminated after 440 cycles.

This cell was constructed to obtain preliminary data prior to the construction of sealed cells. In this cell as in subsequent cells, the V separator, a non-woven polyamide, was used for electrolyte retention.

2. Separator Test Cell No. 1

0.003" 0.009" Ag - R.A.I.** (polyethylene acid membrane) - V - Cd

This cell cycled 88 times prior to failure. The R.A.I. membrane was discolored on both sides and had allowed silver to deposit on the final separator. The R.A.I. separator provides inefficient contact and wetting because approximately 50% of its area is depressed on either side by random grooves. This pattern is clearly

^{*} Table III on Page 11 gives the description of the type and composition of each of these materials.

^{**} Registered Trade Mark - Radiation Applications, Inc.

seen both on the positive plates and on the membrane. The resultant pockets do not provide adequate electrolyte contact to the surface of the plates.

3. Separator Test Cell No. 2

0.004" 0.009" Ag - (Polypor <u>PVA</u> - WB) - V - Cd

This cell developed a short circuit in 66 hours while on a 100 ma charge. The polypor was black on both sides, and the V showed a brown coating.

4. Separator Test Cell No. 3

0.0025" 0.0015" 0.009" Ag - Dynel - Cellophane - V - Cd

This separator system was the same that was tested in cell No. 0 with the exception that cell No. 3 was a sealed cell. The C/10 overcharge voltage and the pressure were recorded. They were 1.56 volts and 35.0 psig respectively. The C/6 overcharge voltage and the pressure obtained were 1.60 volts and 67.0 psig. Figure 3 gives the data on the cell pressure at various overcharge currents.

The cell was cycled 128 times at a 33% depth. The charge voltage and the discharge voltages were at the higher plateaus. The plastic container failed and as a consequence, cycling was terminated.

5. Separator Test Cell No. 4

0.0025" 0.0015" 0.009" Ag_{P.V.P.} - Dynel - Cellophane - V - Cd

Cell No. 4 was identical to cell No. 3 in all respects, with the exception that the positive plates were treated with a 1% solution of polyvinylpyrrolidine (P.V.P.). The P.V.P. was employed to complex the soluble silver. In use, it increased the polarisation of the positive electrodes and reduced the available capacity.

The cell was cycled to a 33% depth and cell failure was experienced after 368 cycles. The failure was caused by the migration and depositing of free silver along the plate edges and the plate connectors. This problem was corrected by applying polystyrene to all of the plate edges and the tabs. The cellophane separator was intact at the plate surfaces but failed at the folds.

6. Separator Test Cell No. 5

0.0025" 0.003" 0.009" Ag = Dynel - R.A.I. (polyethylene acid membrane) - V - Cd

This cell was a repeat of cell No. 1, with the exception that in this cell the dynel was placed against the positive plate while in cell No. 1 the R.A.I. membrane was placed against the positive plate. The cell was cycled manually, placed on open-circuit stand, and allowed to self discharge. Inspection showed that the folds of the separator pack were heavily contaminated with silver deposits.

7. Separator Test Cell No. 6

0.0025" 0.003" 0.009" Ag - Dynel - Polypor WA - V - Cd (Fine nylon base)

The cell was cycled manually and placed on open circuit after a charge. The cell self-discharged rapidly. Inspection showed that the entire separator was heavily contaminated with silver deposits.

8. Separator Test Cell No. 7

This cell was similar to cell No. 3 and was re-run because the plastic container of cell No. 3 had ruptured. The steady state pressure and voltage at a C/10 overcharge were 37.0 psig and 1.55 volts. The cell was cycled 49 times at a 33% depth and placed on open circuit after charge. The cell self-discharged. The cause of failure was silver deposits at the separator folds and in the vicinity of the plate tabs.

9. Separator Test Cell No. 8

0.0025" 0.001" 0.009" Ag - Dynel - Polyvinyl alcohol film - V - Cd

This cell self-discharged on stand after a charge. The cause of failure was the deposition of silver between the connecting tabs and the top edges of the plates of opposite polarity.

10. Separator Test Cell No. 9

0.0025" 0.003" 0.009" Ag - Dynel - Fibrous sausage casing - V - Cd

The steady state voltage and pressure at a C/10 overcharge were 1.60 volts and 41.0 psig. This cell was cycled at a 20% depth and completed 1151 cycles. Inspection showed that the last separator was coated with silver deposits which were most intense at the plate edges. The fibrous sausage casing was intact but completely permeated with silver.

11. Separator Test Cell No. 10

0.0025" 0.003" 0.003" 0.009" Ag = Dynel - Polypor WA - Fibrous sausage casing - V - Cd (Fine nylon base)

The negative and positive plate edges in addition to part of the tab were coated with polystyrene to prevent early shorting caused by silver deposits. The shorting occurs between the positive tabs and the top edge of the negative plates. The cell was cycled so that it was discharged at a 20% depth and charged to return 10C - 110%. The cell completed 2920 cycles. Figure 4 shows the capacity of the cell at cycle numbers 576 and 1820. For cycle number 2058, the discharge voltage was 1.38 volts at t = 0 minutes and 1.35 volts at t = 35 minutes.

12. Separator Test Cell No. 11

0.0025" 0.003" 0.009" Agp_v V_p - Dynel - Fibrous sausage casing - V - Cd

This test was discontinued because of increased polarization resulting from the addition of P.V.P. to the positive electrodes. The same results were noted for cell No. 4.

13. Separator Test Cell No. 12

0.0025" 0.003" 0.003" 0.009" Ag - Dynel - Polypor WA - Fibrous sausage casing - V - Cd (Fine nylon base)

Cell No. 12 employed the same separator system utilized in cell No. 10, but was designed to obtain other information. The cell had smaller electrodes, 24 cm² per side. A higher ratio of negative capacity to positive capacity was used, and a stainless steel container replaced the plastic case. The results showed that the stainless steel container did not affect the cell performance in any way. In addition, a ratio of negative capacity to positive capacity greater than 1.5 was not required. No attempt was made to cycle the cell.

14. Separator Test Cell No. 13

Cell No. 13 employed the same separator system utilized in cell No. 10. However, it was constructed to determine the voltage polarization characteristics for both first and second plateaus at currents up to 6.0 amperes. The results, given in Figure 5, show that for this separator system, the cell resistance is high.

15. Separator Test Cell No. 14

This cell was fabricated with the smaller electrodes used in cell No. 12 and the separator combination employed in cell No. 10 was utilized. The electrode stack consisted of five (5) positives and six (6) negatives. A C/10 rate overcharge was conducted, and the steady state voltage and pressure was 1.54 volts and 39.5 psig. The voltage polarization characteristics were obtained for the first and second plateaus. The results, shown in Figure 6, indicate that the cell resistance is lower than cell No. 13. It may be noted that the linear slopes for the Ag 0 and the Ag₂O plateaus do not differ significantly. Therefore, the voltage differential between the two oxides is relatively constant over the range shown, and is approximately 0.28 volts.

16. Separator Test Cell No. 15

Cell number 15 was fabricated utilizing the 37 cm² plates. The electrode stack consisted of three (3) positive plates and six (6) negative plates. The two extra negative plates were added to ensure that the cell would be positive limiting. The results indicate that the extra negative capacity was not required.

17. Separator Test Cell No. 16

Cells previous to cell No. 16 had a nominal capacity of 6.0 ampere hours. However, it was decided to increase the capacity to 7.0 ampere-hours to take advantage of the first plateau voltage operation during cycling. Cell No. 16 was a prototype for preliminary evaluation. It was operated open and flooded. The separator combination used in cell No. 10 was employed.

This cell and all subsequent cells were fabricated with four (4) positives and five (5) negatives. Each plate in the stack had a surface area of 37 cm².

18. Separator Test Cell No. 17

0.0025" 0.0035" 0.003" 0.009" Ag - Dynel - Nylon (MPV) - Fibrous sausage casing - V - Cd

The nylon (MPV) separator consisted of a 3.5 mil nylon base which was treated with a mixture of colloidal magnesium hydroxide containing 2.3% polyvinylpyrrolidine. The reason for investigating this separator was to find a possible substitute for the standard Polypor WA which has an undesirably high electrical resistance. The results were not encouraging and the cell was discarded.

19. Separator Test Cell No. 18

0.0025" 0.006" 0.003" 0.009" Ag = Dynel = Polypor WA = Fibrous sausage casing = V = Cd (coarse nylon base)

This cell was constructed to determine if the electrical resistance of the separator system could be reduced by substituting Polypor WA on a coarse nylon base for Polypor WA on a fine nylon base. Table 1 gives a list of various separators and their electrical resistance in milli-ohms/inch². Figure 7 shows the test apparatus used to determine the separator resistance.

The cell was cycled by discharging at a 28% depth and charging by the constant current method at a rate of 2.0 amperes for a period of 55 minutes. The cell completed 1262 cycles before the cell was terminated by mechanical failure. The cycling apparatus malfunctioned, allowing the cell to remain on a continuous 2.0 ampere charge for several hours.

20. Separator Test Cell No. 19

This cell represented the first hermetically sealed silver-cadmium cell with ceramic-to-metal seals in addition to a stainless steel case and cover. The separator system was the same used in cell No. 10. Table 2 shows the weight distribution and the percentage of the total weight for the various cell components. In this cell the ratio of negative capacity to the positive capacity was 1.2 : 1.

We have concluded from the foregoing experimental cells that not only is the type of separators employed in the cell important, but the sequence has been shown to play a major role. The system that was selected and used for the cells in this program was:

0.0025" 0.006" 0.003" 0.009" Ag - Dynel - Folypor WA - Fibrous sausage casing - V - Cd (Coarse nylon base)

The dynel was placed against the positive plate to retain electrolyte and to prevent contact with the migration filters. Next in sequence was the Polypor WA with coarse nylon base. This separator was employed in place of the Polypor WA with the fine nylon base to reduce the electrical resistance of the cell. The function of the Polypor WA is to serve as the first, or primary, migration filter.

The fibrous sausage casing was placed against the Polypor WA and served as "back-up", or secondary, migration filter to extend cycle life. The V separator which was against the negative plate, served as the main electrolyte retaining separator.

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TABLE 1.

THICKNESS AND ELECTRICAL RESISTANCE OF SEPARATORS

SEPARATOR	THICKNESS	RESISTANCE @ 30 ⁰ C (milli-ohms/in.	
Dyne1	.0025	18.0	
Polypor WA	.0045	46.0	
Fibrous Sausage Casing	.003	26.3	
V	.009	7.6	
Polypor WA (Fine nylon)	.003	132.5	
Polypor WA (Coarse nylon)	.006	9.0	

NOTE: Table III, Page 11, gives the description of the type and composition of each of these materials.

TABLE 2.

THE WRIGHT OF THE AG-7HS SILVER-CADMIUM CELL AND ITS VARIOUS COMPONENTS

CELL COMPONENT		GRAMS	PERCENT
Positive electrodes		47.7	19.8
Negative electrodes		65.9	27.5
Cover assembly		13.0	5.4
Case		66.1	27.6
Separators		13.2	5.5
Electrolyte		<u> </u>	14.2
	Total	239.8	100.0

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TABLE 3.

DESCRIPTION OF SEPARATOR MATERIALS TESTED

DESIGNATION

DESCRIPTION

Polypor WA (fine)	Ion exchange resin deposited on fine woven nylon base
Polypor WA (coarse)	Ion exchange resin deposited on coarse woven nylon base
Polypor PVA-WB	Ion exchange resin deposited on woven nylon base
v	Non-woven polyamide
R.A.I.	Radiation treated polyethylene acid membrane
Fibrous Sausage Casing	Glycerine-free cellulosic film
Cellophane	Cellulosic film
Dynel	Non-woven copolymer of acrylonitrile and vinyl chloride
Nylon M.P.V.	Nylon treated with Mg (OH) ₂ and polyvinylpyrrolidine
Polyvinyl Alcohol film	Polyvinyl alcohol film

III. B. SILVER ELECTRODE

A new type of silver oxide electrode had been developed prior to this contract. The electrode was prepared by impregnating a compound of silver into a highly porous sintered plate having no free silver metal present, and then thermally decomposing the silver compound at a low temperature, 150° C. The use of a porous base metal allows the deposition of silver within the matrix by thermal or chemical reduction methods. The deposited silver need not be sintered since the silver is held within the pores of the sintered matrix. The deposited silver is extremely fine, and the porosity of the plates is high. The coefficient of utilization of the silver oxide is in the order of 90%. About 50% of the energy is available at the potential level of silver^{II} oxide, and the remainder is available at the silver^I oxide level. The purpose of this study was to investigate the effect of a non-silver, highly porous grid on the silver-cadmium electrode system.

1. Experimental Gulton Electrodes

a. Before Loading:

i.	Weight	7.9 grams	
ii.	Dimensions	6.6 cm. x 5.7 cm. x 0.09 cm	ι.
iii.	Porosity	72%	

b. After Loading:

i .	Weight		12.2	grams
		~		

- ii. Weight of silver 4.3 grams
- iii. Theoretical cap, 2.10 ampere-hours
- iv. Porosity 55%

Table 4 shows discharge data for the Gulton experimental silver-cadmium electrode discharged against standard Gulton cadmium plates (normally used for nickel-cadmium cells).

The performance of this silver electrode indicates a high order of active material utilization, both at the one hour rate, C rate, and at the 5C rate. The discharge proceeds with about 41% of capacity available at the higher potential plateau at the C rate and with 36% available at the 5C rate. These results are attributed mainly to the following properties of this electrode:

- a. High porosity (55%) of the fabricated plate.
- b. Silver deposited at low temperature (100-200°C).
- c. Highly porous supporting matrix, yielding improved conductivity between oxide grains and supporting matrix.

TABLE 4.

DISCHARGE DATA FOR GULTON EXPERIMENTAL SILVER-CADMIUM CELL

Discharge Current	Voltage (volta)		Capacity	Capacity at R.	Total <u>Capacity</u>	
(amperes)	E 1	E ₂	(amb)	(% of total)	(% of theoretical)	
2.0	1.36	1.09	1.86	417	89 %	
10.0	1.28	1.02	1.84	36%	88%	

Note:

- (1) E_1 is the Ag O Potential E_2 is the Ag₂O Potential
- (2) Theoretical capacity = 2.10 ampere-hours
- (3) See Figures 8 and 9 for discharge data

A control run on a commercial silver plate was made for comparison with the findings as indicated below and in Table 5.

2. Commercial Electrode

Physical characteristics of loaded plate

8.	Weight	8.50 grams
b.	Dimensions	6.6 cm. x 6.0 cm. x 0.04 cm.
c.	Porosity	31%
d.	Weight of Silver - (in screen)	7.6 grams
e.	Theoretical Capacity	3.80 ampere-hours

From Table 5 it is seen that the voltage during discharge is lower than for the Gulton experimental electrode. The discharge capacity at E_1 is also lower. The greatest difference, however, is the low coefficient of utilization: only 41% of the theoretical capacity compared to 89% for the Gulton electrode. It should also be noted that the capacity at the first plateau was obtained with no stand time prior to discharge. It is characteristic for this electrode, that the higher silver oxide, Ag^{II}O, becomes reduced, on stand, to the lower oxide, Ag^I₂O.

TABLE 5.

DISCHARGE DATA FOR COMPERCIAL SILVER-OXIDE ELECTRODE

Discharge Current (Amperes)	Volta (volt	ge s) E ₂	<u>Capacity</u> (amphrs.)	<u>Capacity</u> <u>at E1</u> (% of total)	Total Capacity (% of theoretical)
2.0	1.25	1.04	1.56	34.0%	41.0%
Note:					

- (1) E_1 is the Ag 0 Potential E_2 is the Ag₂0 Potential
- (2) Theoretical capacity = 3.80 ampere-hours
- (3) See Figure 10 for discharge data
- 3. Preparation Of Lighter Weight Electrodes

Positive electrodes were prepared using a lighter sintered structure for the supporting matrix, in order to reduce weight. The plates were dipped into the silver solution and dried at 150°C, until the formation of free silver was complete. In production, the process can be made continuous; that is, dip and dry. The characteristics of the experimental electrodes were as follows:

Before loading:

4.	Weight	6.4	gra	26					
ь.	Dimensions	6.6	cm.	x	5.7	cm.	x	0.09	cm.
c.	Porosity	72%							

After loading:

8.	Weight	11.3 - 11.8 grams
Ъ.	Weight of silver	4.9 - 5.4 grams
c.	Theoretical capacity	2.5 - 2.7 ampere-hours per plate
d.	Porosity	47%

Table 6 represents data for a typical plate containing 5.0 grams of silver.

TABLE 6

DISCHARGE DATA FOR SILVER ELECTRODE

Discharge Current (Amperes)	<u>Voltage</u> (volts)		<u>Capacity</u> (amphrs.)	Capacity at E ₁	Total Capacity (% of theoretical	
	^E 1	E ₂		(% of total)		
2.0	1.37	1.08	1.94	39.5%	78%	

Note:

(1)	Ε,	ís	the	Ag 0	Potential
	E ₂	is	the	A g ₂ 0	Potential

- (2) Theoretical capacity = 2.50 ampere-hours
- (3) See Figure 11 for discharge data
- (4) See Figure 12 for charge data (2.1 ampere-hour cell)
- 4. Evaluation Of Gulton 6-AH Cell

A six (6) AH silver-cadmium cell was constructed, using three Gulton positives and four Gulton negatives. The positive plates were treated with polyvinylpyrrolidine, (PVP). The silver positives were wrapped with (PVP) treated woven nylon, followed by a layer of type V separators. The cell was filled with 38% KOH and was of open type construction. The data on this cell was acquired for comparison of the capability of this and other test cells when operating in a sealed container. The electrodes contain active material impregnated into a porous sintered matrix. The V separator is a non-woven polyamide selected on the basis of inertness and ability to hold sufficient electrolyte upon acceleration up to 25G. This separator is also known to be suitable, from the standpoint of oxygen recombination, in sealed nickel-cadmium cells.

TABLE 7.

DISCHARGE DATA FOR 6 AH OPEN CELL

					Total
Dis	charge Current	Voltage	Capacity	Capacity at E1	Capacity
	(Amperes)	(Volts) E ₁ E ₂	(amphrs.)	(% of total) -	(% of theoretical)
		1 2			
	2.0	1.38 1.1	0 6.37	40.8%	85%
	Note:				
	(1)	E ₁ is the Ag	0 Potential		
		\mathbf{E}_2^- is the Ag	20 Potential		
	(2)	Theoretical	capacity = 7 .	5 ampere-hours	
	(3)	See Figure 1	3 for dischar	ge data	
	(4)	See Figure le	4 for charge	data	
	(5)	Total weight	of positive	electrode = 34.2	grams
	(6)	Weight of si	lver = 15.0 g	j tâms	
5.	Evaluation of	Commercial 6	AH Cell		
	The following	data is subm	itted for con	marison to the 6	AH open cell
			TABLE 8		

DISCHARGE DATA FOR COMPERCIAL 6 AH OPEN CELL

Discharge Current (Amperes)	Voltage (Volts) E ₁ E ₂	Capacity (amphrs.)	<u>Capacity at E</u> ₁ (% of Total)	<u>Capacity</u> (% of Theoretical)
2.0	1.34 1.07	6.30	35.8%	55 %
Note: (1)	E ₁ is the Ag E ₂ is the Ag	0 Potential 20 Potential	(no stand time)	
(2)	Theoretical	capacity = 11	.4 ampere-hours	

Total

- (3) See Figure 15 for discharge data
- (4) See Figure 16 for charge data
- (5) Total weight of positive electrode = 26.1 grams
- (6) Weight of silver = 23.4 grams

It should also be noted that, at the 3 hour rate, the open 6 AH cell discharged at higher voltages, with better voltage regulation and with more capacity available at the higher plateau. The charge curve shows that the second plateau is preceded by a small peak, as shown in Figures 14 and 16. This peak is due to the resistance of the Ag_2O layer.

6. Preparation of 24 cm². Silver Electrodes

Smaller plates were prepared so that cells containing five positives and six negatives could be fabricated and compared with the cells containing 37 cm² plates. The average weight of the plates prior to impregnation was 4.2 grams, the weight after impregnation was 7.0 grams, and the theoretical capacity per plate was 1.4 amperehours.

This loading was the same percentage as for the 37 cm² plates. Cell numbers 12 and 14 were made using these positives.

7. Percent Coefficient of Utilization

The efficiency of the electrodes in open cells averaged 86.2% of the theoretical capacity, of which 41.3% was available at the upper voltage plateau. In sealed cells the efficiency was 70% and 41.7% respectively. It should be noted that the percent capacity at the higher voltage plateau is similar for either cell.

8. Electrode Characteristics as a Function of Silver Content

Silver electrodes were prepared containing silver in excess of that needed for the work required in this contract. This was done so that the sintered matrix - silver electrode could be more thoroughly characterized with respect to silver content. Electrodes were prepared in the following weight ranges.

a. 5.0 to 5.3 grams of free silver
b. 5.4 to 5.7 grams of free silver
c. 5.8 to 6.1 grams of free silver
d. 6.2 to 6.5 grams of free silver
e. 6.6 to 6.9 grams of free silver

The (a) group represents the weight of silver used per 37 $cm^2/side$ electrode. These cells were built and evaluated under this contract. The loading was limited by the amount of negative capacity available in the final cell design. The electrode dimensions are 6.6 cm. x 5.6 cm.

x 0.09 cm., or 3.33 cm³. Table 9 summarizes the data for the electrodes containing the different amount of silver.

TABLE 9.

CHARACTERISTICS OF ELECTRODES LOADED WITH VARIOUS AMOUNTS OF SILVER

W <u>t. of Silver</u> (gms.)	Wt. of ₃ Sil- <u>ver/cm. (gms</u> .)	Porosity %	Theoretical <u>Capacity</u> (amp-hrs.)	<u>lA Dischg</u> . (AH to 0.90V)	3 <u>AH/cm.</u>)@1A- 0.90V	Cell Cap. % Theo- retical
5.0-5.3	1.55	47.0	2.58	2.18	0.66	84.5
5.4-5.7	1.67	44.3	2.78	2.28	0.69	82.0
5.8-6.1	1.79	43.0	2.98	2.46	0.74	82.5
6.2-6.5	1.91	42.3	3.18	2.54	0.76	80.0
6.6-6.9	2.02	39.2	3.38	2.78	0.84	82.3

The capacities obtained to 0.90 volts were at a discharge rate of one (1) ampere. The ampere-hour yield, therefore, does not indicate the maximum yield of the electrodes. Higher loadings can be obtained, but no data is available.

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III. C. CALCULATION OF ELECTROLYTE VOLUME

The quantity of electrolyte to use in scaled silver-cadmium cells is based on completely filling the pore volume of all the cell components. In the case of some separators, the pore volume is reduced by the compression between electrodes, and a correction factor must be applied. Using the formula,

$$V_e = V_p + V_s \times C_f$$

where V_p = the total pore volume of the electrodes
V^s = the total pore volume of the separator (no compression)
C_f = the separator compression factor
V_e = volume of electrolyte necessary to fill all the pore
space completely

The following figures were obtained for cell No. 14.

1. The Pore Volume:

Positive pore volume	5.55 ml
Negative pore volume	<u>4.06</u> ml
Total pore volume, V _n	9.61 ml

2. The Electrolyte Content of the Separators

Separator pore volume	8.76 ml
multiplied by the Compression Factor	0.6
$V_{g} \times C_{f} =$	5.26 ml

3. Total Amount of Electrolyte

 $V_e = V_p + V_s \times C_f = 14.90 \text{ mitotal}$

The separator compression factor varies, depending upon the separator used and the inter-electrode spacing. It is a compensation for the reduction of separator pore volume under compression.

Porosity measurements were made on the various separators in use at the present time. These measurements were required in order to determine electrolyte content. The procedure consists of placing a known volume of separator into a known volume of 35% KOH. Vacuum is applied for 5 to 10 minutes in order to remove entrapped air from the separator. The volume of the liquid displaced, subtracted from the volume of the separator, is equal to the volume of the separator, thus:

Void Vol. x 100 Vol. of Separator - % Void or Porosity

TABLE 10

MEASUREMENTS OF SEPARATORS IN SEALED SILVER-CADMIUM CELL

Separator	Thickness, in.	Porosity, %
Dynel	.0025	34.2
Polypor WA (Fine nylon)	.0045	50.7
Fibrous Sausage Casing	.003	19.8
v	.009	72.3
Polypor WA (Coarse Nylon)	.006	65.8

III. D. PRESSURE DECAY

A general formula has been derived for rapidly determining pressure drop versus time when a cell is placed on open circuit stand. The method is useful in comparing pressure decay rates between cells, for setting standards and for general experimental work with separators, electrolyte volume and other components.

In Figure 17 curves are given showing oxygen pressure decay on open circuit stand at 77°F. The cell was fully charged, evacuated and filled with oxygen to the pressures indicated at time zero. Evacuation and addition of oxygen is not required after overcharge unless it is desired to remove traces of hydrogen from the cell stmosphere. The data is presented in two different ways for comparison. The top curve illustrates the decay by plotting log P versus time. The resulting curve is exponential. The lower plot presents the decay as log T versus pressure. The data results in a straight line. The slope of the line is derived from the following equation:

$$k = \frac{P_2 - P_1}{\log T_2 - \log T_1}$$

and \underline{k} in this instance, is equal to -29.0. Other cells tested in this manner gave substantially similar results. Figure 18 shows similar data for cell No. 20.

The pressure, P_2 , at any time, T_2 , can be calculated by modifying equation (1) as follows:

$$\frac{P_2 - P_1}{\log T_2 - \log T_1} = k$$
 (1)

$$\frac{\frac{P_2 - P_1}{2}}{k} = \log\left(\frac{\frac{T_2}{T_1}}{T_1}\right)$$
(2)

$$P_2 - P_1 = k \log \left(\frac{T_2}{T_1}\right)$$
(3)
$$P_2 = k \log \left(\frac{T_2}{T_1}\right) + P_1$$
(4)

we know

k = -29.0, $P_2 = -29 \quad \log\left(\frac{T_2}{T_1}\right) + P_1$ therefore (5)

if we assign T_1 as 20 min, then from Figure 17, log $T_1 = 1.301$, and P1 is 37.5

then

P ₂	-	-29 log T ₂	+	29	(1.301) + 37.5	(6)
	_	-20 1.5 8		97	5 I 27 5	(7)

$$P_2 = -29 \log T_2 + 37.5 + 37.5 \qquad (7)$$

$$P_2 = -29 \log T_2 + 37.5 \qquad (8)$$

$$P_2 = -29.0 \log T_2 + 75$$
 (8)

In Table 11 is shown a test of equation (8) based on experimental data.

TABLE 11

ACTUAL AND CALCULATED CELL PRESSURES

Time (T ₂) (min.)	Log T	-29 log T ₂	P ₂ <u>Calculated</u>	P2 Actual
30	1.477	-42.5	- 32.5	32.5
40	1.602	-46.1	28.9	29.0
50	1.699	-49.0	26.0	26.0
60	1.778	-51.3	23.7	24.0
70	1.845	-53.2	21.8	21.5
80	1.903	-54.7	20.3	20.0

 \blacktriangle similar equation can be derived for any class of cells utilizing a different geometry or a different separator.

III. E. CHARGING PROBLEMS

There are several charging methods which have been used to recharge sealed silver-cadmium batteries. The principle methods are constant current, constant voltage, or a combination of both. Battery charging problems arise from the following:

- a. High pressure due to low overcharge capability
- b. Cell imbalance
- c. Temperature extremes and variations
- d. Short charge time
- e. Thermal effects

The batteries cycled for this program were charged by a constant current routine for half of the cells, and a constant potential routine for the other half, at each of three temperatures, $-20^{\circ}F$, $+78^{\circ}F$, and $120^{\circ}F$.

1. Constant Current

Constant current charging at the rates required to recharge batteries in 55 minutes results in high end-of-charge voltages and pressures. A loss of charge efficiency also occurs when the charge voltage rises above 1.60 V/cell at $+78^{\circ}$ F prior to 100% charge. Successful cycling up to 50% of cell capacity at the first plateau voltage depends on an effective recharge and a complete conversion of Ag₂O to Ag O. Where there is adequate recharge time, constant current charge at low rates is the best method for returning a full charge to all cells in a silver-cadmium battery.

2. Constant Current Charge Acceptance

In these experiments cell No. 18 was discharged at a constant rate of 4.0 amps for 35 minutes removing 2.33 AH. Thereafter the cell was charged at a set current rate until the cell voltage reached 1.60 volts. The charge rate was then reduced to 1.0 amp until the cell voltage again reached 1.60 volts. Charging was then terminated. The procedure was repeated for a series of charge currents from 3.0 A to 1.4 A. The data is presented in Table 12 and Figure 19.

Manual charging is generally terminated when the cell voltage reaches 1.60 volts inasmuch as cell pressure rises rapidly above that voltage. The maximum charge current using constant current charging for cycling is selected on the basis that the cell voltage remains below 1.60 volts for up to 90 - 95% of the charge time available in a given cycle. In applying this data, cell No. 18 was cycled in the following manner: 2.9A discharge for 35 minutes and charge at 2.0 amps for 55 minutes.

It can be seen from Table 12 that the cell readily accepted charge up to a C/2 rate. However, the duration of charge is limited by the cell voltage which should not exceed 1.60 volts for the reason outlined above.

CHARGE RATE ₁ (ANPS)	TDAE (MIN) TO 1.60V	INPUT	CHARGE RATE ₂ (ANPS)	TIME (MIN) TO 1.60V	INPUT	R ₁ +R ₂ TOTAL INPUT (AH)	X (AH) INPUT TO 1.60V B R1
3•0	33•0	1.65	1.0	42.0	0•700	2.35	70.0
2.8	43•3	2.02	1.0	77-17	0.356	2.38	84.8
2.6	1-14	2.07	1.0	19.1	0.318	2.39	86.5
2.4	53.9	2.16	1.0	13.4	0.224	2.38	90.5
2.2	60.8	2.23	1.0	0°6	0*150	2.38	93.5
2.0	68.3	2.28	1.0	7.9	0.132	2.41	94.5
1.8	1.17	2.31	1.0	5.0	0•083	2.39	96.5
1.6	88 . 0	2.35	1.0	3.7	0.062	14.5	97.5
1.4	6•66	2.32	1.0	1 . 8	0•0	2.35	98.6

TABLE 12

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CONSTANT CURRENT CHARGE ACCEPTANCE

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In order to charge within 55 minutes for 40% depths, a current approaching 2.8 amps is required. The cell voltage would reach 1.60 volts at 79% of the charge time. The cell would then build up prohibitive pressure during the remaining 21% of the charge time. The current must be reduced when the cell reaches 1.60 volts. This indicates that a form of stepped constant current charging, or constant potential charging may be required from a given voltage point during charge.

3. Constant Potential

This method of charge is better than constant current with regard to control of end-of-charge voltage and pressure, particularly at low temperatures, by virtue of the fact that the charge current rate is continuously adjusted and reduced towards the end of charge. There are problems arising in constant voltage routines, however, due to individual cell imbalance. As imbalance occurs in a battery of sealed cells, two conditions have been noted: (1) The current remains high for a period of time after some of the cells in the battery are completely charged, and their voltage rises because the cells which are not fully charged are still calling for high currents. This results in high pressure for the cells that are fully charged. (2) Due to the effect of the cells which become fully charged early, the current approaches its low end-of-charge value before all the cells are charged. Therefore, the constant potential method of charging sealed cells results in incomplete charging of some cells which may fall low in voltage or even reverse on subsequent discharges. The use of constant potential routines at elevated temperatures also results in overheating of some cells, and a phenomenon similar to thermal run-away eventually occurs.

4. Constant Current - Constant Potential

The good features of constant current and constant potential can be combined to some extent by the use of constant current - constant potential routines. However, cell imbalances towards the end-of-charge may still reduce the current prematurely for some cells, and this may result in insufficient charge for some of the cells in the battery. Constant current - constant potential routines do provide efficient recharge, and eliminate pressure problems as long as cell imbalance is not too severe.

5. Effect of Charge Method on Operation at First Plateau Voltage

The AG-7HS series of silver-cadmium cells are all capable of operation at the higher voltage plateau, provided the silver is converted to the higher oxide. This implies a complete and effective charge. Under conditions of limited charge time such as 55 minutes, the method of charge determines to a great extent the degree of conversion of Ag_2O to Ag 0 and hence the performance of the cell at the higher voltage plateau. In general, complete conversion takes longer time and lower currents in order to keep the voltage of the sealed cell within acceptable limits so that excessive internal cell pressure is not generated. A better charging method for sealed silver-cadmium cells appears to be a process consisting of starting the charge with a high constant current to replace a specific fraction of the ampere-hours removed, and thereafter reducing the current to a lower value, followed by applying a trickle charge. The constant potential method does not appear to be entirely adequate, in that cells, which have greater polarization, rise in voltage and reduce the battery current, thereby preventing the required ampere-hours from being returned in 55 minutes. This is especially true when the charge time is short. The constant current method requires careful control of overcharge and works fairly well at low rates. When the charge rates are high, the efficiency rapidly drops as polarization increases towards the end of charge, resulting in high pressures and poor conversion of Ag₂0 to Ag 0.

The first plateau capacity can be optimized by a prolonged overcharge, Figures 20, 21, 22. In Figure 20, an open, flooded AG-7HS cell was charged by a low constant current of 0.5 amp to 1.60 volts, followed by continued charge at the same rate for two hours. The input was 11 AH whereas in Figures 21 and 22, the open, flooded AG-7HS cell was charged with a constant potential of 1.60 volts for 20 hours. The charge current varied from 4 amps to 0.2 amp. The constant potential method allows a quick recharge followed by a low rate overcharge. This method is best for complete activation of first plateau capacity (Figures 21 and 22).

When the time specified for recharge is 55 minutes, a combination of constant voltage and constant current methods may be desirable and should be considered, namely, a fast recharge to 1.55 or 1.60 volts using constant current followed by constant potential charge between 1.55 and 1.60 volts. The advantage of this two step charge method is to obtain a maximum overcharge in the time available with a minimum pressure build-up.

6. Charge Retention

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A 14

Nine cells were fully charged and allowed to stand at room temperature $(78^{\circ}F)$ for 21 days. They were then discharged. Figure 23 shows the average performance of the 9 cells. When discharged immediately after stand, similar cells Figure 24, showed a capacity of 3.65 ampere hours to 1.15 volts, and 6.5 ampere-hours to 0.90 volt. After 21 days stand, capacity to 1.15 volts was 3.2 ampere hours, and capacity to 0.9 volt was 6.4 ampere-hours.

Loss of capacity after 21 days stand at 78°F was therefore, 12.3% of the first plateau capacity, but only 1.5% of total cell capacity.

It is interesting to note that while there is some decrease of first plateau capacity, the lower plateau is extended by 12.5%, and the voltage levels on either plateau are not affected.
7. Thermal Coupling

Local overheating of scaled cells was a problem at 120° F in the hot air environmental chamber, due to poor thermal coupling. A method of heat sinking is required, such as an oil bath. The temperature of the cells would be more uniform in an oil bath. Heat conductivity becomes a problem during cycling, and the temperature of operation is dependent upon the amount of heat transfer between the cells and the environment. The results of testing at specified temperatures can vary significantly, depending upon the thermal coupling or ambient medium which is chosen.

III. F. ELECTRICAL TESTING

TEST APPARATUS:

The following equipment was used during either the fabrication or the test phases:

- 1. Charger, Constant Potential, Rapid Electric Co., Type 300-50AVS.
- 2. Charger, Constant Current, Vickers Corp., Type "Controlarc".
- 3. Voltmeter, Recording, 24 Point, Bristol Model H560.
- 4. Voltmeter, Weston Model 911.
- 5. Voltmeter, Weston Model 931.
- 6. Anmeter, Weston Model 931.
- 7. Cycler, Battery (as shown in Figure 1)
- 8. Leak Detector, Veeco, Vacuum Electronics Corp., Model MS-9

All of these instruments were new from the manufacturer and calibrated prior to the start of the program. All cycles were run automatically.

TEST PROCEDURE:

Eight prototype cells were fabricated with different separator combinations and were tested in a preliminary manner to observe performance and electrical characteristics. Sixty cells were then constructed and their electrical characteristics measured. Thereafter, the cells were divided into 5-cell batteries for life cycling under twelve various conditions. The details of the procedures are delineated in the text which follows:

RESULTS OF TESTS:

1. Prototype Cells

Prior to the construction of the sixty-five cells for cycling, eleven prototypes were built. Cell Nos. 50 to 58 were made with the standard Polypor WA on a five nylon base. The two cells, Nos. 59 and 60, were made with the Polypor WA on a coarse nylon base. After formation, the cells were sealed and discharged at 3.0 amperes. Table 13 gives the results.

Cell No. 58 was used for preliminary testing at $-4^{\circ}F$ and at $-20^{\circ}F$. The discharge data is shown in Figure 25. The cell was discharged at 3.0 amperes at $-4^{\circ}F$, and 4.3 ampere-hours was obtained to 0.5 volts. At $-20^{\circ}F$, a capacity of 2.7 ampere-hours was realized at 3.0 amperes. These results pertain only to cells numbered 50 to 58, which contain the standard Polypor WA on a

AMPERES
3.0
AT
DISCHARGED
3
ខ្ព
ß
NOS.
CELL
5
CAPACITIES

AH to 0.60 V	7.1	7.3	7.5	7.3	7-4	7.3	7.5	7.5	7.3	7.5	7.5	
AH to 1.0 V	6.2	6.1	6.2	6•2	6.2	6.1	6.4	6.3	6.1	6•5	6.4	
2nd Plateau Voltage (Volts)	1.063	1.065	1.063	1.064	1.065	1.067	1.066	1.060	1.063	1.072	1.075	
AH to 1.15V (End of lat Plateau)	0•7	3.4	3.4	3.6	3•5	3.8	3.7	3.9	3•5	0•1	3•5	
E _{l5} (min)	1.355	1.353	1.352	1.350	1.355	1•353	1.352	1.353	1.353	1.357	1.356	
E ₀ (min)	1.350	1.352	1.355	1.353	1.356	1.352	1.355	1.355	1.353	1.360	1.356	
Cell No.	8	ц	52	53	54	55	56	57	58	59*	*09	

*Note: Cells 59 and 60 contain the lower resistance grade of Polypor WA, but are otherwise similar

to cell Nos. 50-58.

-29-

fine nylon base, a material which is known to have a high electrical resistance.

2. Electrical Characteristics of AG-7HS Test Cells

These cells are similar in construction to cell Nos. 59 and 60 which were approved as Item 2 of the subject contract. The above cells were fabricated for testing as per Item 4 of the work statement. The cells were formed, sealed, and data was obtained. A group of cells were randomized and placed in electrical series for evaluation. Figure 26 shows a 2.0 amp charge to a cut-off voltage of 1.60 volts on cell Nos. 75, 100, 104 and 110. The data presented is the average performance of the four cells. The average input capacity was 8.45 AH. Figure 27 shows a 1.0 ampere discharge on cell Nos. 70, 67, 64, 66, 73, 83 and 81. The average data gives a first plateau capacity of 3.64 AH, which is 50% of the cell capacity to 0.90 volts. The cell capacity at 0.90 volt cut-off is 7.30 AH. Figure 28 shows a 2.0 amp discharge taken on cell Nos. 77, 63, 68, 75, 78 and 84. The first plateau capacity was 3.66 AH. The capacity to 0.90 volt was 6.70 AH, and 7.12 AH to 0.60 volts. The first plateau capacity is 55% of the 0.90 volt capacity of the cell.

Figure 29 is a 3.0 amp discharge taken on cell Nos. 79, 80, 65, 76, 61 and 85. The data shows that the first plateau capacity was 3.65 AH which represents 56% of the cell capacity to 0.90 volts. The capacity at 0.90 volts was 6.50 AH and 7.00 AH to 0.60 volts.

Figure 30 is a 4.0 amp discharge on cell Nos. 62, 82, 74, 69, 71 and 72. The first plateau capacity was 3.74 AH, which is 62% of the cell capacity to 0.90 volts. The capacity was 6.04 AH to 0.90 volts.

Figure 31 is a 5.0 amp discharge on cell Nos. 101, 103, 108 and 110. The first plateau capacity was 3.12 AH, which is 50% of the cell capacity to 0.90 volts. The capacity at 0.90 volts was 6.25 AH and 6.76 AH to 0.60 volts.

Figure 32 is a discharge at 6.0 amps for cell Nos. 101, 104, 107 and 111. The first plateau capacity was 2.60 AH which is 49% of the cell capacity to 0.90 volts. The capacity to 0.90 volts was 5.35 AH and 6.00 AH to 0.60 volts.

Figure 33 is a 7.0 amp discharge on cell Nos. 102, 105, 106 and 109. The first plateau capacity was 2.65 AH. This is 52% of the cell capacity to 0.90 volts. The capacity to 0.90 volts was 5.10 AH and 6.18 AH to 0.60 volts.

Figure 34 is a voltage polarization curve for both plateaus. The data was taken from the above discharge curves. The first plateau readings were plotted from the 15 minute voltage points, and the second plateau readings were taken 15 minutes after the cell reached 1.15 volts. A summary of results is given in Table 14.

DISCHARGE CHARACTERISTICS OF AG-7HS CELLS

Discharge Current (Amperes)	<u>Volt</u> (Vol ^E 1	<u>age</u> ts) E ₂	Capacity To 1.15V (amp-hrs.)	<u>Capacity To</u> 0.90V (amp-hrs)	<u>Capacity To</u> 0.60V (amp-hrs)
1.0	1.37	1.08	3.64	7.30	7.43
2.0	1.35	1.05	3.66	6.70	7.12
3.0	1.34	1.04	3.65	6.50	7.00
4.0	1.32	1.03	3.74	6.04	6.61
5.0	1.31	1.02	3.12	6.25	6.76
6.0	1.29	1.01	2.60	5.35	6.00
7.0	1.28	0.985	2.65	5.10	6.18

E1 is the mid-point voltage of first plateau (AgO).

 E_2 is the mid-point voltage of second plateau (Ag₂O).

A photograph of a hermetically sealed AG-7HS silver-cadmium cell is shown in Figure 56. Based on the electrical characteristics determined, a Preliminary Prototype Battery Specification was prepared and is included as Appendix I.

3. Cycle Testing

Cycle testing of cells was carried out in accordance with the requirements set forth in Item 4 of the contract work statement. This report describes data on three groups of 20 cells operating as batteries in groups of five cells each. There were four batteries tested in each of the following environments: -20° F, $+78^{\circ}$ F and $+120^{\circ}$ F. For two batteries, the discharge rates were 4.0 amperes and 2.0 amperes followed by a constant current mode of charging. The other two batteries were discharged at 4.0 amperes and 2.0 amperes, followed by charging at constant potential. Cycling was based on a 90 minute period with 35 minutes of discharge and 55 minutes of charge. The constant current was set to return 110% of the charge removed. The constant potential was set at 1.60 volts/cell at the $+78^{\circ}$ F and 120° F test temperature. At the test temperature of -20° F the constant potential charger was set at 1.80 volts/cell. The batteries

were designated as \triangle , B, C and D. At every test temperature, each battery is followed by either 4a or 2a to indicate the discharge current for that battery. Table 15 gives a summary of the cycling performed for each routine.

Figures 35 through 43 show data taken on the actual test batteries at each of the temperatures. During testing, some cells failed earlier than others, due to imbalances between cells. The figures also have an added curve showing the voltage characteristics of a 5 cell battery made up of the best cells.

Figures 44 through 52 show average cell data at each of the temperatures. The end-of-charge voltage in the constant current routimes was very sensitive to the amount of overcharge the cells were receiving. This required slight readjustments in current value from time to time, which caused fluctuations in the end-of-charge voltage.

4. Failure Analysis

The causes of failure and average cycle life for each battery are given in Table 16. The major cause of failure, as shown, is shorting. The shorts were caused in three different manners which deserve special mention. One form of short was through the separator, and was brought about by a high current density region causing a direct breakdown of separators from one electrode to another, which was caused, primarily, in cases where the cells had lost electrolyte. The other two types of shorts were formed by the migration of silver. In one, the capillary forces between the tab and the dynel separator next to the positive plate caused the electrolyte to rise to the top of the separator. Because the separator system does not enclose the electrodes completely at the top, the top edges were wetted and silver, or silver species, migrated across the top of the separators and deposited on the Pellon V, which is against the negative plate. When the silver deposits were heavy, a conductive path was formed.

The second method of shorting by silver migration occurred at the bottom and sides of the pack. The fibrous sausage casing deteriorated only at the folds. The Polypor is an ion exchange resin deposited on a coarse nylon base. After extensive cycling, the Polypor delaminated to some degree. With delamination, openings formed in the separator through which silver migration occurred. When this occurred, the second migration filter pro-

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SUMMARY OF BATTERY TESTS

Battery Designation _20°F	Test Routine	Status
A-42	Discharged at 4a Charged at 2.8a	Stopped at Cycle #50 High charge voltage and pressure
B-2a	Discharge at 2a Charged at 1.4a	Stopped at Cycle #403 High charge voltage and pressure
C-4a	Discharged at 4a Charged at 1.8V/cell	Stopped at Cycle #1027
D-28	Discharged at 2a Charged at 1.8V/cell	Stopped at Cycle #1383 High charge voltage and shorting
<u>78•F</u>		
A-4a	Discharged at 4a Charged at 2.8a	At Cycle #3050
B-2a	Discharged at 2a Charged at 1.4a	At Cycle #3050
C-42	Discharged at 42 Charged at 1.6 V/cell	Stopped at Cycle #2863 Loss of capacity
D-2a	Discharged at 2a Charged at 1.6 V/cell	At Cycle #3050
<u>120°F</u>		
A-4a	Discharged at 4a Charged at 2.8a	Stopped at Cycle #136 Overheating of cells
B-2a	Discharged at 2a Charged at 1.4a	Stopped at Cycle #626 Overheating of cells
C-42	Discharged at 4a Charged at 1.6 V/cell	Stopped at Cycle #1578 Overheating of cells

D-2a

Discharged at 2a Charged at 1.6 V/cell Stopped at Cycle #1578 Overheating of cells

16	
TABLE	

FAILTRE AND CYCLE LIFE OF 7 AMPERE-HOUR CELLS

	ycles		E	E	×	#	z	E	8	z	×	æ	
5	S S	3	27	8	53	t 3	16	£3	5	434	680	680	
MA	•••	3	ğ	ส	2	25	33	25			Ч	Ч	
23													
ION					ч	Ч	Ч	Ч	н	rl.	Ч	1,2	
	е,												
	1.001	E	2	2									
	e To	F	Ŧ	=					sep.	•.			
		z	z	E	stor				lan	ator	ator	ator	
	& 1	E	Ŧ	=	epar	=	t	=	a Li	aper	epar	epar	
	LI 90	F	E	æ	4				otto	- 	4	ส	
	y	F	E	E	H	t	Ŧ	=	ი ა	IJ	L.	чIJ	
	gut				top	2	2	2	top	top	top	top	
LURE	oper	2	F	E	dep.	F	#	F	dep.	dep.	dep.	dep.	
IM	been	E	E	E	YOL				Ver	19A	Ver.	Ver	
S OF					뎡	=	E	E	뒿	7	뒴	7	
MSIE	pres	E	E	Ŧ	rt ¹ 8				rt 's	rt ig	rt's	rt'g	
3	HI I	E	2	z	Sho	z	E	#	Sho	Sho	Sho	Sho	
	Current	Current	Potential	Potential	Current	Current	Potential	Potential	Current	Current	Potential	Potential	
	ert	ent.	mt 1	mt 1	mt.	nt.	mt 1	mt 1	ent.	nt	ent	mt	
CHAI	Consta	Consti	Consti	Consti	Consti	Consti	Consti	Consti	Const	Const	Const	Const	
RCE ANPS)	Ŭ	Ŭ	Ū	•	•	•	•	-	-	-	-	-	
DISCHA RATE (4	3	4	n i	4	2	4	3	4	2	4	6	
ANYPRX	4	ß	U	9	4	Д	U	Ð	4	Ø	U	Ð	
TER	-20-F				78°F	-3	14-		120•F				

NOTES: 1. 2.

Deposits in vicinity of positive tabs. One cell which ran quite hot showed complete separator breakdown and no positive statement can be given as to the exact cause of failure.

vided the sole protection to prevent the silver, or silver species, from reaching the negative electrode. However, in the region of the corners and bottom, where deterioration of the separator occurred, migration protection was lost, and the silver deposit became heavy enough to cause a conductive path.

Further observations were made concerning the appearance of the components of the cells. The following items were examined.

1. Sticking of Pellon to the Negative Plate

In a number of cases the Pellon, a polyamide, was found to be sticking to the negative electrodes, and in two batteries, disintegration was observed.

2. Disintegration of the Folds of the Fibrous Sausage Casing

This phenomena was described in preceding paragraphs.

3. Percent Delamination of the Polypor

Described earlier.

4. Pinholes in Dynel

In some cases, small pinholes were observed in the Dynel.

5. Plastic Coating

A polystyrene coating is applied to the edges of the electrodes to slow the process of shorting due to the migration of silver at the edges of the plates. The condition of this coating was observed.

6. Nylon Envelope

The nylon envelope is the insulator placed on the outside of the electrode assembly to insulate the electrode stack from the metal cell case.

7. Positive Electrode

The appearance of the positive electrodes was examined. The observations are shown in Table 17.

The major conclusions that were drawn from the failure analysis are:

1. At the low temperatures, the major cause of failure can be attributed to the method of charging. It caused high pressure, opening of the cell, and loss of electrolyte.

APPEARANCE OF COMPONENTS UPON FAILURE ANALISIS

POSITIVE ELECTRODE	Very Good	Very Good	Very Good	Very Good					
ASTIC NYLON ATING ENVELOPE	t. Cond. Ex. Cond.	c. Cond. Good - <mark> </mark> -	od** Ex. Cond.	c. Cond. Ex. Cond.	c. Cond. Ex. Cond.				
PINHOLES PI	Fer	None E	Pev E	Pev B	Pew E	None E	None Go	None Eb	None Eb
% DELAMINA- TION POLYPOR	0	35	45	JO	ŝ	45	35	65	85
DISINTSCRA'N AT FOLDS FLEROUS SAUSAGE CAS'G	Yes	Tes	Yes	Yes	Yes	Tes	Yes	Yes	Yes
STICKING OF PELLON TO NEGATIVE PLATE	None	Light	Некту	Light	Heavy	Невуу	Heavy	Невуу	Heavy
BATTUREY	*	¥	Ø	υ	Ð	4	æ	υ	Ð
1902.	-20•F	78°F			-36-	120-7			

The batteries A - B - C could not be extensively cycled at the low temperature, and failure was by overpressure rather than by wearout of components. *

The plastic costing in one cell was embrittled on both positive and negative plates \$

-1- The nylon envelope in one cell was cracked and brittle.

2. The method of charging at the elevated temperature caused the cell temperature to rise excessively and accelerated deterioration, particularly, of the separator system. This is borne out by noting the amount of delamination of the Polypor at the elevated temperature as compared to room temperature.

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- 3. At 78°F, cells eventually failed because of silver deposits which caused shorting between the electrodes. The deposits occurred, for the most part, in the region of the positive tab.
- 4. The electrodes, in general, were in very good condition. The positive electrodes, in particular, showed no appreciable deterioration.

TEST APPARATUS:

- 1. Acceleration
 - a. Genesco "G" Accelerator Drawing 50078
 - b. Voltmeter, Weston model #931
 - C. Gulton Test Fixture
- 2. Vibration
 - a. Ling Vibration System Model 245
 - b. Gulton Accelerometer, Model A396TMU
 - c. Gulton Cathode Follower, Model F408M
 - d. Tektronix Scope Type 535
 - e. Power Supply, Lambda Model LA-100-03A
 - f. Voltmeter Weston #931
 - g. Ammeter Weston #931
 - h. Gulton Tri-axial Fixture (Drawing 0172)
 - i. Gulton Cycling Timer
- 3. Shock
 - a. Berry Shock Table 150-400 VD medium impact shock machine
 - b. Gulton Accelerometer Model A396TMU
 - c. Gulton Cathode Follower, Model F408-M
 - d. Tektronix Scope Type 535
 - e. Voltmeter, Weston, Model 931
 - f. Gulton Tri-axial Fixture (Drawing 0172)

TEST PROCEDURE:

The test items were subjected to the following test sequence

<u>Cell No</u> .	Acceleration	Vibration	<u>Shock</u>
131	1	2	3
133	1	2	3

Details of the tests are included in the text which follows.

RESULTS OF TESTS:

1. Acceleration

The test items were fully charged. The cell under test was mounted on the arm of the centrifuge and subjected to an 18g acceleration force for (1) minute in each direction along its three mutually perpendicular axis, as shown in the following sketch.



The order of conducting acceleration along each of the axes was as follows:

<u>Cell 131</u>	. <u>Cell 133</u>
X	x
x'	x'
Y '	Y
¥	y '
g	£
B	z'

In order to obtain data on the operation of the cells that were to be tested, the two cells were cycled thirty-one times. They were then subjected to the acceleration test. To insure that the cells were functioning properly, they were cycled twelve times after the test. Each cycle consisted of a (2.0) ampere discharge for 35 minutes and a 1.4 ampere charge for 55 minutes.

In order to check for leaks both before and after subjecting the cells to the acceleration test, they were either sprayed or brushed with phenolphthalein solution.

Figure 53 and Table 18 show the observed cell voltage at several points in the test.

1. At open circuit voltage

2. During discharge immediately before conducting acceleration tests

3. At the point where the cell attains an 18g acceleration

4. At the point where the 18g acceleration is being released

The acceleration tests yielded the following conclusions:

- 1. No electrical discontinuity or abnormality was observed during the test.
- 2. No electrical discontinuity or abnormality was observed during cycling after the test.
- 3. No leakage of electrolyte was noticed when tested on either occasion after spraying or brushing with phenolphthalein solution.
- 4. No cell deformation was observed on either occasion.
- 2. Vibration

1.,4

Cell Nos. 131 and 133 were tested for vibration resistance. During the entire test the cells were cycled by discharging at 2.0 amps for 35 minutes, and charging at 1.4 amps for 55 minutes. The cells were vibrated in accordance with the test specifications which call for vibrating the cells at 10g from 20 cps. logarithmically to 2000 cps. and back to 20 cps. in one hour. The duration of the test was two hours. After the completion of this phase, the cells were surveyed for resonance points in the range of 5 up to 20 cps.

Cell Nos. 131 and 133 were connected in series electrically. Switching from the charge and discharge positions was done with an electrical timing unit which has been used for previous work.

The order of vibration along each axis was:

E	No vibration axis
No vibration axis	£
x	Y
Y	X
<u>Cell 131</u>	<u>Cell 133</u>

Both cells were surveyed for resonance along each axis as set forth in 4:7:14:2 of MIL-E-5272C(ASG). Before and after the vibration test, the cells were sprayed with a phenolphthalein solution to check for leakage. Both the current carrying wires and the cell voltage monitoring wires were soldered to the terminals.

Figure 54 shows cell voltage during the vibration tests. The cells were placed on open circuit for several days between the acceleration test and the vibration test which illowed the state-of-charge to decrease. As the vibration test was continued, the maximum state-of-charge was obtained over a number of cycles. This is graphically illustrated by the rise in the end-of-charge voltages.

The results of the vibration tests were as follows:

- 1. No red discoloration was noticed after spraying with phenolphthalein.
- 2. No resonances were detected.
- 3. No unusual fluctuation or discontinuities in cell voltages were noticed.
- 4. No cell deformation was observed at the end of the test
- 3. Shock

The two experimental cells, number 131 and number 133, were subjected to a shock test of 40g magnitude. Three impacts were conducted in each direction along the three perpendicular axes of the cells. After each series of three impacts, the cells were brushed with a phenolphthalein solution to determine if any rupture of the sealed assembly could be detected. In addition, the open circuit voltage was monitored after each three impacts to detect the presence of a short circuit.

The order in which the axes of the cells were tested was:

<u>Cell No. 131</u>	<u>Cell No. 133</u>
X	Y
x	Y
Y	x
Y'	x'
z	z
Z	2

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The shock tests yielded the following conclusions:

- 1. The open circuit voltage remained at the level prior to the initiation of the shock test.
- At no time was any red discoloration observed (indicating leakage of electrolyte) when the cells were brushed with phenolphthalein solution.
- 3. At no time was any cell deformation observed.
- 4. Cycling after the test showed no electrical abnormality.

After completion of the environmental tests, the two test cells were cycled continuously. The discharge was at 2.0 amperes for 35 minutes followed by charge at 1.4 amperes for 55 minutes. Figure 55 shows cycles 48 and 49 recorded during vibration testing, and also cycle 271 showing no significant change of cell characteristics brought about by the environmental testing.

VOLTAGE OF AG-7HS CELLS DURING ACCELERATION TESTS

Cell No. 131

Cell No. 133

		Axis	Discharge Time (Min.)	Cell Voltage (Volts)	Axis	Discharge Time (Min.)	Cell Voltage (Volts)
Open Circuit Volta	ge	-	0	1.40	-	0	1.40
Start Discharge @	2 amps	-	0.6	1.37	-	0.1	1.37
18g Acceleration	Beginning	x	1.0	-	x	0.3	1.36
	End	x	2.0	1.36	x	1.3	1.36
	Beginning	X,	2.7	1.36	X'	1.9	1.36
	End	X'	3.7	1.36	X1	2.9	1.36
	Beginning	Y	4.5	1.36	Y'	3.8	1.36
	End	Y	5.5	1.36	T.	4.8	1.36
	Beginning	¥,	6.1	1.36	Y	5.4	1.36
	End	יצ	7.1	1.36	Y	6.4	1.36
	Beginning	2	7.6	1.36	2	7.0	1.36
	End	2	8.6	1.36	2	8.0	1.36
	Beginning	Z۱	9.2	1.36	Z†	8.6	1.36
	End	Z'	10.2	1.36	Z!	9.6	1.36

IV. CONCLUSIONS AND RECOMMENDATIONS

Following is a brief summary of the major achievements of this program.

- 1. Construction of 7 AH cells to meet cycle life requirements.
- 2. Fabrication of environmentally resistant hermetically sealed units with ceramic-to-metal seals.
- 3. Development of improved separator.
- 4. Cycle life up to 3000 cycles at 20% depth in 90 minute period.
- 5. Operation on the Ag^{II} oxide plateau voltage.
- 6. Output of 15 20 watt-hours per pound depending on discharge rate.
- 7. Good shelf stand.

As a result of the work on this contract, sufficient knowledge has been gained to provide an insight into the continued R & D required to bring silver-cadmium cells to a higher level of performance as sealed cells. This R & D would include:

- 1. Further improvement of the separator system so as to decrease electrical resistance, reduce overcharge pressure and improve cycle life.
- 2. Increase the watt-hours per pound by increased loading of the silver electrode and by using thinner plates.
- 3. Increase the watt-hours per pound by effecting engineering improvements of the container and the electrode-to-terminal connections.
- 4. Reduce the electrolyte content and the cell weight by decreasing separator bulk.





FIGURE 2 CYCLING CIRCUIT



















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6AH COMMERCIAL SILVER-CADMIUM CELL, 2 AMP DISCHARGE FIGURE 15

6AH COMMERCIAL SILVER-CADMIUM CELL, 2 ANP CHARGE FIGURE 16





FIGURE 17 CELL NO. 18 (FULLY CHARGED), PRESSURE DECAY 77°F -61-



FIGURE 18 CELL NO. 20 (FULLY CHARGED) PRESSURE DECAY, 77°F
















FIGURE 23





















AG-7HS SILVER-CADMIUM CELLS, 3.0 AMP DISCHARGE (CELL NOS. 79, 80, 65, 76, 61, 85) FIGURE 29















FIGURE 34 AG-7HS SILVER-CADMIUM CELL, POLARIZATION POTENTIAL



AG-7 HS SILVER-CADMIUM BATTERIES A, B, C, & D TEMPERATURE -20°F, CYCLE NO. 7, 5 CELL BATTERIES FIGURE 35















FIGURE 39







AG-THS SILVER-CADMIUM BATTERY D, TEMPERATURE 78°F, CYCLE NO. 2543, 5 CELLS, 2 AMP DISCHARGE AND CONSTANT POTENTIAL CHARGE FIGURE 41











AG-7HS SILVER-CADMIUM CELLS, BATTERY B-2a, TEMPERATURE -20°F, 2 AMP DISCHARGE CONSTANT CURRENT CHARGE

FIGURE 44






































FIGURE 56 AG-7HS SILVER-CADMIUM CELL -100-

APPENDIX I.

PRELIMINARY PROTOTYPE BATTERY

SPECIFICATION

.

No. 81162

8 November, 1962.

MILITARY SPECIFICATION

PRELIMINARY PROTOTYPE BATTERY

- 1. SCOPE
- 1.1 SCOPE

This specification covers the requirements for batteries of a 27.5 nominal voltage using sintered flat plate sealed silvercadmium secondary cells.

- 2. APPLICABLE DOCUMENTS
- 2.1 The following documents, of the issue in effect on date of invitation for bids, form a part of this specification.

SPECIFICATIONS

MILITARY

MIL-E-5272C(ASG) Environmental Testing, Aeronautical and Associated Equipment, General Specification for

2.2 The following non-government indexes of drawings form a part of this specification to the extent specified herein:

Gulton Industries, Inc., Alkaline Battery Division drawings

Figure	Title
1	AG-7HS Silver-Cadmium Cell
2	Battery Assembly, 22 AG~7HS Cells

- 3. REQUIREMENTS
- 3.1 DESIGN
- 3.1.1 MECHANICAL DESIGN
- 3.1.1.1 The dimensions of each cell will conform to the drawing as shown in Figure 1 of the Appendix.

3.1.1.2 The weight of each cell will be 0.553 pounds.

- 3.1.1.3 The cell cases and combs will be of 300 series type stainless steel. The terminals and covers will be of alloy #52.
- 3.1.1.4 The cells shall be hermetically sealed with ceramic-to-metal seals.
- 3.1.1.5 The cells shall have a rectangular cross-section.
- 3.1.1.6 The cell case shall not be one of the poles of the battery.
- 3.1.1.7 The weight of the battery shall be kept to a minimum with a design goal of 6.5 pounds.
- 3.1.1.8 The battery will consist of 22 cells connected in series.
- 3.1.1.9 The volume of the battery shall be maintained at a minimum.
- 3.1.1.10 The materials used for the battery assembly will be those shown in the attached Battery Assembly Drawings.
- 3.1.2 Thermal Design
- 3.1.2.1 The thermal design will be such that the battery will operate within the limits as specified in 3.3.1.
- 3.2 CONSTRUCTION
- 3.2.1 The battery shall be capable of withstanding acceleration in accordance with Procedure III of Specification MIL-5272C(ASG) except that 18G will be used in lieu of 14G.
- 3.2.2 The battery shall be capable of withstanding vibration as specified in accordance with Procedure XIV of Specification MIL-5272C(ASG) except that 10G will be used in lieu of 20G.
- 3.2.3 The battery shall be capable of withstanding shock as outlined in paragraph 4.15.5.1 of MIL 5272C(ASG) except that 40G shall be used in lieu of 15G.
- 3.3 PERFORMANCE
- 3.3.1 The battery shall be capable of operating in a vacuum of 10^{-9} psi.
- 3.3.2 The battery shall be capable of operating in a zero G environment.
- 3.3.3 The battery shall be capable of operating in any position.
- 3.3.4 The battery shall be capable of operation without maintenance throughout its entire cycle life.
- 3.3.5 The battery shall be able to deliver 4 amperes for 35 minutes at 27.5 volts +1.5 volts -4.5 volts.

- 3.3.6 The battery shall be capable of storing enough energy in 55 minutes to satisfy the requirements of 3.3.5.
- 3.3.7 The battery shall be capable of 11,000 discharge-charge cycles as outlined in paragraphs 3.3.5 and 3.3.6 above while operating in a temperature range of -20° F to $+120^{\circ}$ F.

3.4 WEIGHT

3.4.1 The weight of the individual components are:

Weight of 22 cells	5528.6 grams
Weight of straps	12.2 "
Weight of battery case and plastic	
insulators	476.7 "
Weight of intercell insulators	165.3 "
Weight of plug plus bracket (typical)	22.9 ^u

- 3.4.2 The total weight of the battery is 6205.7 " (13.7 lbs.)
- 4. QUALITY ASSURANCE PROVISIONS
- 4.1 Not applicable
- 5. PREPARATION FOR DELIVERY
- 5.1 Not applicable
- 6. NOTES
- 6.1 Should environmental conditions necessitate faster heat rejection from the battery, a mixture of aluminum dust and epoxy resin can be added to fill any voids that exist between the cells, or between the cells and the battery case.



FIGURE 1A AG-7HS, SILVER-CADMIUM CELL



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φ Aerospace Batteries In ASTIA collection Inc., Mctuchen, N.J IV. Rampel, G., Liska, I. AFSC Project 8173. III. Gulton Industries. Silver Electrodes J., Shair, F. C. AF 33(600)-42397 Task 817ju4-11 Aerospace Batte
Silver-Cadmium Electrolytic II. Contract No. V. Aval fr OTS Betteries Batteries ۰I۷ m.+ (over) was found that a charge routine consisting of search and development program leading to im-Dynel-Polypor WA (coarse nylon base) - Fibrous seusage casing - V. each enclosing the stant current charging or constant potential This report covers the second phase of a resystems were tested with regard to obtaining Aeronautical Systems Division, Dir/Aero-mechanics, Flight Accessories Lah., Wrightsilver electrode was utilized which yielded up to 50% of its capacity at the $Ag^{I\,I}$ oxide sand cycles were achieved at a 17% depth at Sixty 7 ampere-hour cells, the AF-7HS, were life tested in a 90 minute cycle at several depths of discharge and at several tempera-Patterson AFB. Ohio. Rpt Nr WADD TR 61-131, Pt. II. SILVER-CADMI:M BATTERY PROCRAM. Final report, Mar maximum cycle life. The best separator comstant voltage recharge methods. Three thou-Unclassified report tures, utilizing constant current and cona combination of constant current followed by constant potential was better than convoltage plateau and the balance at the Ag^{I} 78°F. Charging problems are discussed. It proved. long life. sealed silver-cadmium oxide voltage plateau. Several separator positive electrodes in the order listed. batteries for aerospace applications. A bination consisted of single layers of 63. 106p., incl. illus., tables. . í charging alone. į ÷ Aerospace Batteries Inc., Metuchen, N.J. In ASTIA collection Rampel, G., Liska, Gulton Industries, AFSC Project 8173. Silver Electrodes J., Shair, R. C. AF 33(600)-42397 Task 817304-11 Silver-Cadmium Electrolytic Contract No. Aval fr OTS Batteries Batteries 12 N. ٧. ۲I. н H > (over) was found that a charge routine consisting of search and development program leading to imsystems were tested with regard to obtaining This report covers the second phase of a rebrous sausage casing - V. each enclosing the stant current charging or constant potential mechanics. Flight Accessories Lah., Wrightsilver electrode was utilized which yielded up to 50% of its capacity at the Ag^{LL} oxide maximum cycle life. The best separator com-Sixty 7 ampere-hour cells, the AF-7HS, were sand cycles were achieved at a 17% depth at CADMILS BATTERY PROGRAM. Final report, Mar Unclassified report life tested in a 90 minute cycle at several depths of discharge and at several temperastant voltage recharge methods. Three thouvoltage plateau and the balance at the AgIa combination of constant current followed Dynel-Polypor WA (coarse nylon base) - Fitures, utilizing constant current and conby constant potential was better than con-78°F. Charging problems are discussed. It positive electrodes in the order listed. proved. long life, sealed silver-cadmium Aeronautical Systems Division, Dir/Aerooxide voltage plateau. Several separator batteries for aerospace applications. A Rpt Nr WADD TR 61-131, Pt. II. SILVERbination consisted of single layers of 63. 106p., incl. illus., tables. Patterson AFB. Ohio. charging alone.