General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.
- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.
- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.
- This document is paginated as submitted by the original source.
- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

Produced by the NASA Center for Aerospace Information (CASI)

GPO PRICE \$ CSFTI PRICE(S) \$	
Hard copy (HC) <u>3.00</u> Microfiche (MF) <u>65</u> HI653 July 65	
THE CALL OF THE OF THE OF AD NUMBER) (CATEGORY)	
EXIDE MISSILE AND ELECTRONICS DIV	/ISION
Norld's Bargest Producer of Packaged 200005'	



DEVELOPMENT OF IMPROVED SEALED Ag-Zn BATTERY

FOR MARINER 1969

JPL CONTRACT 951927

NAS 7-100



DEVELOPMENT OF IMPROVED SEALED Ag-Zn BATTERY

FOR

MARINER 1969

JPL CONTRACT 951927

NAS 7-100

PART I

COVERING PERIOD NOVEMBER 6, 1967

ΤO

MAY 3, 1968

ESB REPORT NO. E-24-68

(J.O. 83988)

Prepared By:

A. M. Chreitzberg Ass't. Dir. of Engineering

Approved By:

G. S. Hartman Director of Engineering



EXIDE MISSILE & ELECTRONICS DIVISION RALEIGH, NORTH CAROLINA

19 August 1968

Ŧ

TABLE OF CONTENTS

•

	PAGE
CONTRACT OBJECTIVES	1-2
PRELIMINARY CELL TESTS	2-11
DESIGN DEVELOPMENT	Ц.
SEAL DESIGN IMPROVEMENTS	4-5
SEPARATOR SYSTEM MODIFICATIONS	5-6
PLATE LEAD PROTECTION	6
EPOXY PLATE-LOCK	6-7
PROCESS DEVELOPMENT	7
POSITIVE PLATE SINTERING	7
SEALING PROCESSES	7-8
MOLDED PARTS	8-9
OMEGA BENDS IN PLATE LEADS	9-
PHYSICAL PROPERTIES OF CELL DESIGN TYPES	10
ELECTROCHEMICAL PROPERTIES	10-11
EVALUATION TESTS AT JPL: (DESIGNS A, B, C, & D)	11-12
EVALUATION AT JPL OF FINAL DESIGN MONOBLOCKS	12-13
INVESTIGATION OF HIGH TEMPERATURE PRESSURE PROBLEM	13-16
CONCLUSIONS AND RECOMMENDATIONS	16-17



LIST OF TABLES

PAGE

TABLE	I	-	PRELIMINARY DESIGN FROOFING CELL FORMATION CHARGE DATA	18
TABLE	II	-	CELL DISSECTION AND FAILURE ANALYSIS DATA AT ESB	19
TABLE	III	-	MODEL 257 TEST MONOBLOCK DESIGNS	20
TABLE	IV	-	PROPERTIES OF POSITIVE PLATE INTERSEPARATOR.	21
TABLE	V	-	MRB ACTION ON PRODUCTION OF 120 3-CELL MONOBLOCKS	22
TABLE	VI	-	ABS TENSILE TESTS ON LOT 1220 CELL CASES	23
TABLE	VII	-	COMPARISON OF WEIGHTS AND ELECTRICAL TEST DATA MODEL 257 MONOBLOCK DESIGNS A, B, C, D, E,	24
TABLE	VIII		FORMATION CHARGE VOLTAGES OF MODEL 257 CELLS	25
TABLE	IX	-	EFFECTS OF VIBRATION ON "D" MONOBLOCKS	26
TABLE	х	-	ABS MATERIAL STRENGTH IN TYPE E, VERSUS MARINER 67 CELL CASES	27

iii

LIST OF FIGURES

4

R

PAGE

FIGURE 1	-	REDUCTION OF CHARGE VOLTAGES WITH EM-476 ABSORBERS AND RETAINERS	28
FIGURE 2	-	DISCHARGE OF MODEL 257 TYPE B AND C MONOBLOCKS AT 32°C	29
FIGURE 3	-	DISCHARGE OF MODEL 257 TYPE B & C MONOBLOCKS AT 140°F	30
FIGURE 4	-	PRESSURE RISE IN PARTIALLY CHARGED MODEL 257 TYPE "E" CELLS AT 140°F	31
FIGURE 5		PRESSURE RISE IN CHARGED MODEL 257 CELLS AT 140°F	32
FIGURE 6	-	PRESSURE RISE ON MODEL 257 CELLS AT 140°F AFTER TOP-OFF CHARGE	33
FIGURE 7	-	EFFECT OF COMPONENTS OF EPOXY PLATE-LOCK ON GASSING OF MODEL 257 CELLS AT 140°F	34



.

CONTRACT OBJECTIVES

JPL Contract 951297 was awarded to ESB Incorporated, Exide Missile and Electronics Division to improve the design of the Mariner '67 sealed Ag-Zn battery to obtain:

- o Higher "g" level vibration capability
- o Higher seal reliability
- o Improved charge acceptance

The statement of work provided for the manufacture and delivery to JPL for tests five (5) each 3-cell monoblocks of four designs: A, B, C, and D.

Design "A" proofed the changes in cement, sealant, and a modification in one molded part of the cell seal.

Design "B" proofed the changes in positive plate absorber.

Design "C" proofed the change in negative plate retainer and addition of a protective heat shrinkable tubing to plate lead wires.

Design "D" proofed addition of epoxy to bottom of plates in their jars and plastic hold down shims to minimize plate movement during vibration.

Contract modification No. 1 added Design "E" which proofed an "Omega" bend to provide slack in the plate lead wires to permit some plate movement without lead breakage. One-hundred (100) design "E" monoblocks were ordered



to be manufactured for a total of 120 3-cell monoblocks (50 AH each cell) as deliverable items.

PRELIMINARY CELL TESTS

To provide experimental evidence of the extent of plate motion in the Mariner 4 and Mariner 67 cell design during sine vibration tests ESB assembled six 50 AH cells with the following design modifications:

<u>Ceil Type</u>	Modification
1	Epoxy in corners of jar locking plates to jar bottom.
2	Felt sleeve impregnated with above epoxy wrapped
	around cell pack along edge of plates from top of
	plates on one side down, under, and up opposite
	side to top of plates.
3	Cell Type 2 except to height of 3/4" up side of
	plates.
4	Cell Type l plus plastic hold down to compress
	cellophane separator system.
5	Hold down without epoxy. Hold down 0.10" x 1.00"
	x 0.20".
6	Hold down without epoxy. Hold down twice as wide
	with separators compression area doubled: i.e.

0.10" x 1.00" x 0.40".

The six cells were assembled in two 3-cell monoblocks using clear polysulfone jars to permit visual observations of plate movement. Table I

gives formation charge test data obtained at ESB before seal and shipment

to JPL. Open-circuit and loaded voltage measurements at 20 amps were

obtained during vibration testing from 13.5 g rms to 40 g rms. Cell

-2-

design Type 5 with the least plate motion restrictions failed during the first 30 second exposure to 40 g rms at 600 cps frequency. Based on loaded voltage drop, which increases as plate lead wires snap during vibration, the order of designs with most improved vibration capability was predicted to be:

Cell Design <u>Rating</u>	Type	Feature	Observed Voltage Drop mv	Number Plates With Broken Leads
(Best) I	6	Wide area hold down to com- press separators	-1	3
II	2	Epoxy saturated felt full	8	*
		plate wrap around		
III	3	Epoxy saturated felt bottom	11	6
		and up 3/4" wrap around		
IV	4	Epoxy in bottom corners of	37	13
		jar + wide area hold down		
V	l	Epoxy in bottom corners of	86	1.3
		jar only		
VI	5	Narrow low area hold down	226	12
		compressing separators		

(*) Cell was not dissected.

Table II gives findings of cell dissections. Plate lead breakage was predominant at the intersection of active material and lead wires: 8/10 in negatives and 22/37 in positives. Breakage within the straight teflon tube was 15/37 in positives and 1/10 in negatives. Thirty-seven positive leads were broken to 10 negative leads tending to follow their

-3-

individual charged plate weight ratio 18.4 gms/11.6 gms.

Cell Type 2, having the full epoxy impregnated felt wrap, was stored unsupported wet-charged after a formation charge of 56.4 AH on 26 April 1967 to 23 February 1968 at room ambient. After a top-off of 11.9 AH at 0.6 amp to 1.97 volts, the cell delivered 55.5 AH at 10 amps with good voltage regulation. A top-off of 6-11 AH at this rate was expected. Chemical compatibility of the epoxy in the cell environment thus did not appear to be a problem.

DESIGN DEVELOPMENT

ESB drawings for all components with material or dimensional changes were released on a prototype basis to procurement and the Engineering Pilot Plant to obtain modified parts and to construct the cells for delivery to JPL, Table III summarizes part names and changes by design type. Reasons for each change as proposed by ESB are listed in the sections to follow.

Seal Design Improvements

Two modes of failure by electrolyte leakage were discovered by ESB during 15 month float tests on a 15-cell battery: creepage along negative plate lead wires and along a corner boss of the cell subcover. The boss was deleted by a mold change making all four subcover corners identical. Clear visual inspection of the entire primary subcover to cell case seal is now possible. The boss had been essential to a former cell seal design where the tops of all plates were locked to the jar with an epoxy. During

Mariner 4 battery development this platelock was deleted to increase free

volume and reduce cell pressures.



The polystyrene subcover and vent plug components in the case seal were converted to Cycolac* T-2502 white ABS plastic. This material is more resilient and less sensitive to crazing by sealing cements. A new catalyzed ABS cement was also adopted on the entire cell seal. This proprietary cement was developed by The C. F. Norberg Research Center of ESB to eliminate solvent attack on ABS during early curing stages. The new cementing process also has additional viscosity controls not previously available.

Two sealing components - the split wire slot cover and the monoblock cover - were retained as clear polystyrene (RMD-4511 sheet) to permit a visual inspection for voids in the sealants beneath. The 25 cc void below the monoblock cover and above the subcover in each cell was formerly potted with a low density epoxy. To improve bond strength to cavity walls this epoxy was replaced by PPG 639/CH2 epoxy which has reproducibly better tensile butt strength to ABS and polystyrene: 2,600 psi vs 1970 psi.

All seal design changes were imposed as a common design factor on all test cell types: A, B, C, D, & E.

Separator System Modifications

The interseparator, or absorber, between the positive plate and the first layer of cellophane was changed from Kendall EM-312 nylon-dynel to Kendall EM-476 polypropylene. Table IV compares the physical properties of the two materials. When manually wetted and allowed to

-5-

drip free suspended vertically, EM~312 retains more electrolyte in

(*) Marbon Chemical Company.

(**) Pittsburgh Plate Glass Company. in mg/in²/mil of wet thickness in the ratio 1.3:1.0. Its spontaneous wicking capability when 1.0 inch wide strips are suspended into 45% KOH electrolyte is only 1/4 of the wicking height of EM-476. The latter factor was given most weight in order to maintain a wet positive plate throughout cell life. The absorber height was also increased to extend 0.060 inch above the cellophane to permit wicking of electrolyte down into starved positive "U" folds on long low rate charges. Figure 1 shows the combined effects in reducing formation charge voltages at end of the formation charge.

Dissection of aged Mariner 4 cells revealed almost complete disintegration of negative plate cellulosic retainers. Retainers normally cut from non-woven Viskon cellulosic felt are dry pressed around the plate to hold the active material within 2/0 Ag grid until the plate is formed. ESB proposed to substitute EM-476 polypropylene felt for this material to eliminate the degradation reaction and remove soluble hydrolysis products from the cell electrolyte during long term float.

Plate Lead Protection

Mariner 4 cell plate leads were protected by an epoxy coating only. Teflon heat shrinkable tubing was tested first over the plate leads between the top of the plates and the bottom of the subcover. The design which proved most desirable provided for protection of the leads with flexible Ray-Clad RNF-100 heat shrinkable polyolefin tubing.



As a compromise to the epoxy impregnated felt plate wrap of preliminary

design 2 a plate-lock of 3-4 cc PPG 639/CH2* epoxy was added to the outer

-6-

(*) Pittsburgh Plate Glass Company.

bottom corners of each cell. Initial cure was 16 hours at room temperature. Under these conditions the epoxy diffused into the negative plates approximately 1/8 inch 1/3 way across the cell bottom and up the side wall 1/4 inch. Some epoxy also flowed into the "U" fold of cellphane (6L per plate) and locked each "U" fold to the jar bottom.

PROCESS DEVELOPMENT

During the production of the 120 monoblocks process development was found to be necessary to correct problems encountered in plate manufacturing, sealing operations, molding of parts, and testing. Table V summarizes Material Review Board action required and remedial action for each item. Details of process development are given in the sections to follow.

Positive Plate Sintering

Quality of sintered Ag bisquits was improved by sintering beneath a wrapping of asbestos cloth, a process developed for the Model 205 Surveyor battery. The asbestos reduced air oxidation of the hot Ag powder as it emerges from the oven. Yellow gold spots, found to be largely pure silicon on analysis, were also eliminated by this approach.

Sealing Processes

Leakage through the split wire seal* was eliminated by selection of ABS cement with the proper viscosity to flow around each lead wire. Improper location of the subcover was solved by fabrication of alignment

fixtures (T-25722) to hold the subcover down on the jar ledge until cement

cure was complete. Crazing around the vent hole was encountered again

-7-

(*) U.S. Patent 3,223,558, 12-14-65.

during installation of the top RMD-4511 monoblock cover. New tools (T-25721) were machined from wood and lined with neoprene on the bearing surface. Doubling the bearing surface and control of torque eliminated this problem. The number of rejects and rework parts was decreased from 50 percent to five percent after process development.

Molded Parts

The ESB vendor qualified on Mariner 4 to mold ABS jars, subcovers and vent plugs suffered personnel losses. Considerable effort on the part of ESB Q.C. engineers and the JPL resident inspector was necessary to retrain the molder to ESB/JPL part standards. NASA tooling for the jar 257-2001 was modified to mold a 4.38" x 0.50" x 0.125" tensile test bar with each case. The vendor now submits one test bar for each case. These bars are stacked and machined down to 0.380" (2.0" radius) to form a tensile test paddle. Table VI gives the tensile strength obtained on a random sample of 20 such specimens taken from the first molded lot of cases. Marbon Chemical gives in Bulletin 3A a value of 5900 psi for injection molded Cycolac T ABS specimens molded and tested per ASTM D-638-64T. Using a normal variation of ±15%, limits of 5000 minimum to 6800 maximum would apply to this material. Bulletins from Marbon have reported tensile strengths as low as 5500 in 1959 to 6400 in 1962. ESB accepted the above lot of cases based on the measured tensile strength \bar{X} ±3 s (5,449 ± 672), the actual range of 4,956 to 5,778 psi, and the calculated coefficient of variation $(S/X \times 100)$ of 4.1%. Annealing conditions for these parts were 12-16 hours at 175 ±5°F.

Ŋ

All jars were given a static pressure test of 50 psig (end walls supported) before acceptance as test monoblocks.

-8-

One lot of ABS subcovers molded by the same vendor was rejected and later replaced after a change in molding conditions was found to be necessary to eliminate radial cracks around the activation hole. No defective pieces were found in the replacement lot.

<u>Omega Bends in Plate Leads</u>

Preliminary cell tests* demonstrated that a full epoxy wrap between plate edges and the jar would prevent plate motion relative to the cell jar adequately to withstand 40 "g" sine in the frequency range 600 to 2000 Hz, but that bottom corner plate-locks using much less epoxy would fail with lead wire breakage. ESB ultimately installed plates leaving slack (an "Omega bend") in the leads between the top of the plates and the cover seal. This "Omega bend" design, previously developed for the Saturn project by ESB,** was modified for the Mariner cells by addition of a flexible polyolefin covering thermally shrunk over the bend.

Two problems were encountered and solved: (1) deforming of bend during thermal shrinking operation, and (2) over-flattening of tubing. Both solutions involved modification of tooling and process. The Engineering Pilot Plant installed all the "Omega" bends of plates for the 120 monoblocks with very few rejects for dimensions or splits in the tubing.

- (*) (Page 2 this report, cell types 2 and 3).
- (**) NAA Contract M3J7XSA-939503, Failure Analysis Report 259-5, 5-5-65.

-9-

PHYSICAL PROPERTIES OF CELL DESIGN TYPES

Table VII summarizes means and ranges for four test parameters of the 15-cell groups in Designs A, B, C, D, and E for comparison to the Mariner '67 cell design. Dry 3-cell monoblocks increased in weight as follows:

Ø	-	New sealants, cements, ABS parts	Ŧ	25	gms
Ø		Replacement of EM-312 by EM-476 for	+	13	gms
		absorbers and retainers			

• - Epoxy plate-lock + 13 gms

• - Total of all changes + 51 gms

Electrolyte weight per 3-cell monoblock decreases with changes in the separator system and addition of the plate-lock:

Ø	-	Total of	all cha	anges				-]	.0	gms
Ø		Addition	of epox	ky pla	ate-lock	¢.			2	gms
Ø	-	Retainer	change	from	Viskon	to	EM-476		6	gms
Ø		Absorber	change	from	EM-312	to	EM-476		2	gms

Associated with the change from EM-312/Viskon to the all EM-476 absorberretainer system is an increase in dry cell capacitance from 21-24 to $27-29 \times 10^{-4}$ mmfd.

ELECTROCHEMICAL PROPERTIES

ESB gave a formation charge to all cells prior to electrolyte level adjustment and final seal. Table VIII shows the decrease in charge voltage

at 2.0 to 30.5 hours of charge at 1.85 amperes achieved by the increase in

height and substitution of EM-476 absorber in cell designs B, C, D, and E

for EM-312 in design A and in Mariner '67 cells. In each case the data

-10-

recorded is the minimum and maximum voltage of at least 15 cells in 5 monoblocks treated alike. After final seal all monoblocks were delivered to JPL for environmental and cycling tests.

EVALUATION TESTS AT JPL: (DESIGNS A, B, C, & D)

After shipment of the contract deliverable items to JPL, monoblocks of each design were given acceptance tests and then vibrated through the frequency range 600-2000-600 Hz at 10 octave per minute at "g" levels of 13.5, 20, and 40 g rms. Table IX summarizes loaded voltages at the 10 amp discharge rate before and after vibration of "D" type monoblocks. The cells of each monoblock contained the following variations of vibration clamping devices:

lst cell	Epoxy plate-lock only					
Center cell	Wide area hold down and plate-lock					
3rd cell	Hold down only					

No lead wire breakage was observed at 13.5 or 20.0 "g" rms. At 40 "g" rms breakage was observed and dissection of cells revealed the breakage frequency shown in Table IX. Least frequent lead breakage occurred with the plate-lock alone. The plastic hold down compressed the top of the cellophane folds in order to hold the cell pack down in the jar, but by this action the lead wires were placed in tension and lead breakage was increased. Compression of cellophane also increased the chances of zinc dendrites shorting the cell by growth in the compression site. When the bottom corners of plates are locked down, plates will stretch and spring back in the $\pm \mathbf{Z}$ vibration plane without damage provided sufficient slack is provided in the lead wires to every

-11-

plate. In cell design D no slack was available and one wire broke in the test cell in spite of the plate-lock. A need for the "Omega Bend" lead wire design was thus demonstrated. All design E cells were therefore equipped with "Omega Bends" in both positive and negative leads.

Monoblock designs B and C were evaluated by low temperature discharges to determine the effect of EM-312 versus EM-476 absorbers and EM-476 versus Viskon retainers. Figures 2 and 3 show the discharge of 6 cell groups of the "B" and "C" designs at 32°F and at 140°F. At the 10 amp rate replacing the Viskon cellulosic retainer with polypropylene EM-476 retainers of equal thickness decreased voltage 120 mv at 32°F and 35 mv per cell at 140°F. At this point JPL authorized continued use of Viskon negative plate retainers.

EVALUATION AT JPL OF FINAL DESIGN MONOBLOCKS

A lot of 100 monoblocks (design E) was manufactured and shipped to JPL for vibration tests at 20 and 40 "g" rms and for extensive evaluation tests to determine battery life as a function of operating and wet charged storage time. Design "E" cells survived 20 and 40 "g" vibration tests with no broken wires over the frequency range 600 to 2000 Hz.

Another test was a 14-day stand 50% discharged at 140°F. After 12 days of this test on cell S/N 840-842, electrolyte leakage was observed through vertical cracks in the case walls of each cell at locations of maximum stress. Open-circuit voltages were 1.599 volts on each cell.

Capacity was measured by a 10 amp discharge to 1.30 volts per cell yielding 18.8 AH each cell. A capacity loss of 40% of the 31.4 AH remaining in

-12-

the cells after the 50% depth discharge before storage thus occurred in 12 days at 140°F, or a rate of 100% per month at 140°F. This loss is substantially greater than expected. Cells S/N 837, 8 and 9 were stored fully charged (67.6 AH after top-off charge) for a 14-day period at 140°F. Electrolyte leakage through a vertical crack in the side wall of cell 838 was detected. All unsupported walls exhibited distinct bulging from high internal pressure. Steps were immediately taken to determine the cause of the high pressure, not common to Mariner 64 and 67 cells, and to verify the material strength of the Cycolac cases. Table X summarizes tensile tests performed to relate the tensile strength of the ABS material in the failing cell cases to Mariner 67 cell cases of a previous mold lot. This data confirmed normal case material strength and indicated the "E" design had a high temperature pressure problem.

INVESTIGATION OF HIGH TEMPERATURE PRESSURE PROBLEM

Contract 951927 was altered by Modification 3 dated 9 April 1968 to determine the amount and cause of gassing when design "E" cells are stored at 140°F. Suspected components in the cell design were: EM-476 polypropylene, cellophane, and the epoxy plate-lock. A 3-cell monoblock was sealed with a pressure gage in each cell, no plate pack, but 105 cc 45% KOH plus -

> Cell 1: 3 EM-476 absorbers (41 in² each) Cell 2: 3 190-PUDO cellophane pieces (234 in² each)

Cell 3: 3-4 cc plate-lock epoxy in each bottom corner

cured 16 hours at room temperature

-13-

During oven storage at 140°F the pressure rose immediately to 2.0-3.0 psig and remained at that pressure for 6 days dropping to 1.5 psig by the 14th day at 140°F. This experiment eliminated single components from suspicion but not interactions. ESB then equipped a spare monoblock type "E" with pressure gages in cells 893, 894, and 895, discharged the cells down to a residual capacity of 20.4 AH, and then stored at 140°F in an oven. Figure 4 shows the individual cell pressure increases:

- - 0-11 psig on open-circuit stand 5 hours, then
- o to 12-26 psig in 9 hours on charge at 1.8A, then
- to 34-45 psig in 9 hours on final o.c. stand.

This test verified JPL pressure rise findings for the "E" design, especially during and after charge at 1.8A at 140°F.

For the next test ESB selected cells from a group returned by JPL for dissection analysis: three each Model A, B, and C. Open-circuit voltages were observed to be 1.859 to 1.860 on each of the 9 cells. Each 3-cell monoblock was equipped with pressure gages and valves on the two outer cells. Type A cells were Mariner 67 cells and were the controls for the experiment. Type B and C cells have progressively more EM-476 polypropylene - B as an absorber (244 in²/cell), C as absorber and as retainer (548 in²/cell). If pressure rise were from EM-476, then in cell Types A, B, and C the ratio of cell pressures would be 1:X:2.2X. As a gassing control, Type "E" cells S/N 893, 4, and 5 were discharged (51.0 AH), recharged (58.8 AH) at 1.85, tapered to 1.0 ampere, vented and resealed with new pressure gages, and stored at 140°F with the other 9 cells. Figure 5 gives the observed pressure rise curves.

Type "E" cells

containing the epoxy plate-lock again exhibited severe pressure rise: - 36

psig in 14 hours at 140°F. Type "C" cells with most EM-476 reached peak



pressures of only 8.1 psig during 45 hours exposure at 140°F. It was noted in the data that cells with peak voltages during the previous charge gave higher pressures. To determine the magnitude of the charge effect on pressure rise cells Types A, B, and C were checked for leakage, charged until <u>each cell</u> reached 1.97-1.98 volts, and stored again. Figure 6 gives the pressure rise curves over an 86 hour period at 140 ±4°F. Maximum pressures noted were:

S/N	758	Type	13	22	psig
S/N	756	Type	В	11	psig
s/n	785	Type	С	13	psig
S/N	783	Type	С	8	psig
s/n	746	Type	A	11	psig
s/n	744	Type	A	8	psig

All cells were within a pressure range of 6-14 psig by the end of the storage period, compared with 6-9 psig for the first experiment. The effect of full charge is thus to increase pressures 1.5 to 2 times but only temporarily, and EM-476 was not the cause of sustained high pressures.

A final investigation was then directed at determining which component of the epoxy plate-lock accelerated normal gassing rates. For this test cells having pressure gage-valve assemblies were vented, and then inoculated with 3 cc portions of one of the following:

• - Cell electrolyte (control)

-15-

• - Electrolyte + 0.7 gm epoxy Catalyst A*

- - Electrolyte & 1.0 gm epoxy Catalyst B
- - Electrolyte extract from 8.3 gms epoxy resin.

(*) Portion required for epoxy plate-lock in each cell.

After sealing and checking for leaks, the cells were stored charged at $140^{\circ}F$. Figure 7 shows the pressure rise curves. The extract from the epoxy resin produced twice the pressure of either control or catalysts A and B. The gas from this cell was analyzed with a Fisher gas chromatograph and found to be 70% hydrogen and 30% nitrogen. It has been concluded, therefore, that the epoxy resin in the plate-lock, or its filler, is interacting with charged negative plates to increase normal hydrogen evolution rates at elevated temperatures (140°F).

Testing should be continued to establish what component of the epoxy i.s. resin, filler, or diluent, accelerates the gassing of negative plates. Other epoxies of a different chemical type should also be investigated to find an inert plate-lock for this cell system.

CONCLUSIONS AND RECOMMENDATIONS

1. Mariner '67 cells have been modified to improve seal reliability, charge acceptance, and "g" level vibration capability.

2. Epoxy plate-locks on each side of the plate pack at the inside bottom of the cell jar together with an omega bend in the plate leads have effectively increased vibration "g" level capability above the 20 "g" rms anticipated for Mariner '69 type approval tests.

3. The epoxy selected for the plate-lock interacts with 45% KOH electrolyte and the negative plates to accelerate hydrogen evolution at 140°F.

4. Cell pressures reach an equilibrium value of 35-40 psig during a

the second second as we will be used the description of a second s



immediate high temperature exposure after a top-off charge.

*(c %)

5. It is recommended that several chemical types of epoxies and catalysts be tested to find a combination that is stable chemically in 45% KOH, provides mechanical support for the plate pack, and does not accelerate hydrogen gassing rates.

4



TABLE I

r y

PRELIMINARY DESIGN PROOFING CELL FORMATION CHARGE DATA

	Cell Voltages By Cell Design Type						
Charge	1.	2	3	Lt	5	6	Charge
Time	Epoxy in	Epoxy Felt	Epoxy Felt	(1)plus(6)	Hold Down	Hold Down	Current
(Hrs)	Corners	Full Wrap	3/4 Wrap	Hold Down	Area A	Area 2A	(Amps)
0	-0.152	-0.532	-0.539	-0.569	-0.578	-0.520	0
1	1.204	1.195	1.201	1,201	1.198	1.212	1.85
2	1.656	1.658	1.656	1.654	1.653	1.657	1.85
3	1.666	1.677	1.672	1.668	1.663	1.676	1,85
4	1,682	1.698	1.869	1.682	1.675	1.710	1.85
5	1.910	1.908	1.907	1.906	1.904	1.909	1.85
10	1.913	1.913	1.912	1.912	1.911	1,914	1.85
16	1.909	1.915	1.911	1.910	1.906	1.918	1.85
22	1.918	1.922	1.920	1.918	1.914	1.922	1.85
26	1.923	1.933	1.926	1.924	1.922	1.943	1.85
28	1.928	1.946	1,933	1.929	1.925	2.021	1.85
30,5	1.956	2.046	1,972	1.960	1.941	**	1.85*
32	1.866	1.893	1.876	1.869	1.862	1.873	0
		,,	A.C. Impe	dance, Ohms			
Before Charge	.142	.157	.156	.150	.150	.150	
After Charge	.038	.033	.028	.018	.047	.032	

- (*) Charge at 1.85 amps for 30.5 hrs = 56.43 AH each cell.
- (**) Cell reached 2,101 V at 28.2 hrs. Was charged to an input of 56.43 AH at 0.92 amps.

-18-

۳"

TABLE II

\$

CELL DISSECTION AND FAILURE ANALYSIS DATA AT ESB

Test		Observation By Cell Design Type						
0	bservation	1	2	3	14	5	6	Total
1. 2.	Voltages at EMED, volts A.C. Impedance, mohms, õ0 c/s	1.84 10	1.84 0.7	1.84 1.5	1.85 11.1	1.84 13.0	1.85 0.1	
3.	Broken Leads Negatives: Positives	2 11	N o t	1 5	6 7	1 11	0 3	10 37
4.	Total: Location of Lead Breaks:	13	D i	6	13	12	3	47
	<u>In Negatives</u> : At plate edge At subcover In teflon tube	2/2	s s c+	1/1 	4/6 1/6 1/6	1/1 		8 1 1
	<u>In Positives:</u> At plate edge At subcover In teflon tube	4/11 7/11	e d.	2/5 3/5	7 /7 	6/11 5/11	3/3 	22 15
5.	Loaded Voltage Drop, mv. (20 amp load)	86	8	11	37	226	-1	



TABLE III

MODEL 257 TEST MONOBLOCK DESIGNS

1 GS

Des	ign	Application By Design Type						
Mod	ification	A	B	С	מ	E		
1.	Elimination of corner boss on 257-2002 subcover. Material change: RMD-4511 polystyrene to Cycolac T-2502 ABS.	x	x	x	х	х		
2.	Vent plug 257-2003 material change: RMD-4511 polystyrene to Cycolac T-2502 ABS.	x	x	х	x	х		
3.	Change epoxy sealant.	х	x	x	х	х		
4.	Change case sealing cement from catalyzed polystyrene to catalyzed ABS cement.	x	x	x	х	х		
5.	Change positive plate absorber 257-2007 from EM-312 to EM-476 and increase height 0.13 inch.	x	x	x	х	х		
6.	Change negative plate retainer 257-2006 from Viskon to EM-476 polypropylene.			x	x			
7.	Change teflon tubing on all plate leads to heat shrinkable polyolefin tubing.			x				
8.	Add epoxy to bottom of plates in corner of jar as a plate- lock.				x	х		
9.	Add "omega" bend slack in plate lead wires with polyolefin tubing over wires.					х		



TABLE IV

PROPERTIES OF POSITIVE PLATE INTERSEPARATOR

T	est Parameter	Unit	<u>EM-47</u>	<u>5</u>	<u>EM-312</u>
			⊼	Ŕ	
1.	Thickness (1) (2) Dry Wet (30% KOH)	mils	3.9 4.0	0.6 0.7	4-6 5.5-8.5
2.	Weight Dry Wet (30% KOH) Wet (30% KOH)	mg/in ² " mg/in ² /mil	23 51 13	2.6 12.	22 85 17
3.	Electrolyte Retention (3)	%	221	41.	380
4,	Wet Out Time (30% KOH)	sec.	4-6		2-6
5.	Wicking Height With grain Against grain	in (45% KOH) after 24 hrs.	6-7 1.8-2.2		0.9-1.8 0.2-0.3
6.	Composition	~~	100% Polypropy-		25% dynel 75% nylon
7.	Supplier		lene Kendall		Kendall

(1) 5 lots EM-476 in population mean \bar{X} with mean range \bar{R} from 4 specimens each lot. NOTES:

> 3 lots EM-312, 2 specimens per lot; data is population range. (2)

(3) Immersion in 30% KOH for 1 hour then suspended 3-5 minutes vertically until drip free: wet weight/dry weight x 100.

TABLE V

MRB ACTION ON PRODUCTION OF 120 3-CELL MONOBLOCKS

MRB		
<u>NO.</u>	Problem	Remedial Action
7707 7862	Yellow spots and Ag20 spots on positive bisquits	Sinter with plates wrapped in asbestor cloth. Yellow is silicon from fire brick.
7717 7933	A.C. Impedance too high on 20 "E" and 32 "F" monoblocks	Instrumentation problem. Distribution normal and tight. Change to Keithley Model 502 millohmmeter.
7718 7929	Top cover crazed around vent hole, (2/20).	Decrease torque on hole- down bolt and increase bearing surface of tool.
7735	Potting cover cracks around vent holes (161/200)	Reject and return to vendor.
7737	Leaks in primary "E" sub- cover seal (2/13) through cracks in subcover vent hole. See 7735	Sealed with additional ABS cement. Vendor contacted. Mold conditions changed for next let and new ABS material ordered from Marbon Chemical.
7738	Brown fibers embedded in EM-312 absorber (213/1500)	Kendall Mills stated brown fiber was from brown paper bag in which they receive their raw material prior to the felting operation. Rejected and returned to vendor.
7934	Scratches and flow lines on monoblock cases	100% inspection of cases at Receiving Inspection ordered. Case classified as critical cell component.

Mold modified to add tensile test bar to be molded with each cell jar.

Tool T-25722 made to position subcover correctly.

8768 Top covers misaligned



TABLE VI

ABS TENSILE TESTS ON LOT 1220 CELL CASES

Test No.	Jar No.	Force to Break * <u>(lbs.)</u>	Thickness at Break 	Break Area <u>(in²)</u>	Tensile Strength (psi)
1 2 3 4 5 7 8 9 10 11 12 13 14 15 17 18 20	108 85 96 39 24 10 30 101 43 58 83 14 3 69 21 100 17 9 38 7	$\begin{array}{c} 245\\ 225\\ 220\\ 235\\ 245\\ 260\\ 250\\ 250\\ 240\\ 250\\ 240\\ 235\\ 250\\ 245\\ 235\\ 250\\ 245\\ 250\\ 255\\ 255\\ 255\\ 255\\ 245\end{array}$	<pre>.119 .121 .117 .117 .119 .120 .120 .120 .118 .120 .119 .119 .121 .120 .121 .120 .121 .118 .118 .119 .118 .120 .118 .120 .119 .118</pre>	0446 0454 0439 0446 0450 0450 0443 0450 0446 0446 0450 0450 0450 0450 0450 04443 04443 04443 04450 04443 04450 04443 04450 0450 0450 0450 0450 0450 0450 0450 0450 0450 0450 0450 0450 0450 0450 0450 0450 0450	5,493 4,956 min. 5,011 5,270 5,444 5,778 max. 5,643 5,556 5,381 5,610 5,286 5,222 5,556 5,396 5,396 5,304 5,605 5,643 5,643 5,643 5,643 5,643 5,643
x		244	.1194	。0449	5,449
S					224
± 3 ;	S				672
Min.	(X - 3 s)				4,777
Max.	(X + 3 s)				6,121
(*)	Dillon Teste Test date:	r: Speed 1/4 4-10-68	in/minute.		



TABLE VII

COMPARISON OF WEIGHTS AND ELECTRICAL TEST DATA MODEL 257 MONOBLOCK DESIGNS A, B, C, D, E

	Test	Unit	Observation By Monoblock Design						
	Parameter			Mariner 67	A	В	С	D	E
1.	Dry Weight	Х R	gms	1476 9	1501 15	1501 10	1514 16	1527 11	1510 14
2.	Electrolyte Weight	Х́ R	gms	466 3	463 3	461. 9	455 10	453 6	456 12
3.	Capacitance Dry	R	mmfd X 10 ⁻⁴	21- 24	23- 24	25- 32	27- 29	26- 29	23- 26
4.	A.C. Impedance	Х R	ohms	.210 .090	.238 .130	.281 .017	.291 .009	.279 .011	.323 .060



TABLE VIII

FORMATION CHARGE VOLTAGES OF MODEL 257 CELLS

	щ	Min. Max.	1.652 1.661 1.906 1.920 1.916 1.922 1.921 1.929 1.927 1.941 1.929 1.945	56,6	12-11-67	67–127	EM-476 Viskon Epoxy	
gn Type	D	fin. Max.	1.661 1.666 1.909 1.919 1.925 1.927 1.930 1.936 1.937 1.948 1.941 1.954	56.4	6-6-67	67 - 063	EM-476 EM-476 Epoxy	
odified Cell Desig	 U	Min. Max. N	1.652 1.659 1.673 1.700 1.916 1.921 1.926 1.929 1.929 1.933 1.931 1.937	56.4	6-12-67	67-063	EM-476 EM-476 None	
Ŵ	B	Min. Max.	1.652 1.658 1.903 1.911 1.922 1.926 1.931 1.927 1.941 1.962 1.943 1.968	56 . 4	6-5-67	67-063	EM-476 Viskon None	
	A	Min. Max.		56.	5-30-67	67-063	EM-312 Viskon None	
Mariner	67	Min. Max.	1.637 1.668 1.909 1.921 1.916 1.921 1.935 1.996 1.933 2.092 1.951 2.100	56 . t	3-23-67	67-037	EM-312 Viskon None	
Charge	Time	(Hrs.)	2.0 6.0 20.0 27.5 29.5 30.5	2. Input, AH	3. Date of Test	4, Reference TWO No.	5. Design: Absorber Retainer Platelock	

(*) Rate: 1.85 amperes for 30.5 hours = 56.4 AH

ą

-25-

TABLE IX

The second second

EFFECTS OF VIBRATION ON "D" MONOBLOCKS

	1			T			1		-	1			+
		Cell	S/N	765	771	774	766	772	775	767	773	776	
	Total	Break-	аде	1	0	Т	Ţ	0	Ŧ	1	0	6	It
	ve Leads	In	Tubes	1	0	0	1	0	0	J	0	ى	0
ations	Positi	At	Cover		0	G	I	0	2	1	Ū	7	Ģ
n Observa	Broken	At	Plates	1	0	Т	I	0	I	J	0	r1	m
issectio	e Leads	In	Tube	I J	0	0	ţ	0	0	1	0	0	0
D	Negativ	At	Cover	I I	0	0	ţ	0	l	ţ	0	0	
	Broken	At	Plates	1	0	0	1	0	0	ł	0	Т	-1
	Volts	ZV	MV	-4	0	+65	+42	+2	+29	+23	+21	-22	1
	/ol.tage	After	.drv	l.330	L.305	1.370	1.345	1.310	1.359	l.328	l.308	l.272	
	Loaded V	Before	.drv	1.334	1,305	1.305	l.303	1.308	1.38U	1.305	1. 287	1.294	1
	Vibration	"G"	телет	13.5	20.0	ц0.0	13 . 5	20.0	40.0	13 . 5	20.0	40.0	All
		Vibration	vampener	Epoxy	Platelock	Only	Hold Down	and	Platelock	Hold Down	Only		Totals:

-26-

TABLE X.

ABS MATERIAL STRENGTH IN TYPE E VS MARINER 67 CELL CASES

Specimen Number	Material <u>Application</u>	Break Force <u>(lbs.)</u>	Break Dimensions (In.)	Tensile Strength (psi)
1	"E "	315	.102 X .667	4,630
2	Monoblocks	415	.117 X .675	5,250
3		390	.109 X .675	5,300
ц	Mariner	310	.085 X .675	5,400
5	67	350	.095 X .675	5,520
6		340	.094 X .675	5,360

(*) ESB Dillon tester at .25 in/min. manual rate.

Ð



FIGURE 1

REDUCTION OF CHARGE VOLTAGES WITH EM-476 ABSORBERS & RETAINERS





Ľ

-29-

FIGURE 2

COLUMN STATES

36

FIGURE 3

DISCHARGE OF MODEL 257 TYPE B AND C MONOBLOCKS AT 140°F

Rate: 10.0 Amps

Sample: n = 6 Cells



Discharge Time - Hours





. . .

8 . It







Ť.

Į,





	Ę	I	G	l	JR	E	7
--	---	---	---	---	----	---	---



