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Lithium Battery Session

EVALUATION OF DESIGNS FOR SAFE OPERATION OF LITHIUM BATTERIES

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Introduction

Early in the ECOM lithium-organic electrolyte battery program it became apparent that design for safety would be one of the paramount factors in the development of batteries for military applications.

In order to resolve this problem, ECOM initiated a safety program with three companies, Eagle-Picher Industries, Inc., Power Conversion Inc., and Mallory, who had demonstrated successful electrical performance with a lithium cell.

Some of the conditions to which the cells and batteries were exposed were considered to be extreme in nature and, in some instances, beyond what would be encountered in field conditions; however, it was felt necessary to perform these tests to determine the safety limitations of the lithium/organic cell and battery structure.

Cell Tests

The following tests were conducted by each contractor on "D" cells on both fresh (100% capacity) cells and on cells which had been discharged to 50% of their capacity.

a. The short circuit test was conducted by shorting the terminals of the cell (0.01 ohm or less), measuring the temperature rise, and determining the length of time required to vent or deactivate (rendering the cell incapable of delivering current) the cell.

b. The increasing load test was initiated at the C/5 rate and the load increased by 1 ampere per minute until the cell deactivated or vented.

c. The hot plate test consisted of placing a cell on a hot plate. The cell temperature was increased by approximately 20°F per minute (temperature measured by a thermocouple placed on the cell) until deactivation or venting occurred.

d. The cell deformation test required that the lower half of the cell be crushed while leaving the crimp seal intact. The

crushing action was applied slowly while the voltage and temperature of the cell were monitored. When a voltage drop indicated a short circuit, further crushing was terminated but the pressure on the cell was maintained until the temperature started to drop or the cell deactivated or vented.

e. The dynamic environment test consisted of stressing the cell with either a shock or vibration at a resonance point until voltage readings indicated that an internal short or open circuit occurred in the cell.

f. Case Rupture Test consisted of boring through the side of a "D" cell about halfway between top and bottom with a high speed drill approximately 0.25" in diameter.

g. Incineration Test required that the flame of a torch be applied to an unprotected side of a cell until venting or deactivation occurred.

Battery Tests

The batteries were subjected to the following tests:

- a. Short Circuit Test
b. Increasing Load Test
c. Hot Plate Test
d. Immersion Test
e. "Reverse" Discharge Test

The short circuit, increasing load, and the hot plate tests are described in the section on cell tests. In the immersion test the battery (with its connector covered with waterproof tape) was immersed in water until air bubbles no longer emerged from the battery.

Technical Approach

Two of the contractors, Power Conversion Inc. and Mallory, employed the lithium-organic electrolyte-sulfur dioxide system in their batteries while Eagle-Picher Industries used the lithium-organic electrolyte-carbon monofluoride system.

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This type of fusing has an advantage over venting as the contents of the cell are retained and not spewed to the atmosphere. Both companies found that this was not a valid approach to follow, since no fuse was available which could withstand the internal environment of the cell. Eagle-Picher also investigated the use of a cell separator which would soften when subjected to the heat developed in a short circuited cell. It would then lose its porous qualities and cause the internal resistance to increase considerably, thereby lowering the cells current producing capability. Results of cell tests revealed that this technique was not as reproducible as desired. Mallory investigated the use of a battery can containing material which would react with SO_2 . In the event of cell venting, the battery would retain as much of the sulfur dioxide as possible which would be consumed by the reactant. Such a design would be extremely desirable where personnel must remain with the battery in an unventilated space from which they cannot easily vacate. However, the price of such a battery can, along with an impervious connector, was found to be cost prohibitive for high quantity, general military use.

All companies recognized that venting, although neither desirable nor the ultimate solution, would be preferable to a fire or explosion. In this approach any internal pressures created in the cell by heating due to short circuits or incineration would be relieved when the cell reached a specified pressure level. The volatiles and electrolytes would then be forced from the cell, rendering it inert. This is not a desirable feature for the sulfur dioxide system because of the irritant nature of sulfur dioxide.

Eagle-Picher, for their cell venting mechanism, adapted the "beer can opener" pressure relief device (Figure 1). This

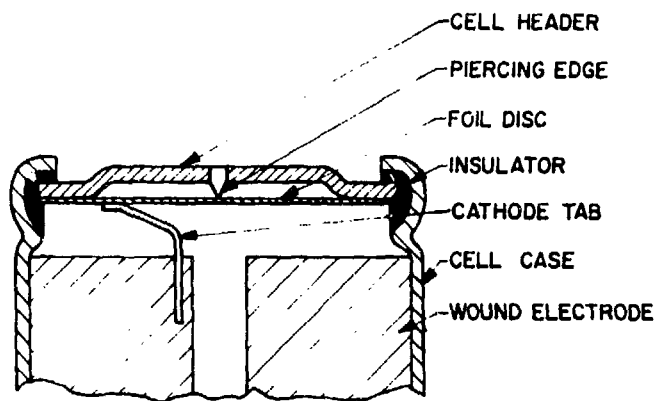


Figure 1. Eagle Picher Cell Design.

consists of a metal cap (which has been perforated to produce a triangular like piercing edge) and a thin nickel foil disc, approximately 3 mils thick, placed beneath this edge at a fixed distance across the entire opening of the cell. Pressure buildup within the cell causes the foil to distend outward so as to be cut by the triangular piercing edge. Eagle-Picher subjected their cell to all of the tests that were described earlier. Although their cell design, on occasion, passed the short circuit tests without fire or explosion, there were a few instances in which a fire and explosion did occur. It is believed that the

vent opening was blocked by cell material that was forced into the opening by the sudden release of high pressure when the nickel foil was pierced. Eagle-Picher is now working on an improvement in their venting design.

Power Conversion utilized the vent mechanism shown in Figure 2. Basically, the construction consists of a two piece

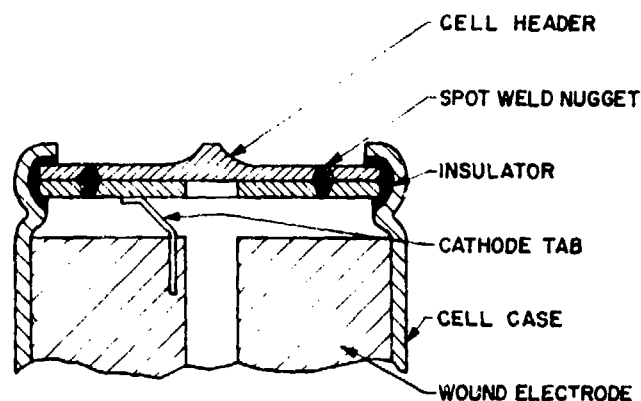


Figure 2. Power Conversion Inc. Cell Design.

aluminum cover welded together in such a way as to produce a rupture in the seal under conditions of high internal cell pressure. The location, number, and size of the welds determines the magnitude of the pressure required to rupture the seal.

The Mallory design (Figure 3) employs a septum which

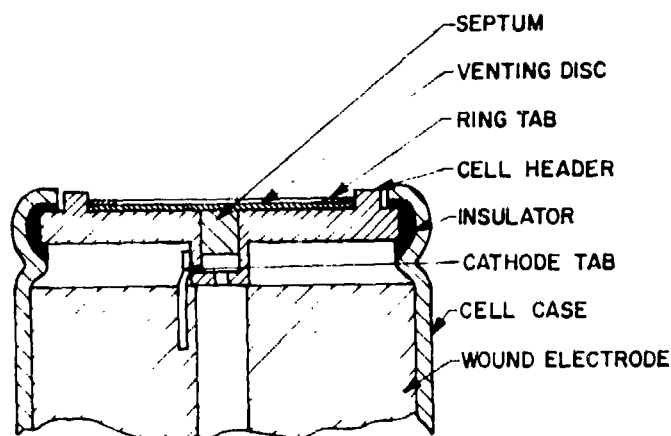


Figure 3. Mallory Cell Design.

is forced fitted into a well in the cell header. It is further retained by a foil which is ultrasonically welded over this septum. As pressure is developed in the cell, the septum is forced upward against the foil. At a pressure level of approximately 400 psi, the foil is ruptured by the septum which is ejected from the well in the header permitting the pressures that have developed to escape through the vent hole.

Test Results

Table I summarizes the results of the tests performed on

TABLE I
SAFETY EVALUATION OF LITHIUM ORGANIC ELECTROLYTE CELLS

CELL TESTS	POWER CONVERSION, INC.			MALLORY		
	TEMPERATURE (°F)	VENT TIME (MIN.)	REMARKS	TEMPERATURE (°F)	VENT TIME (MIN.)	REMARKS
SHORT CIRCUIT	93-145*	1-1.5	20 A PEAK	140-175*	6-15**	20 A PEAK
INCREASING LOAD	175-152*	10-14	27 CWP LOAD	150-160*	17-18	10 A PEAK
HOT PLATE	260-300*	12-16	---	170-210*	---	NOT RECORDED
CELL DEFORMATION	100-155*	0.5-1	---	---	---	NOT RECORDED
CASE RUPTURE	---	---	NO ADVERSE EFFECT	---	---	NO ADVERSE EFFECT
INCINERATION	NOT RECORDED	1.2-1.75	---	NOT RECORDED	0.5-1.5	---

*TEMPERATURE AT THE TIME OF VENTING.

**SOME CELLS DID NOT VENT.

NONE OF THE CELLS EXPLODED OR CAUGHT FIRE.

DYNAMIC ENVIRONMENT SHOCK TEST HAD NO EFFECT ON POWER CONVERSION CELL.

DYNAMIC ENVIRONMENT VIBRATION TEST HAD NO EFFECT ON MALLORY CELL.

Power Conversion, Inc. and Mallory "D" cells.^{1,2} Five (5) sample cells were used on each test. None of the cells caught fire or exploded under any of the tests. Under short circuit conditions, the time to cell venting varied although some of the Mallory cells did not vent at all. No flame was noted when the torch was applied to the cell vent opening; however, this test was conducted 10 minutes after venting. The cells vented safely during the increasing load and hot plate tests. Under the cell deformation test, internal shorts were produced in some cells causing them to vent. Others vented prematurely before the cells were sufficiently crushed to cause internal shorts. On the case rupture or drilling test, the cells did not catch fire under room temperature conditions although they did heat up slightly. A cell preheated above 200°F (this was done as an additional experiment using a Mallory cell) caught fire when drilled through. The incineration test, which is considered to be the most stringent of all the test conditions, showed that both manufacturers' cells vented properly. However, continued heating resulted in melting the lithium anode which then burned. The dynamic test (Power Conversion, Inc. performed a 1000 "g", 0.5 ms shock test on each axis, Mallory a 75 "g", 2000 Hz vibration test for 15 minutes on each axis) demonstrated the ability of the cell design to withstand these environmental conditions.

Table II summarizes the data on the battery tests.^{1,2} Each contractor tested three batteries under each test condition.

The short circuit test conducted on Power Conversion batteries, which were not fused, vented normally. However, the short circuit test on the Mallory batteries caused the fuse to blow in approximately one-half minute. Batteries of both manufacturers vented normally on the hot plate tests. Reduced performance was obtained, as expected, after the salt water-fresh water immersion tests.

The "reverse" discharge test conducted at the C/5 rate (1 ampere) on the Power Conversion battery caused the cells to open (no voltage). The reverse discharge test on the Mallory battery was conducted at 2 A and resulted in the battery venting after 16 hours, in another test an explosion and fire occurred within 45 seconds. A repeat of this test was performed by Mallory, only this time the safety vent port of the cells was increased in diameter and the cells vented safely.

TABLE II
SAFETY EVALUATION OF LITHIUM ORGANIC ELECTROLYTE BATTERIES

BATTERY TESTS	POWER CONVERSION, INC.			MALLORY		
	FIRE OR EXPLOSION	VENT TIME	REMARKS	FIRE OR EXPLOSION	VENT TIME	REMARKS
SHORT CIRCUIT	NONE	0.5-1.5 MIN.	---	NONE	1/2 MIN.*	BATTERY WAS FUSED AT 10 A.
INCREASING LOAD	NONE	7-9 MIN.	2.5 CWP	NONE	8-10 MIN.	10 A MAX CURRENT
HOT PLATE	NONE	10 MIN.	HOT PLATE 600°F.	NONE	NOT RECORDED	---
IMMERSION	NONE	NONE	VARIED LOSS IN CAPACITY	NONE	NONE	SOME LOSS IN CAPACITY WAS EXPERIENCED.
REVERSE DISCHARGE	NONE	NONE	OPEN CIRCUIT DEVELOPED IN CELLS OF EACH BATTERY.	1 OF 3 BATTERIES HAD AN EXPLOSION AND A FIRE.	16 HOURS	---

*FUSE BLEN

**TEST WAS REPEATED USING A LARGER VENT HOLE.

CELLS THEN VENTED WITH NO EXPLOSION OR FIRE OCCURRING.

Conclusions

Two manufacturers of lithium organic batteries, Power Conversion and Mallory, have completed the safety test program. They have demonstrated that their cells and batteries maintained their integrity or vented without explosion or fire under a variety of adverse test conditions. During the venting process it is recognized that sulfur dioxide and other organic vapors are released to the atmosphere; sulfur dioxide is classified as an irritant and an asphyxiant gas.³ Although there are no known systemic effects from exposure to sulfur dioxide, concentrations as small as 8-12 ppm cause throat irritation, coughing, tearing and smarting of the eyes.² Concentrations in the order of 400-500 ppm are considered dangerous even for short exposure.³ The irritation caused by a relatively low sulfur dioxide atmosphere is considered so severe that one could not remain in such an atmosphere unless he were trapped or unconscious. Daily exposure to sulfur dioxide to a recommended threshold value of 5 ppm has shown no chronic systemic effects in workers who were so exposed. In order to minimize the number of occasions when venting of sulfur dioxide will occur and as an extra precautionary measure, all major size batteries will be required to be fused to prevent venting in the event of external short circuits.

Certainly, at this time, the lithium battery has demonstrated substantial performance advantages over other primary batteries to make it a prime candidate for military and commercial use. The evaluation programs of the safety features incorporated in the cell and battery designs have indicated the ability of the battery to withstand many of the adverse conditions that may be expected to arise during its use. This area will be continuously explored, as a large number of batteries are procured and the development program moves from the laboratory to field use, including problems of distribution, shipment, and disposal.

REFERENCES

1. Preliminary Design and Visualization Plan, "Non-Hazardous Lithium Battery BA-5590 ()/U," dated 15 October 1973, Contract DAAB07-73-C-0242 (ECOM), Power Conversion Inc.
2. Preliminary Design and Visualization Plan, "Non-Hazardous Primary Lithium Organic Electrolyte Battery BA-5590," dated 11 January 1974, Contract DAAB07-73-C-0282 (ECOM), Mallory.
3. Encyclopedia of Chemical Technology, Kirk-Gamer Section Edition, vol. 19, (John Wiley & Sons, Inc., New York, 1969), p. 417.

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