Performance and Safety to NAVSEA Instruction 9310.1A of Lithium-Thionyl Chloride Reserve Batteries

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1. Introduction

Reserve-bipolar Li/$SOCl_2$ batteries are preferred for military applications which require:

- Prolonged uncontrolled storage. In the reserve mode the storability of a Li/$SOCl_2$ battery is essentially indefinite.
- Safety prior to use. As the two active battery materials are stored in separate hermetic containers there is no possibility of a hazardous runaway reaction. It should be noted that this is not necessarily the case for reserve batteries employing solid anode and cathode materials.
- Very high specific power levels due to the bipolar design and the liquid catholyte.

This paper describes the design, performance and safety of a fully engineered, self-contained Li/$SOCl_2$ battery as the power source for an underwater Navy application. In addition to meeting the performance standards of the end user this battery has been successfully tested under the rigorous safety conditions of NAVSEA Instruction 9310.1A for use on land, aircraft and surface ships.

2. Battery Design and Performance

A schematic cross section of the battery is given in Figure 1. Prior to activation the catholyte and dry battery stack are separated by a burst disk in the central bulkhead. The stack itself consists of ten 25 cell series modules. During construction the dry stack is potted in epoxy with individual bus wires running down the outer surface of the epoxy shell.

The bus wires run to a terminal board at the base of the battery. The individual modules are connected in parallel to yield the required capacity and voltage upon activation. Per NAVSEA Instruction 9310.1A the modules are connected through protective diodes to prevent charging. In addition each module is protected from short circuit by fusing both the negative and positive bus wires.

Undersea activation of the battery occurs when water pressure bursts the disk above the piston and a bursting pressure is transmitted to the disk between the reservoir and the dry stack. As the device sinks increasing hydrostatic pressure fills the battery stack with electrolyte.

In its intended application the battery is required to provide hotel power and multi-kilowatt pulse power. A typical discharge curve for the battery is given in Figure 2. The total energy drained from the battery corresponds to 850 Wh.

The complete battery measures 29.5 cm in length, 12.7 cm in diameter and weighs 11.4 kg. This yields energy densities of 0230 Wh/l and 75 Wh/kg. The gravemetric energy density is strongly influenced by the heavy case (60% of the battery weight) required for deep undersea operation.

3. Safety

Operational Safety: The battery is intended for operation in unmanned devices and hence safety of activated batteries during discharge is not an issue. It is an issue during development and if device recovery is contemplated.

During preliminary development of the battery venting after discharge but prior to full energy depletion (approximately 24 hrs) was observed approximately 50% of time. The source of these vents was identified as the growth of lithium dendrites driven by the leakage currents in the common electrolyte bipolar filling manifold.

The solution to this problem was to clear the manifold of electrolyte after battery activation. This is accomplished by partially filling the reservoir with argon. Once the battery is filled the electrolyte bursts a rupture disk between the stack and an overflow reservoir. Upon rupture of this disk the piston forces electrolyte out and argon into the filling manifold. By clearing the manifold leakage currents are virtually eliminated and no dendritic ventings have been observed in six consecutive tests.

Short Circuit Safety: By design the battery is fused to assure complete safety during short circuit. This is combined with internal depletion resistors to fully deactivate the battery prior to retrieval.

Nonetheless, NAVSEA Instruction 9310.1A calls for short circuit tests with all fuses and diodes removed. This test was carried out at the systems level by heating the electrolyte reservoir of a shorted battery.

After 26 minutes of heating the reservoir temperature reached 230°C and the battery activated. The behavior of the battery after activation is depicted in Figure 3. To summarize, 54 seconds after activation there was a mild vent with no visible movement of the system. The maximum temperature reached was 506°C 10 minutes and 15 seconds after activation. Maximum short circuit current was 42 amps and a 10 psig pressure spike was observed above the battery vent. The battery presented no fire or explosive hazards.

Reserve Safety: The two areas of concern for an unactivated battery are:

- Maintenance of reserve integrity during shock and vibration
- Safety during a conflagration test

Batteries of an early design passed vibration testing but failed shock by rupture of the electrolyte burst disk when subjected to 330g for 1 msec. A failure analysis led to the conclusion that this resulted from mixing of the argon with the electrolyte and the development of stress concentrations at the disk.

The solution was to place the baffle shown in Figure 1 between the bulk of the reservoir and the burst disk. With the baffle design the batteries are capable of:

- Passing both shock and vibration
- Delivery of full capacity after both shock and vibration
- A 3.8 to 1 safety margin in the shock test

Conflagration tests in accordance with NAVSEA Instruction 9310.1A have been carried out at the systems level. Acceptance, while subjective is generally deemed as the absence of any fragmentation or flame.

An extensive testing, analysis and design program was implemented to meet this standard. Specific activities have included:

- Analytical calculation of reaction rates and battery internal pressure.

- Structural analysis of the battery casing and design as required to assure its integrity in a worst case situation.

o Introduction of a nonfragmentary burst disk.

Results of the reaction time-pressure analysis are summarized in Figure 4. The analysis showed reaction times of:

200	msec	worst case
500	msec	best estimate
1000	msec	best case

Based on this analysis the bulkhead between the reservoir and the stack was designed to accomodate the worst case reaction time. In Figure 4 results of experimental verification of the case integrity are given.

The safety vent was changed to a nonfragmentary design with an increased rim thickness to assure weld integrity. This redesign was accompanied by modification of the vent hole pattern in the piston as shown in Figure 5. The new design eliminates excessive pressure at the center of the safety disk and reduces the blow torch phenomena typical of bipolar batteries venting up the fill hole.

The result of this through analysis and design to conflagration safety standards is graphically demonstrated in Figure 6. Although the system shows the effects of conflagration no fragmentation has occured and no flame was emitted during the test.

4. Conclusions

The $Li/SOCl_2$ system has potentially the highest energy and power density of any primary power source. Concerns with regard to battery safety increase with both energy and power density.

Development of the battery described in this report demonstrates that with careful engineering safe-reserve-bipolar $Li/SOCl_2$ are achievable.

To our knowledge this is the first reserve $Li/SOCl_2$ battery to have complied with the standards in NAVSEA Instruction 9310.1A. The lessons learned in this program are presently being applied at Altus to the development of larger, higher energy density batteries.

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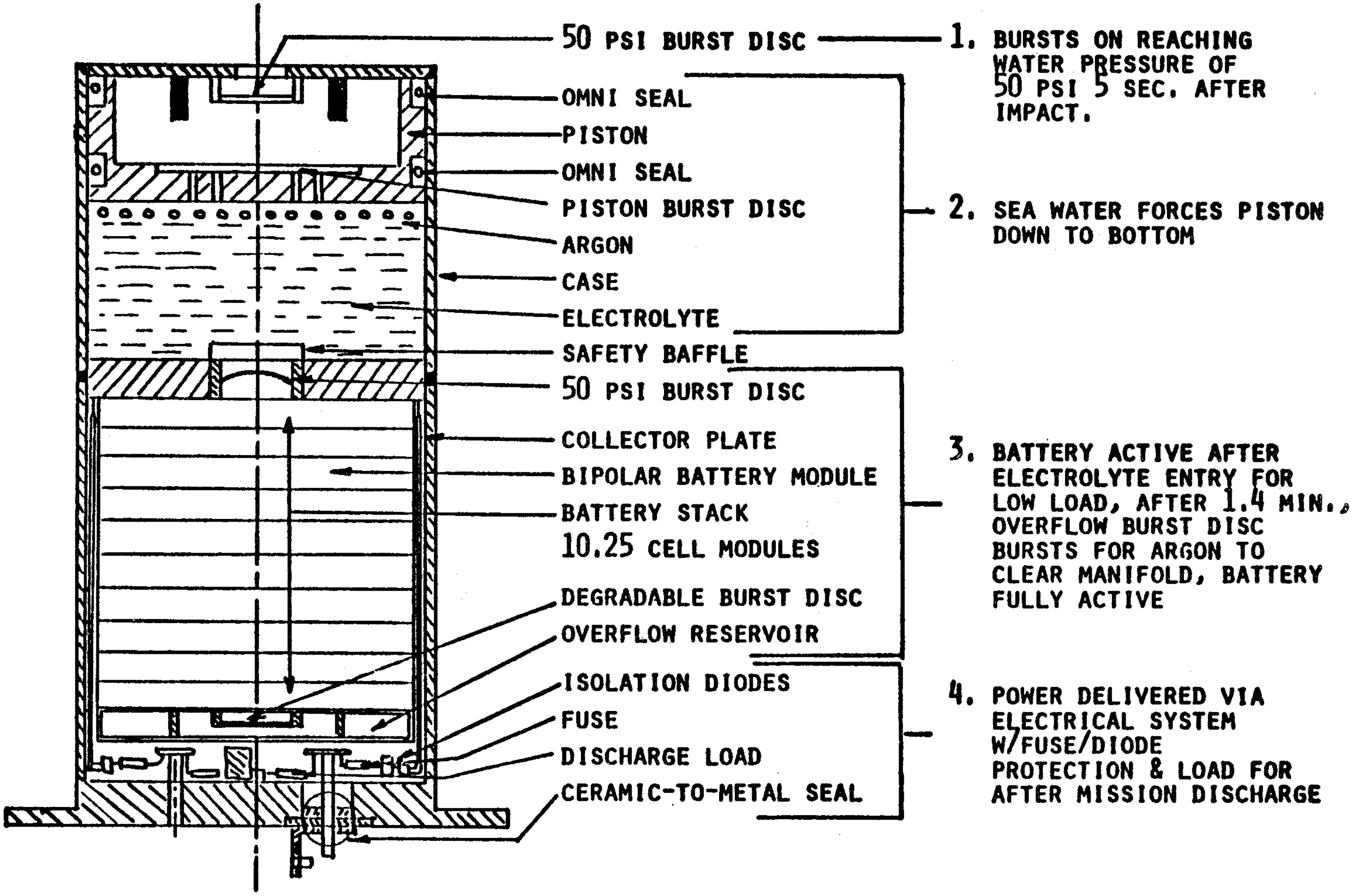


1. BURSTS ON REACHING WATER PRESSURE OF 50 PSI 5 SEC. AFTER IMPACT.

2. SEA WATER FORCES PISTON DOWN TO BOTTOM

3. BATTERY ACTIVE AFTER ELECTROLYTE ENTRY FOR LOW LOAD, AFTER 1.4 MIN., OVERFLOW BURST DISC BURSTS FOR ARGON TO CLEAR MANIFOLD, BATTERY FULLY ACTIVE

4. POWER DELIVERED VIA ELECTRICAL SYSTEM W/FUSE/DIODE PROTECTION & LOAD FOR AFTER MISSION DISCHARGE

WT 25 LBS SIZE 4.94 IN DIA X 11.6 IN

Figure 1. Li/$SOCl_2$ reserve battery system.

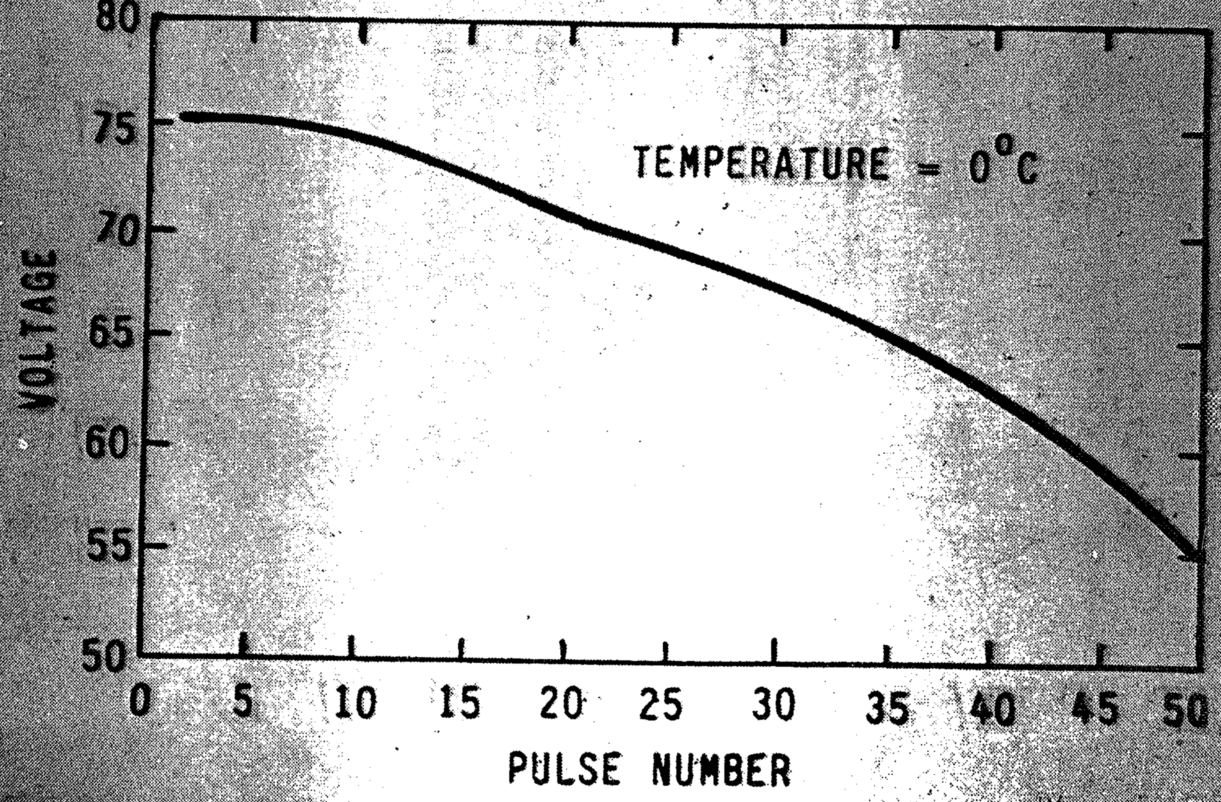


Figure 2. Discharge curve.

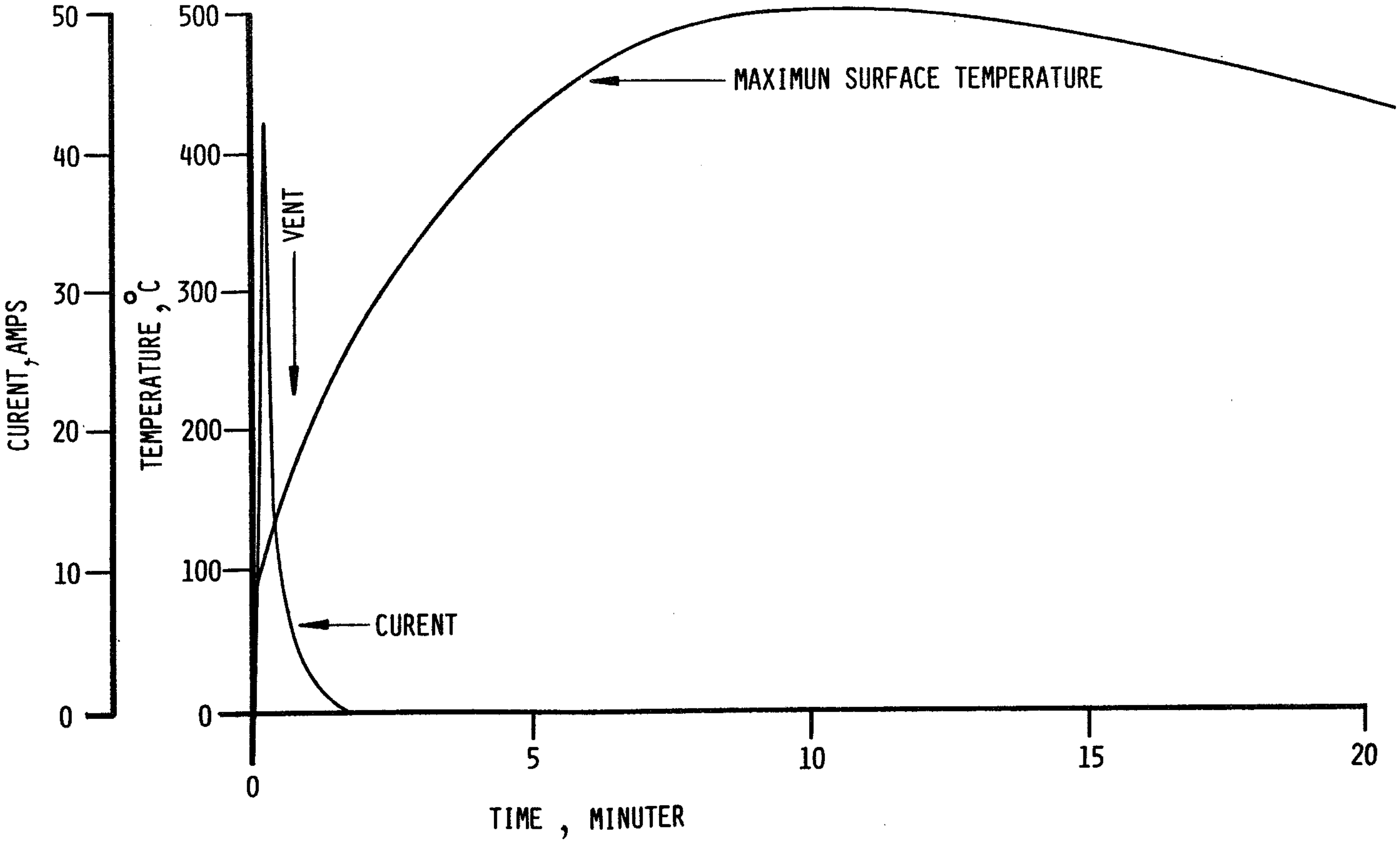
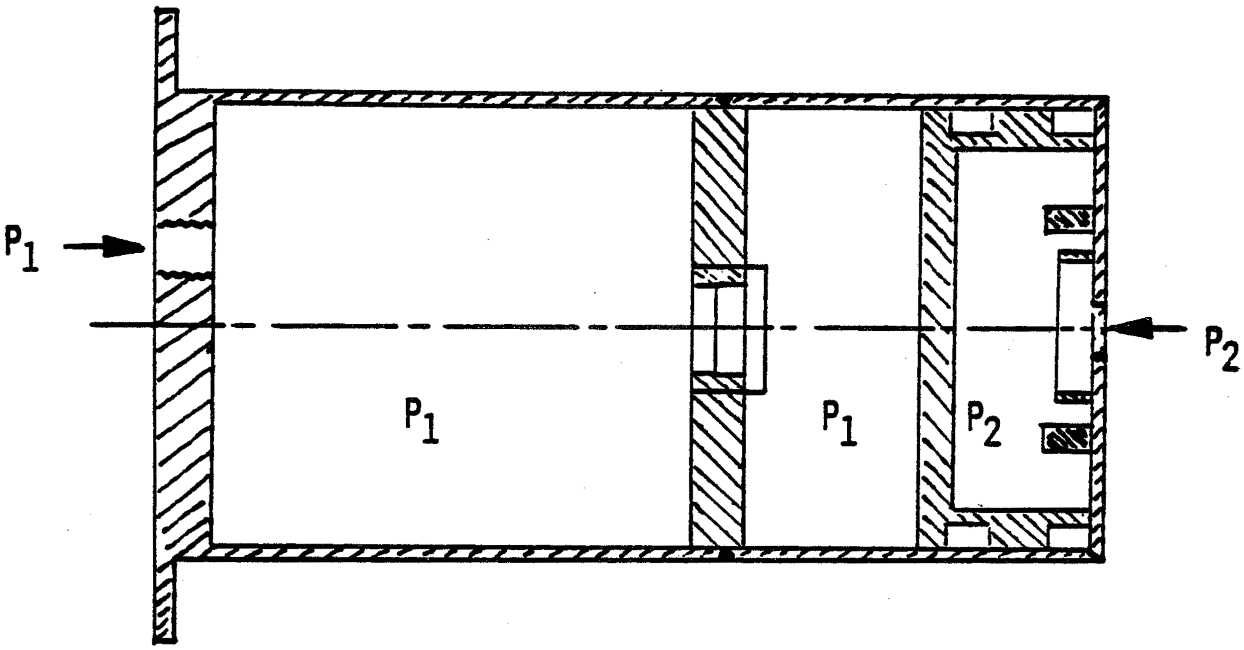


Figure 3. Short circuit test data.



THEORETICAL PRESSURES

REACTION TIME (SECS)	P_1 (PSI)	P_2 (PSI)
0.500	1345	1088
0.200	2588	2058
0.080	3508	2720
0.000	4347	3579

TEST PRESSURES

	P_1 (PSI)	P_2 (PSI)
	1000	550
	1350	1000
*Lost pressure	2000	1500
**Battery top failed	2550	1950
	3000	2500
	3500	*2806
	**3750	0

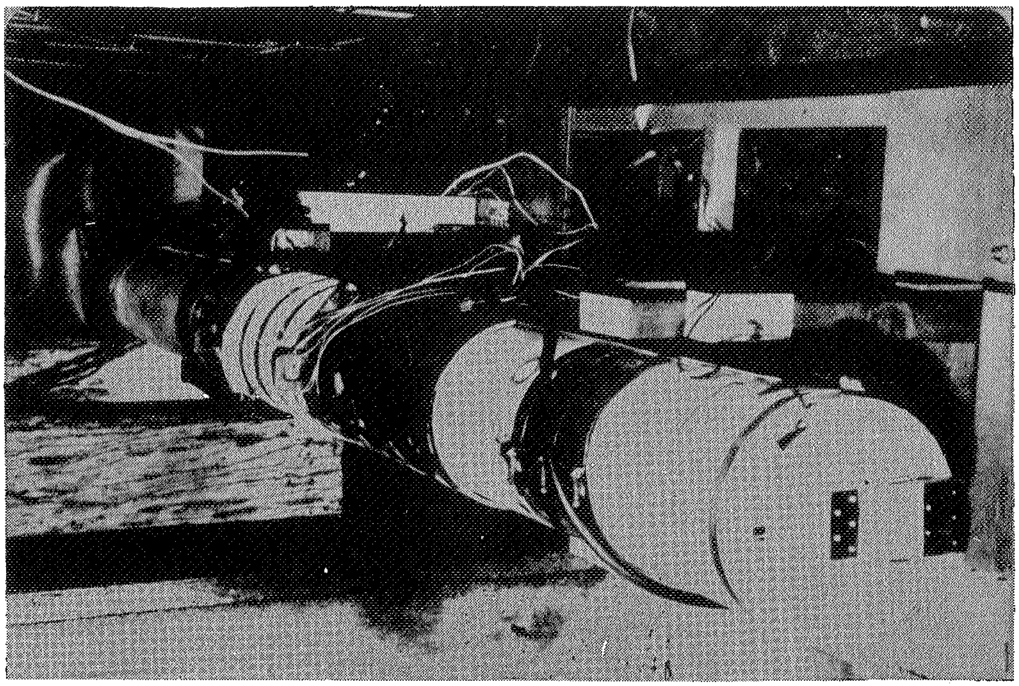
Figure 4. Battery pressure test.

OLD DESIGN

NEW DESIGN

Figure 5. Change to piston safety disc hole pattern.

AFTER



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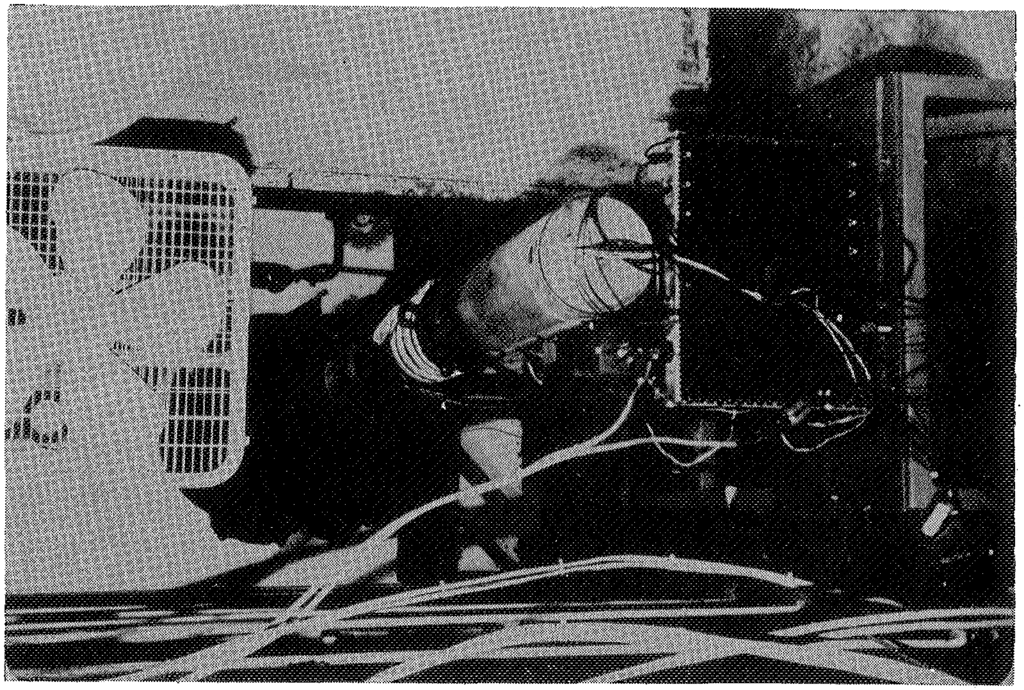

Figure 6. System level battery conflagration test.