HEAT STERILIZABLE Ni-Cd BATTERY DEVELOPMENT

Jet Propulsion Laboratory
Contract No. 951972

Report for First Quarter
1967
(1 July 1967 to 30 September 1967)

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ABSTRACT

Contractual work conducted during the first quarterly reporting period was concerned with construction of testing stations, preliminary separator and seal evaluation and definition of the basic problems associated with the effects of heat sterilization on the electrochemistry of the Ni-Cd system. Early in the program a panel consisting of 60 test stations which monitor current, voltage and resistance of the cells was constructed. This panel was subsequently integrated into our existing data acquisition system which automatically records the pertinent electrochemical parameters.

Several polypropylene separators were selected for further evaluation on the basis of their thermal and chemical stability in 7N KOH. Approximately forty cylindrical cells were constructed using these separators. Pellon 14019 separator is the most promising in terms of lower voltage, lower resistance, higher capacity and lower uniformity both before and after sterilization. All cells evaluated exhibit an increase in end-of-charge voltage after sterilization. This effect cannot be explained by resistance increases and is believed associated with morphological changes at the cadmium electrode.

At present glass-to-metal seals which are protected by a KOH resistant coating have been the most successful in undergoing heat sterilization. A decision on the final design as well as materials of construction will be made during the second quarter.

INTRODUCTION

The heat sterilization of certain spacecrafts required to prevent contamination of planets while searching for extra terrestrial life has created the problem that some components are unable to withstand the severe temperatures used for sterilization. This appears to be especially true of rechargeable batteries which must function satisfactorily over hundreds of charge-discharge cycles after being subjected to the rigors of heat-sterilization. Since no such storage battery is currently available, the Jet Propulsion Laboratory (JPL) has undertaken a systematic program to develop such batteries. The general objectives of the JPL program as outlined in the "Spacecraft Sterilization Technology"(1) are: (1) To obtain basic and new information regarding batteries and battery components subjected to heat sterilization procedures. (2) To develop technology to assist in the proper designing and fabrication of heat-sterilizable batteries. (3) To test and to evaluate components and units of heat-sterilizable batteries. (4) To produce a battery which will satisfactorily meet flight program requirements.

The goal of the present Research and Development contract is to perform studies and to design, develop, fabricate and test sealed, rechargeable, nickel-cadmium batteries capable of surviving heat sterilization.

The heat sterilization requirements include testing at 135°C for type approval, and 125°C testing for flight acceptance. At the 135°C sterilization temperature, the heating rate is 19°C/hour. The chamber is held at this temperature for sixty-four hours and then cooled to room temperature at the same rate at which it was heated. Two such cycles are required. For preliminary testing one 120-hour cycle may be used.

Commercially produced Ni-Cd cells are not designed to withstand the rigors of the heat sterilization process and the factors responsible for the deterioration in the performance of Ni-Cd cells need to be investigated and understood before a reliable, hermetically sealed, rechargeable cell with long cycle life and satisfactory performance characteristics can be developed. The specific tasks under this contract, therefore, include the following:

A. TASK I - Electrochemistry

Use statistical factorial programs to perform studies to characterize electrodes, electrolyte solutions and separators of the nickel-cadmium system. This effort shall consist of, but not necessarily be limited to, the following studies:

1. Electrolyte Solution
    - a. Effect of heat sterilization on cell performance at various concentrations of KOH.
    - b. Effect of the addition of lithium (Li^+), sodium (Na^+), and bismuth (Bi^{3+}) ions and of surfactants to the electrolyte solution.
2. Nickel Electrode
    - a. Effect of heat sterilization on the structure and behavior of the nickel electrode.
    - b. Efficacy of various formulation and fabrication methods to produce more efficient, heat sterilization-resistant electrodes.
    - c. Effect of the addition of cobaltous ion (Co^{++}) to the electrode.
3. Cadmium Electrode
    - a. Effect of heat sterilization on the structure and behavior of the cadmium electrode.

b. Efficacy of various formulation and fabrication methods to produce more efficient heat sterilization-resistant electrodes.

c. Effect of the addition of thallium (Tl^+) and indium (In^+) to the electrode.

4. Separator

Behavior of various separators in cells comprised of selected electrodes and electrolyte solutions under conditions of heat sterilization and subsequent electrical cycling.

B. TASK II - Cell Case

Develop, design, fabricate, and test cell case materials, which shall be sealed after activation, and which are intended to be capable of withstanding a storage life of twelve (12) months after activation and sealing, and a minimum of twelve (12) months after sterilization.

C. TASK III - Fabrication and Test

Fabricate and test cells of a prismatic configuration of about four (4) AH capacity at the contractor's facilities in a parallel effort to support a JPL in-house test program.

1. Develop a procedure for the characterization of nickel-cadmium cells which shall include, but not necessarily be limited to, the following:
   a. One or more sterilization cycles.
   b. Electrical cycling at various rates, depths of discharge, and temperature.
   c. Cell internal pressure measurements for various conditions.

    - d. Cell voltage regulation with cycling.
    - e. Cell voltage and/or capacity stability for a period of time at fifty degrees centigrade (50°C) on a charged stand test after sterilization and electrical cycling.

2. Perform the characterization in accordance with the plan approved by Jet Propulsion Laboratories.
3. Test cells at the contractor's facility for the capability of withstanding the shock and vibration requirements stated in the applicable specifications listed in Exhibit I.
4. Fabricate and characterize nickel-cadmium cells utilizing the electrochemical and mechanical design developed in Tasks I and II, and as approved by Jet Propulsion Laboratories, of a sealed cell capable of successfully surviving heat sterilization, shock and vibration environments as defined in Jet Propulsion Laboratories' specification GMP-50436-DSN-B.
    - a. Develop a test plan to prove the design.
    - b. Perform the tests in accordance with the test plan, as approved by Jet Propulsion Laboratories.

This report summarizes the work performed during the first quarter of the contract.

RESULTS AND DISCUSSION

TASK I - Electrochemistry

Separator Evaluation

Information obtained from Jet Propulsion Laboratories and other pertinent literature indicate that polyalkanes and polyhalocarbons are suitable as separators in alkaline secondary cells and batteries. The requirement of heat sterilizability (i.e., exposure to 135°C for 128 hours in $\sim$30% KOH) further limits the selection of suitable separator materials to felted or porous polypropylene, "Teflon" and fluorohalocarbons. Membrane type separators, developed mainly for Ag-Zn and Ag-Cd batteries to prevent internal short-circuiting via dendrite growth, were not considered suitable for this application. These polymetric materials are characterized by a relatively high resistance which increases internal parasitic power losses and low permeability to oxygen gas which inhibits rapid oxygen recombination in the overcharge mode, causing high internal pressure.

Several brands of nonwoven polypropylene and polypropylene-nylon mixtures were evaluated as to their stability under sterilization conditions. Nylon felt was included as a control standard. These data are shown in Table I. Another important characteristic of these separators is their effect on the electrochemical behavior of hermetically sealed cells. These data were obtained in the initial screening program. Typical results are shown in Table II. Considering the thermal and chemical stability data presented in Table I and the electrochemical performance data presented in Table II, three polypropylene type separators were selected for further evaluation.

TABLE I

THERMAL/CHEMICAL STABILITY OF VARIOUS SEPARATORS

Separator Type		Appearance After Sterilization
Material (Felt)	Manufacturer	
Nylon	Pellon #2505	Dissolved
Polypropylene	Pellon #25/249	Not Visibly Attacked
Polypropylene	Pellon #25/242	Not Visibly Attacked
Polypropylene	Pellon 14019	Not Visibly Attacked
Polypropylene	Pellon 14020	Not Visibly Attacked
Polypropylene/Nylon	Pellon 1243	Nylon Portion Dissolved
Dynel	Kendall M1401	Dissolved
Polypropylene	Kendall EM476	Not Visibly Attacked
Polypropylene/Nylon	Kendall EM490	Nylon Portion Attacked
Nylon	Kendall	Dissolved

TABLE II

PRELIMINARY ELECTROCHEMICAL SCREENING OF SEPARATOR MATERIALS FOR HEAT STERILIZABLE Ni-Cd CELLS

Positive limited, sealed cylindrical cells with 0.6 AH nominal capacity were filled with 30% KOH. Eighty percent of the pore volume was filled with the electrolyte.
DUTY CYCLE: Charge 60 mA, 24 hrs; discharge 500 mA to 1.000 volts

Separator (Felts) (3 cells tested)	Brand		Cell Capacity (AH) At Cycle No.				End of Charge Volt.(volts) At Cycle No.				End of Discharge Resis.(mΩ) At Cycle No.			
			1	2	3	100	1	2	3	100	1	3	3	100
Nylon (Control)	Pellon #2505	Avg.	.734	.711	.688	.668	1.409	1.413	1.412	1.428	12.56	11.44	10.22	14.20
		* Δ	.034	.042	.038	.096	.004	.007	.003	.005	2.0	1.0	0.3	2.04
Polypropylene	Pellon #25/249	Avg.	.605	.542	.508	.557	1.412	1.422	1.424	1.450	25.89	26.11	24.67	32.43
		Δ	.066	.092	.092	.075	.003	.005	.011	.005	8.3	8.3	8.3	10.7
Polypropylene	Pellon #25/242	Avg.	.616	.563	.529	.646	1.408	1.416	1.419	1.449	33.00	31.67	29.00	36.5
		Δ	One cell		tested									
Polypropylene	Pellon 14019	Avg.	.780	.746	.723	.711	1.417	1.421	1.419	1.437	12.10	12.44	11.89	15.28
		Δ	.058	.067	.062	.067	.023	.006	.005	.002	.30	.30	.30	.60
Polypropylene	Pellon 14020	Avg.	.533	.520	.511	.522	1.421	1.426	1.431	1.466	17.45	18.11	17.33	21.30
		Δ	.016	.013	.008	.017	.002	.005	.008	.017	2.0	1.0	2.3	1.8
Dynel	Kendall M1401	Avg.	.532	.518	.493	.458	1.412	1.418	1.421	1.419	37.42	32.77	30.89	36.16
		Δ	.019	.013	.016	.006	.002	.002	.001	.003	7.19	6.46	6.04	8.74
Polypropylene 2 Layers	Kendall EM476	Avg.	.614	.653	.660	.586	1.409	1.416	1.421	1.416	19.44	18.87	18.44	18.43
		Δ	.010	.041	.060	.013	.002	.002	.002	.001	1.00	1.57	1.67	1.73
Polypropylene 50% Nylon 50% 50%	Kendall EM490	Avg.	.426	.635	.611	.566	1.409	1.413	1.416	1.415	16.55	14.46	16.15	17.10
		Δ	.272	.012	.032	.035	.002	.002	.003	.001	0.29	0.33	0.76	1.41
Polypropylene and Nylon	Pellon 1243	Avg.	.632	.674	.684	.585	1.415	1.419	1.423	1.420	15.61	15.61	15.22	16.92
		Δ	.042	.028	.024	.064	.002	.002	.002	.006	2.19	2.15	2.09	2.39
Nylon	Kendall	Avg.	.719	.778	.799	.671	1.416	1.422	1.430	1.413	13.47	12.98	12.79	17.30
		Δ	.042	.010	.023	-	.008	.005	.005	-	3.69	3.37	3.33	-

*Δ is the difference between high and low values of the three cells tested.

Again referring to the data presented in Table II, it is apparent that these felted polypropylenes supplied by the various manufacturers vary widely in their electrochemical behavior. This variability is noted in such parameters as the electrochemical capacity, the internal cell resistance, the end-of-charge voltage and, presumably, internal pressure during overcharge. These parameters are affected and in part controlled by the electrolyte wetting, absorption and retention properties of the separator materials. Characteristically pure polyalkanes (e.g., polypropylene) have relatively poor wetting properties (i.e., contact angle ~90°) in concentrated alkaline solutions. Often these separators are treated with surfactants during the manufacturing process. Past experience in our laboratories has shown that some of these additives or their constituents (e.g., chloride ions) may be detrimental to battery performance due to their oxidizing or reducing characteristics in the cell environment. The selected separators, mentioned previously, were therefore analyzed for trace "impurities" using a mass spectrometer. Results of these analyses are shown in Table III.

TABLE III

SPECTROSCOPIC ANALYSES OF SEPARATOR MATERIALS

Separator	Ash %	Major Constituent of Ash	Cations Present (ppm) Si	Al	Mg	Zn	Fe	Cu	Na
Kendall EM476	0.2	-	200	20	10	<10	10	100	<1
Pellon 14019	1.3	Zn	1000	200	20	-	20	300	500
Pellon 25/249	11.1	Mg	100	<1	-	<10	20	200	1000

From these data there appear to be no cations present in sufficient quantity to adversely affect the cell performance. The separators and cell electrolytes will be analyzed for anions as well as cations routinely during post-sterilization analyses.

An attempt was made to enhance the wetting properties of the polypropylene separators by replacing and/or adding a known surface active agent. Based on wetting characteristics, thermal stability and compatibility with potassium hydroxide solutions, as described by the manufacturers, three surfactants were chosen for evaluation. Pertinent chemical and physical properties supplied by the manufacturers are shown in Table A in the Appendix. To determine the effectiveness of these surfactants in enhancing the wetting characteristics of the separators, samples of the various felts as received were impregnated with the surfactant solutions. In another set of experiments, the separator samples were washed free of the surfactants incorporated by the manufacturer and were then treated with the surface active agents to determine their effectiveness on electrolyte wetting, absorption and retention characteristics of the separators. Efficacy of the surfactants was measured in terms of grams of 31 weight percent KOH solution absorbed per gram of dry separator. Untreated separators were used as control samples. These data are shown in Table IV for surfactants Triton X-100; FC-95; and FC-98 with water or methanol as solvents.

These data show that the attempts to date to enhance the wetting and absorption properties of these polypropylene separators by the leaching and/or addition of surfactants have been unsuccessful. From independent studies conducted in these laboratories the addition of surfactants to the electrolytes appears more promising. This course of action will be followed if it is found that

TABLE IV

ABSORPTION OF KOH BY VARIOUS SEPARATORS

(gm of 31% KOH/gm of dry separator)

	Separator Material		
Separator Treatment and Surfactant Used	Kendall EM476	Pellon 25/249	Pellon 14019
Material Untreated (control sample)	3.2	2.2	10.9
Material Unwashed FC-95 in H_2O 1:1000	2.5	2.2	9.9
Material Unwashed Triton X-100 in H_2O 1:1000	2.5	2.7	10.1
Material Washed FC-98 in CH_3OH 7.5% Soln.	1.8	1.2	2.8
Material Unwashed FC-98 in CH_3OH 7.5 Soln.	3.5	1.5	2.7
Material Washed Triton X-100 in H_2O 1:1	3.0	3.0	4.7
Material Unwashed Triton X-100 in H_2O 1:1	2.5	2.0	4.6
Material Unwashed FC98 in CH_3OH 1:100	2.2	2.2	3.1
Material Unwashed Triton X-100 in H_2O 1:100	3.2	2.1	7.7
Unwashed Samples FC-98 in 30% KOH 500 ppm	2.0	2.6	10.1

the surfactants incorporated in the separators by the manufacturer are destroyed or rendered inefficient by the sterilization process. Final selection of the separator will be made when the evaluation, including further electrochemical testing, is completed.

A total of approximately 40 cylindrical 0.6 Ah sealed cells were made for electrolyte and further separator optimization studies. The cells have undergone five presterilization characterization cycles. The data obtained include (1) electrochemical capacity, (2) end-of-charge voltage, (3) end-of-charge resistance, and (4) end-of-discharge resistance. These data are shown in Tables V to VII.

These data indicate the electrochemical performance of cells is strongly influenced by the separator used in that system. The lack of reproducibility in those cells containing separators EM476 and 25/249 is reflected in the standard deviation (σ) of the capacity and resistance values. The variability among cells containing separator 14019 is notably smaller. The lack of reproducibility of cell performance containing different separators may be attributed largely to the nonuniformity of the separator materials since all other parameters (e.g. plate area, plate capacity, cell volume, etc.) are held constant. Thus separator 14019 is considered more uniform in its effect on cell performance. In addition, those cells containing separator 14019 exhibit better electrochemical characteristics (e.g. higher capacity, lower internal resistance) than cells with the other separators.

The decrease in capacity from cycle to cycle is common to all cells tested, although this effect occurs to a lesser degree in those cells containing separator 14019. Nevertheless, the cause of this behavior must be determined

TABLE V

Cell Capacity - 0.600 Ah nominal, cylindrical type
Electrolyte - 30% KOH, 80% pore volume filled (calculated)
Charge Rate - 60 Milliamperes for 24 hours
Discharge Rate - 1.5 Amperes to 1.000 volts
Separator - Kendall EM476; 2 layers

Cell No.	Capacity (amp-hrs)					End-of-Charge Voltage (volts)				
	Cycles: 1	2	3	4	5	Cycles: 1	2	3	4	5
1	.475	.400	.264	.163	.138	1.420	1.409	1.402	1.407	1.405
2	.564	.463	.363	.339	.264	1.423	1.411	1.402	1.409	1.408
3	.513	.475	.388	.238	.213	1.419	1.418	1.410	1.416	1.422
4	.489	.438	.363	.264	.264	1.420	1.414	1.406	1.411	1.410
5	.613	.538	.438	.274	.325	1.422	1.413	1.402	1.409	1.407
6	.424	.363	.264	.163	.189	1.407	1.399	1.392	1.398	1.398
7	.525	.438	.349	.238	.225	1.418	1.406	1.398	1.404	1.403
8	.400	.349	.288	.199	.189	1.411	1.409	1.402	1.406	1.405
9	.414	.363	.288	.199	.175	1.408	1.403	1.401	1.413	1.413
Avg.	.491	.425	.334	.231	.221	1.416	1.409	1.402	1.408	1.408
σ	.068	.059	.057	.054	.052	0.005	0.005	0.005	0.005	0.006

Cell No.	End Charge Resistance (milliohms)					End Discharge Resistance (milliohms)				
	Cycles: 1	2	3	4	5	Cycles: 1	2	3	4	5
1	38.64	34.46	38.68	35.55	40.53	22.82	24.76	25.55	22.09	21.63
2	22.41	20.29	20.52	19.47	19.87	17.04	19.22	18.32	17.67	17.39
3	26.50	23.32	23.87	23.55	24.96	17.19	18.76	19.12	17.20	17.29
4	35.77	33.14	34.34	32.46	34.90	21.93	23.56	24.46	21.73	21.33
5	27.12	26.15	25.64	23.67	23.78	19.01	21.76	22.09	20.06	19.66
6	29.70	25.32	24.52	23.04	24.19	22.53	24.20	22.59	21.90	21.10
7	29.35	25.96	25.07	22.97	22.98	18.57	21.38	21.49	19.52	19.64
8	36.84	33.25	32.80	29.51	30.44	21.35	24.26	24.73	21.73	21.12
9	34.66	32.75	32.21	28.01	29.12	21.32	23.77	24.24	21.96	21.00
Avg.	31.22	28.22	28.63	26.47	27.89	20.20	22.41	22.51	20.43	20.02
σ	5.18	4.87	5.67	5.02	6.27	2.20	2.12	2.01	1.81	1.59

TABLE VI

Cell Capacity - 0.600 Ah nominal, cylindrical type
Electrolyte - 30% KOH, 80% calculated pores filled
Charge Rate - 60 Milliamperes for 24 hours
Discharge Rate - 1.5 Amperes to 1.000 volts
Separator - Pellon 25/249

PRESTERILIZATION DATA

Cell No	Capacity (amp-hrs) Cycles: 1	2	3	4	5	End-of-Charge Voltage (volts) Cycles: 1	2	3	4	5
11	.339	.189	.300	.114	.075	1.421	1.410	1.406	1.406	1.409
12	.450	.363	.264	.150	.124	1.424	1.412	1.406	1.407	1.406
13	.463	.424	.339	.264	.274	1.422	1.411	1.407	1.408	1.413
14	.463	.388	.288	.189	.163	1.424	1.414	1.408	1.412	1.412
15	.499	.438	.339	.213	.213	1.427	1.417	1.409	1.411	1.413
16	.513	.475	.388	.288	.264	1.433	1.420	1.411	1.416	1.419
17	.538	.489	.414	.375	.375	1.421	1.408	1.420	1.410	1.409
Avg.	.466	.395	.333	.228	.198	1.424	1.413	1.410	1.410	1.412
σ	.064	.101	.054	.089	.103	0.004	0.004	0.005	0.003	0.004

Cell No.	End-of-Charge Resistance (mΩ) Cycle: 1	2	3	4	5	End-of-Discharge Resistance (mΩ) Cycle: 1	2	3	4	5
11	39.98	38.43	37.38	34.53	34.99	29.14	33.63	34.20	28.17	27.10
12	42.97	38.99	38.20	33.56	34.39	30.21	38.40	35.84	31.79	30.09
13	41.32	40.14	40.00	36.17	38.31	32.11	39.29	38.76	32.46	31.18
14	44.26	44.18	44.84	41.51	44.09	30.97	33.55	33.91	29.13	28.86
15	36.86	33.06	33.13	31.42	32.80	28.81	32.08	30.55	26.15	25.16
16	45.25	43.97	45.30	42.93	45.21	31.45	34.74	34.21	30.41	30.03
17	40.48	44.14	39.30	43.64	41.44	37.01	40.37	38.55	39.91	38.51
Avg.	41.59	40.42	39.74	37.39	38.75	31.38	36.00	35.14	31.14	30.13
σ	2.82	4.08	4.26	4.75	4.87	2.75	3.22	2.87	4.42	4.22

TABLE VII

Cell Capacity - 0.600 Ah nominal, cylindrical type
Electrolyte - 30% KOH, 80% calculated pores filled
Charge Rate - 60 Milliamperes for 24 hours
Discharge Rate - 1.5 Amperes to 1.000 volts
Separator - Pellon 14019

PRESTERILIZATION DATA

Cell No.	Capacity (amp-hrs) Cycles: 1	2	3	4	5	End-of-Charge Voltage (volts) Cycles: 1	2	3	4	5
19	.625	.489	.400	.424	.450	1.412	1.400	1.400	1.402	1.402
20	.613	.499	.424	.450	.475	1.410	1.398	1.396	1.399	1.401
21	.639	.499	.414	.414	.450	1.412	1.399	1.399	1.400	1.401
23	.613	.489	.414	.438	.475	1.412	1.399	1.400	1.398	1.401
24	.600	.485	.400	.438	.450	1.410	1.398	1.399	1.398	1.399
25	.613	.475	.400	.414	.424	1.410	1.397	1.400	1.401	1.401
27	.675	.525	.414	.424	.438	1.420	1.398	1.396	1.396	1.397
Avg.	.625	.494	.409	.429	.452	1.412	1.398	1.399	1.399	1.400
σ	.025	.016	.009	.014	.019	0.003	0.001	0.002	0.002	0.002

Cell No.	End-of-Charge Resistance (m Ω) Cycle: 1	2	3	4	5	End-of-Discharge Resistance (m Ω) Cycle: 1	2	3	4	5
19	14.76	15.26	14.50	15.98	14.69	14.38	14.04	14.21	14.92	14.09
20	14.35	14.70	14.54	15.63	14.13	14.50	14.29	15.13	16.09	14.82
21	16.10	16.42	15.43	16.83	15.41	16.18	15.46	16.01	16.19	15.21
23	15.44	16.30	15.73	16.75	15.46	15.18	15.38	14.99	15.29	14.56
24	14.30	14.79	14.02	14.97	14.10	14.67	14.50	15.21	15.13	14.83
25	14.52	15.45	14.73	15.79	14.34	15.01	14.78	15.18	15.92	15.10
27	13.91	14.68	14.04	15.28	14.16	13.39	13.26	13.79	13.99	13.41
Avg.	14.77	15.38	14.71	15.89	14.61	14.77	14.53	14.93	15.36	14.57
σ	1.01	0.73	0.54	0.75	0.60	0.65	0.77	0.73	0.78	0.63

since cell-to-cell as well as cycle-to-cycle uniformity is important before a meaningful statistical program can be implemented. Previous experience in the laboratory indicates that the decreasing capacity as a function of short-term cycling may be associated with electrolyte redistribution which, in turn, depends on cell geometry.

The capacity decrease on cycling is not significant in 4 Ah prismatic cells, as is shown in Table VIII. The cell-to-cell variation is associated with the difference in pore volume filling by KOH, not necessarily lack of uniformity of the separator material.

Post sterilization behavior of the cyclindrical cells is characterized by increased capacity and increased end-of-charge voltage. These data are presented in Tables IX to XI.

Without exception, the cells exhibited a higher end-of-charge voltage after sterilization. This increase in voltage cannot be fully explained by the small increase in cell resistance after sterilization. From independent studies conducted in these laboratories it appears that this higher end-of-charge voltage is associated with morphological changes at the cadmium (negative) electrode during sterilization which results in inefficiency upon the subsequent charging cycle. Charge voltages greater than 1.5 volts are normally associated with hydrogen evolution at the cadmium (negative) electrode.

This aspect of the electrochemistry is being investigated further with the aid of specially designed cells with plastic and prismatic stainless steel cases. These cells are equipped with pressure gages to monitor the gas pressure during the charge and discharge cycles. In addition, gas analyses can

TABLE VIII

Cell Capacity - 4.0 Ah nominal, prismatic type
Electrolyte - 30% KOH, pore filling as shown
Charge Rate - 2.000 Amperes for 3 hours
Discharge Rate - 4.000 Amperes to 1.000 volt cutoff
Separator - Pellon 14019

PRESTERILIZATION DATA

Cell No.	Capacity (amp-hrs) Cycles: 1	2	3	4	End-of-Charge Voltage (volts) Cycles: 1	2	3	4	% Fill
PA-1	3.904	3.968	3.868	3,836	1.460	1.470	1.463	1.457	70
PA-2	4.436	4.504	4.400	4.436	1.465	1.486	1.483	1.482	80
PA-3	4.332	-	-	4.032	1.455	-	-	1.437	90
PA-4	4.636	4.568	4.468	4.468	1.482	1.485	1.480	1.476	80

Cell No.	End Charge Resistance (mΩ) Cycles: 1	2	3	4	End Discharge Resistance (mΩ) Cycles: 1	2	3	4	% Fill
PA-1	5.66	6.09	5.87	6.10	5.76	5.91	5.93	6.17	70
PA-2	5.53	5.97	5.70	5.91	5.49	5.70	5.68	5.89	80
PA-3	5.82	-	-	6.09	5.80	-	-	6.22	90
PA-4	5.80	5.81	5.58	5.66	5.61	5.49	5.48	5.74	80

TABLE IX

Cell Capacity - 0.600 Ah nominal, cylindrical type
Electrolyte - 30% KOH, 80% calculated pores filled
Charge Rate - 60 Milliamperes for 24 hours
Discharge Rate - 1.5 Amperes to 1.000 volts

POST-STERILIZATION DATA

Cell No.	Capacity (amp-hrs) Cycles: 6	7	8	9	10	End Charge Voltage (volts) Cycles: 6	7	8	9	10	Separator
5	.763	.789	.775	.700	.700	1.483	1.481	1.474	1.469	1.464	Kendall EM 476
6	.799	.789	.775	.675	.663	1.485	1.486	1.476	1.475	1.470	
7	.700	.714	.714	.639	.639	1.487	1.487	1.479	1.476	1.473	
*AVG. (1)	.754	.764	.755	.671	.661	1.485	1.485	1.476	1.473	1.469	
**AVG.(2)	.521	.466	.350	.225	.246	1.416	1.406	1.397	1.404	1.403	

Cell No.	End Charge Resistance (mΩ) Cycles: 6	7	8	9	10	End Discharge Resistance (mΩ) Cycles: 6	7	8	9	10	Separator
5	25.64	28.67	28.32	26.49	29.99	22.89	22.38	23.10	23.09	23.64	Kendall EM476
6	28.06	29.40	29.48	27.19	32.24	24.74	24.35	25.07	25.46	25.11	
7	25.33	29.40	29.17	27.19	30.30	23.39	22.94	23.85	24.13	23.95	
*Avg.(1)	26.34	29.16	28.99	26.96	30.84	23.76	23.22	24.01	24.23	24.23	
**Avg.(2)	28.72	25.81	25.08	23.23	23.65	20.04	22.45	22.22	20.49	20.62	

* Average of 3 cells after sterilization
** Average of 3 cells prior to sterilization

TABLE X

Cell Capacity - 0.600 Ah nominal, cylindrical type
Electrolyte - 30% KOH, 80% calculated pores filled
Charge Rate - 60 Milliamperes for 24 hours
Discharge Rate - 1.5 Amperes to 1.000 volts

POST-STERILIZATION

Cell No.	Capacity (amp-hrs)					End-of-Charge Voltage (volts)					Separator
	Cycles: 6	7	8	9	10	Cycles: 6	7	8	9	10	Pellon 25/240
13	.613	.564	.564	.513	.513	1.507	1.511	1.504	1.497	1.492	
15	.613	.463	.424	.375	.339	1.500	1.510	1.497	1.493	1.485	
16	.600	.600	.538	.463	.438	1.505	1.521	1.500	1.490	1.483	
*Avg.(1)	.609	.542	.509	.450	.430	1.504	1.514	1.500	1.493	1.487	
**Avg(2)	.492	.446	.322	.255	.250	1.427	1.416	1.409	1.412	1.415	

Cell No.	End-of-Charge Resistance (m Ω)					End-of-Discharge Resistance (m Ω)					Separator
	Cycles: 6	7	8	9	10	Cycles: 6	7	8	9	10	Pellon 25/249
13	45.37	51.45	48.09	42.98	49.20	42.44	36.02	35.92	36.87	36.13	
15	48.19	52.43	47.76	47.11	49.77	38.95	33.74	37.55	38.21	36.28	
16	57.78	63.35	59.04	56.57	61.45	45.37	39.28	38.60	45.12	41.11	
*Avg.(1)	50.45	55.84	51.63	48.89	53.47	42.25	36.35	37.36	40.07	37.84	
**Avg.(2)	41.14	39.06	39.48	36.84	38.54	30.79	35.37	34.51	29.67	28.79	

* Average of 3 cells after sterilization
** Average of 3 cells prior to sterilization

TABLE XI

POST-STERILIZATION BEHAVIOR OF CYLINDRICAL CELLS

Cell Capacity - 0.600 AH nominal, cylindrical type
Electrolyte - 30% KOH, 70% calculated pores filled
Charge Rate - 60 mA for 24 hrs
Discharge Rate - 1.5 A to 1.000 volts

Cell No.	Capacity (amp-hrs)					End-of-Charge Voltage (volts)					Separator 14019
	Cycles: 6	7	8	9	10	Cycles: 6	7	8	9	10	
19	.714	.738	.775	.750	.750	1.489	1.497	1.490	1.480	1.472	
20	.825	.825	.838	.813	.825	1.503	1.512	1.501	1.483	1.477	
21	.763	.724	.738	.738	.738	1.484	1.490	1.492	1.477	1.471	
*Avg(1)	.767	.762	.784	.767	.771	1.492	1.500	1.494	1.480	1.473	
**Avg(2)	.626	.496	.413	.429	.458	1.411	1.399	1.398	1.401	1.401	

Cell No.	End Charge Resistance (mΩ)					End Discharge Resistance (m)					Separator 14019
	Cycles: 6	7	8	9	10	6	7	8	9	10	
19	19.84	19.94	18.37	17.54	17.84	19.40	17.93	18.04	18.54	18.20	
20	19.88	18.90	17.71	17.33	17.56	19.70	17.85	18.53	18.89	18.49	
21	26.04	24.87	22.61	21.08	21.28	23.25	21.64	19.86	20.36	19.64	
*Avg(1)	21.92	21.24	19.56	18.65	18.89	20.78	20.25	18.81	19.26	18.78	
**Avg(2)	15.07	15.46	14.82	16.15	14.74	15.02	14.60	15.07	15.73	14.71	

* Average of 3 cells after sterilization
** Average of 3 cells prior to sterilization

be performed at any time to determine the composition of evolved gases. An associated problem is devising a suitable reference electrode that will also survive the heat sterilization cycle. The commonly employed Hg/HgO electrode cannot be used in this geometry. The partially charged $Ni(OH)_2/NiOOH$ electrode decomposes to the uncharged $Ni(OH)_2$ at the sterilization temperature of 135°C, thus shifting its potential and introducing uncertainty into the potential values obtained. Previously the stainless steel cell case itself has been used as an empirical reference electrode, in these laboratories, with success. This approach will be pursued further.

The increase in capacity observed in the cylindrical cells is considered atypical of the behavior normally expected and previously reported on heat sterilized nickel-cadmium cells. In no case, however, do the capacity values exceed those normally expected for these cells using conventional nylon separators. Several 4 Ah prismatic cells were heat sterilized to determine the stability of the design of the hermetic seal. The findings concerned with the behavior of the seal will be discussed later. The electrochemical behavior of these cells, shown in Table XII, was similar to that of the cylindrical cells except for a decrease in capacity. Again, our best knowledge to date indicates this capacity loss is due to changes in the morphology of the cadmium electrodes which reduces its efficiency on charge and results in decreased capacity. This area of investigation will be actively pursued during the next quarter when the appropriate separators are selected and cell case and seal design are finalized.

TABLE XII

Cell Capacity - 4.0 Ah nominal, prismatic type
Electrolyte - 30% KOH, pore filling as shown
Charge Rate - 2.000 amperes for 3 hours
Discharge Rate - 4.000 amperes to 1.000 volt cutoff
Separator - Pellon 14019

POST-STERILIZATION DATA

Cell No.	Capacity (amp-hr) Cycles: 5	6	7	End Charge Voltage Cycles: 5	6	7	% Fill
PA-1	2.468	3.268	3.132	1.479	1.730	1.748	70
PA-2	3.436	Short	Short	1.552	-	-	80
PA-3	3.236	3.968	3.932	1.626	1.709	1.726	90
PA-4	3.304	3.868	3.668	1.544	1.717	1.743	80

Cell No.	End Charge Resist. Cycles: 5	6	7	End Discharge Resist. Cycles: 5	6	7	% Fill
PA-1	6.18	6.66	6.73	5.73	7.71	9.42	70
PA-2	6.36	-	-	5.74	-	-	80
PA-3	7.68	5.99	5.89	6.05	5.96	5.72	90
PA-4	6.17	6.55	6.29	5.76	6.36	7.65	80

TASK II. Cell Cases and Seals

Two cell and seal designs were selected for experimental use. Preliminary testing (i.e. separator screening) was carried out in cylindrical cells with polypropylene seals. Because of the inconsistencies previously mentioned the major portion of the experimental program will be conducted using the prismatic configuration. The 304 stainless steel prismatic cases have successfully passed the required two sterilization cycles.

The seals are of the glass-to-metal type whose construction is shown in Figs 2,3 in the appendix. Mass-produced, hermetically sealed glass-to-metal seals of this type are used extensively in the electronic industry for diodes, transistors, etc., and for electrical feed-throughs. We have had considerable experience in the fabrication and testing of these seals for electronic devices. Since glass is not resistant to KOH at sterilization temperatures, it must be protected from chemical attack. Work performed prior to this contract with epoxy coated glass seals have shown no leakage over a one-year period at room temperature and several weeks at 145°F. After a review of the literature and contact with several vendors, we have selected KEL-F, Durafilm K (an epoxy) and Stycast (an epoxy) for further evaluation as protective coatings. These materials were applied to several case tops and hermetic seals by the Durafilm Company who specialize in protective coating technology. The coating is applied in four or five steps, each step involves spraying and baking.

The tops and seals were assembled into cells. The cells were electrochemically characterized (see Table VIII), sterilized, recharacterized (see Table XII) and subsequently opened for examination. The coatings applied to the tops and sealed were not attacked by KOH during and after the heat sterilization process.

Although the adhesion of the coating to the metallic surfaces was poor, the seals themselves were protected and did not leak. Adherence of the coatings to the case tops can be improved by design changes and/or additional pretreatments to the metal surfaces. Cell tops and seals incorporating such changes were manufactured and are currently being assembled into cells. The factorial experimental program will be undertaken when a uniform separator and a reliable seal are obtained.

TASK III. Fabrication and Tests

A test panel, complete with control stations, was built for electrochemical characterization of cells and plates prior to and following heat sterilization. The test stations were connected to our automatic data acquisition system which records all pertinent electrochemical characteristics of the cells. The data which is recorded on punchcards is then processed by an IBM 360-30 computer according to programs available in the system's library. A typical computer print-out is shown in the appendix in Table B. This facility is routinely being used for all the characterization of cells under this program.

CONCLUSIONS

1. Polypropylene separators are thermally and chemically stable in KOH at sterilization temperatures of 135°C.

2. The carding or wetting agents present in the separator materials do not contain harmful cations in sufficient quantity to adversely affect cell performance.

3. Of the several non-woven polypropylene types evaluated, namely, Pellon's FT2140, 25/249, 14019 and Kendall's EM476, separator 14019 appears superior in terms of uniformity and contributing to lower cell resistance and higher cell capacity.

4. The results obtained to date indicate that much of the loss in capacity which occurs in cylindrical cells from cycle to cycle is associated with geometry factors. This behavior is not observed in prismatic cells.

5. At present glass-to-metal seals coated with KOH resistant coatings (KEL-F and Durafilm K) appear to withstand heat sterilization at 135°C as well as subsequent pressure cycling without any leakage.

CONFERENCES

1. On August 28, 1967, Dr. Ralph Lutwack from Jet Propulsion Laboratories visited our Research and Development laboratories to review the progress of the work under this contract. The experimental data and the design of the statistical experiments were discussed with Dr. Lutwack. He also reviewed the test facilities and inspected the cells that were sterilized and cut open for failure analysis.

2. Drs. Ralph Lutwack, Aiji A. Uchiyama and Gordon L. Juvinall from the Spacecraft Power Section, Jet Propulsion Laboratories, visited our Research and Development laboratories and manufacturing facilities on Friday, October 6, 1967. They reviewed the contract work as well as our electrochemical test facilities and Ni-Cd battery production facilities in connection with spacecraft power requirements.

APPENDIX

APPENDIX

TABLE A

Surfactant - FC 98(2)
Manufacturer - 3M Company
Type - Anionic Fluorochemical Solid
Solubility - In H_2O 10 gm/1000 gm H_2O
In CH_3OH 40 gm/1000 gm CH_3OH
Decomposition Temperature - 350°C
Surface Tension

Concentration (ppm)	Surface Tension (dynes/cm) In 30% KOH	In H_2O
0	83	72
1	36	-
10	26	60
100	22	46
1000*	22	40

*Surfactant not completely dissolved.

Surfactant - FC 95(3)
Manufacturer - 3M Company
Type - Anionic Fluorochemical Solid
Solubility - In H_2O 2 gm/1000 gm H_2O
In CH_3OH 60 gm/1000 gm CH_3OH
Decomposition Temperature - 390°C
Surface Tension

Concentration (ppm)	Surface Tension (dynes/cm) In 30% KOH	In H_2O
0	83	72
1	72	-
10	26	65
100	24	45
1000*	24	22

* Surfactant not completely dissolved.

APPENDIX
(Contd)

Surfactant - Triton X-100(4)
Manufacturer - Rohm & Haas Company
Type - Nonionic Akylaryl Polyether Alcohol (liquid)
Solubility - In H_2O, completely miscible
Decomposition
Temperature - > 70°C
Surface Tension

Concentration (ppm)	Surface Tension (dynes/cm)
0	72
10	46
100	31
1000	30
10000	30

// EXEC

TABLE B

JPL SEPARATOR EVALUATION =1

NI-CD, SUB-C, SINTERED PLATE, HERMETICALLY SEALED CELLS.

CELLS 1-9 SEPARATOR KENDALL EM476
CELLS 10-16 SEPARATOR PELLON 25/249
CELLS 17-23 SEPARATOR PELLON 14019

TEST NO. 0 CYCLE NO. 1 DATE. 8/18/1967 TEMP. DEGREES C. 22

	CURRENT AMPS	TIME HR(S)	TIME MIN(S)	RATE	LEVEL (P/C)
CHARGE.	0.060	24	0	C/ 0.0	0
DISCHARGE.	1.500, TO 1 VOLT CUT-OFF.			C/ 0.0	

OPEN CIRCUIT STAND TIME. 0 HR(S)., 0 MIN(S).

					CELL VOLTAGE AT VARIOUS DISCHARGE LEVELS											
					25 PER CENT		50 PER CENT		75 PER CENT							
CELL NUMBER	ECV (V)	ECN-R (V)	OCV (V)	OCN-R (V)	T-V (V)	N-R (V)	T-V (V)	N-R (V)	T-V (V)	N-R (V)	ECR MILLI OHMS	EDR MILLI OHMS	ECP PSIA	EDP PSIA	ECC AMP-HRS	EFF
1	1.420	0.0	1.391	0.0	0.0	0.0	1.174	0.0	0.0	0.0	38.64	22.82	0.0	0.0	0.475	0.0
2	1.423	0.0	1.391	0.0	0.0	0.0	1.195	0.0	0.0	0.0	22.41	17.04	0.0	0.0	0.564	0.0
3	1.419	0.0	1.386	0.0	0.0	0.0	1.193	0.0	0.0	0.0	26.50	17.19	0.0	0.0	0.513	0.0
4	1.420	0.0	1.387	0.0	0.0	0.0	1.170	0.0	0.0	0.0	35.77	21.93	0.0	0.0	0.489	0.0
5	1.422	0.0	1.394	0.0	0.0	0.0	1.198	0.0	0.0	0.0	27.12	19.01	0.0	0.0	0.613	0.0
6	1.407	0.0	1.381	0.0	0.0	0.0	1.159	0.0	0.0	0.0	29.70	22.53	0.0	0.0	0.424	0.0
7	1.418	0.0	1.389	0.0	0.0	0.0	1.188	0.0	0.0	0.0	29.35	18.57	0.0	0.0	0.525	0.0
8	1.411	0.0	1.392	0.0	0.0	0.0	1.155	0.0	0.0	0.0	36.84	21.35	0.0	0.0	0.400	0.0
9	1.408	0.0	1.383	0.0	0.0	0.0	1.158	0.0	0.0	0.0	34.66	21.32	0.0	0.0	0.414	0.0
10	1.420	0.0	1.389	0.0	0.0	0.0	1.147	0.0	0.0	0.0	39.98	29.14	0.0	0.0	0.339	0.0
11	1.424	0.0	1.392	0.0	0.0	0.0	1.150	0.0	0.0	0.0	42.97	30.21	0.0	0.0	0.450	0.0
12	1.422	0.0	1.387	0.0	0.0	0.0	1.141	0.0	0.0	0.0	41.32	32.11	0.0	0.0	0.463	0.0
13	1.424	0.0	1.389	0.0	0.0	0.0	1.154	0.0	0.0	0.0	44.26	30.97	0.0	0.0	0.463	0.0
14	1.427	0.0	1.393	0.0	0.0	0.0	1.170	0.0	0.0	0.0	36.86	28.81	0.0	0.0	0.499	0.0
15	1.433	0.0	1.395	0.0	0.0	0.0	1.162	0.0	0.0	0.0	45.25	31.45	0.0	0.0	0.513	0.0
16	1.421	0.0	1.374	0.0	0.0	0.0	1.148	0.0	0.0	0.0	40.48	37.01	0.0	0.0	0.538	0.0
17	1.412	0.0	1.375	0.0	0.0	0.0	1.216	0.0	0.0	0.0	14.76	14.38	0.0	0.0	0.625	0.0
18	1.410	0.0	1.377	0.0	0.0	0.0	1.217	0.0	0.0	0.0	14.35	14.50	0.0	0.0	0.613	0.0
19	1.412	0.0	1.375	0.0	0.0	0.0	1.210	0.0	0.0	0.0	16.10	16.18	0.0	0.0	0.639	0.0
20	1.412	0.0	1.376	0.0	0.0	0.0	1.212	0.0	0.0	0.0	15.44	15.18	0.0	0.0	0.613	0.0
21	1.410	0.0	1.376	0.0	0.0	0.0	[illegible]	0.0	0.0	0.0	14.30	14.67	0.0	0.0	0.600	0.0
22	1.410	0.0	1.374	0.0	0.0	0.0	[illegible]	0.0	0.0	0.0	14.52	15.01	0.0	0.0	0.613	0.0
23	1.420	0.0	1.379	0.0	0.0	0.0	1.219	0.0	0.0	0.0	13.91	13.39	0.0	0.0	0.675	0.0
MEAN	1.418	0.0	[illegible]	0.0	0.0	0.0	1.181	0.0	0.0	0.0	29.37	21.95	0.0	0.0	0.525	0.0
STAND. DEV.	0.007	0.0	[illegible]	0.0	0.0	0.0	0.027	0.0	0.0	0.0	11.16	6.93	0.0	0.0	0.087	0.0

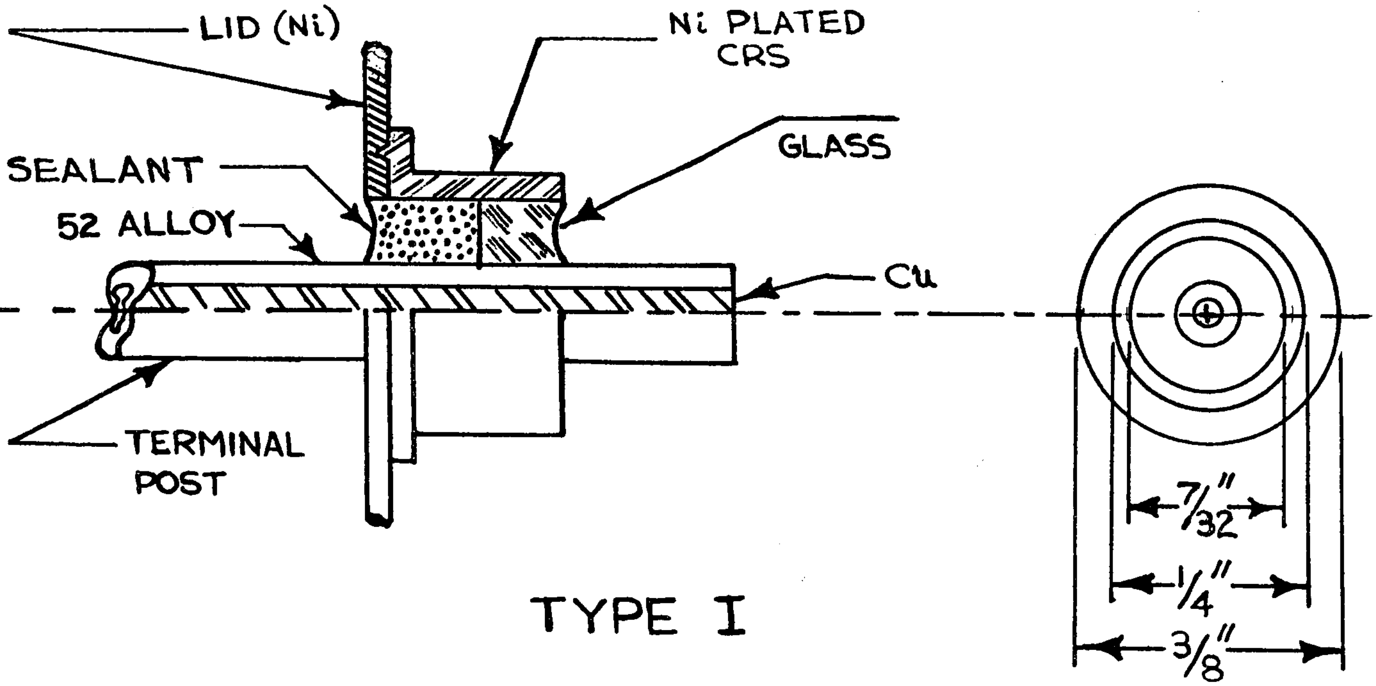
FIGURE 1

KEY

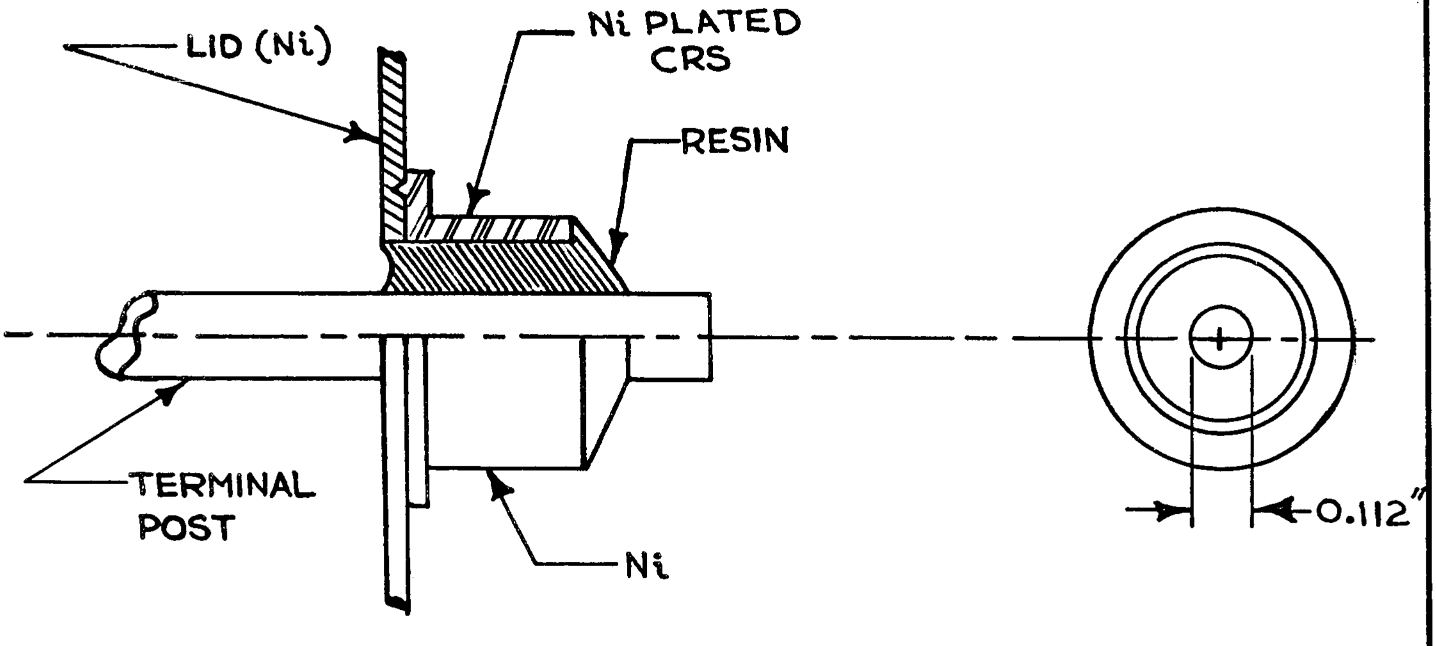
ECV	END OF CHARGE CELL VOLTAGE	
* ECN-R	END OF CHARGE NEG VS. REF	
OCV	OPEN CIRCUIT CELL VOLTAGE	
* OCN-R	OPEN CIRCUIT NEG VS. REF	
T-V	CELL VOLTAGE	AT SPECIFIED DISCHARGE LEVELS
* N-R	NEG VS. REF VOLTAGE	
ECR	END OF CHARGE RESISTANCE	
EDR	END OF DISCHARGE RESISTANCE	
* ECP	END OF CHARGE PRESSURE	
* EDP	END OF DISCHARGE PRESSURE	
ECC	ELECTROCHEMICAL CAPACITY	
* EFF	EFFICIENCY	
* LEVEL		
* RATE CHARGE		
* DISCHARGE		

* NOT APPLICABLE FOR THIS DATA

FIGURE 2



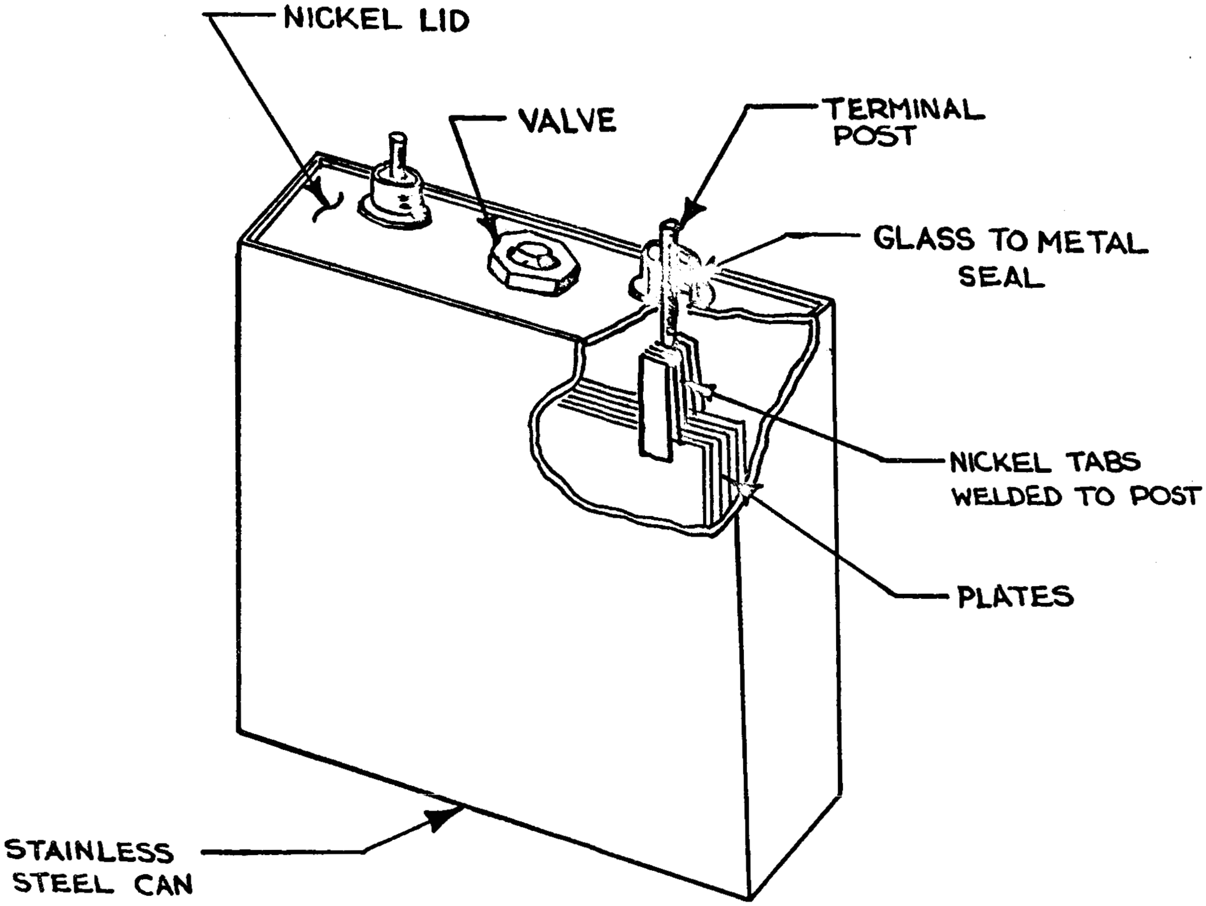
TYPE I



TYPE II

HEAT STERILIZABLE HERMETIC SEAL

FIGURE 3



HEAT STERILIZABLE NICKEL-CADMIUM CELL

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(2) Technical Information Bulletin No. Y-IT98, 3M Company.

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