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INVESTIGATIONS LEADING TO THE DEVELOPMENT OF A PRIMARY ZINC-SILVER OXIDE BATTERY OF IMPROVED PERFORMANCE CHARACTERISTICS

PROGRESS REPORT NO. 11
Contract No. NAS 8-5493
Control Number TP3-83728 (1F)
CPB 13-1600-63
GEORGE C. MARSHALL SPACE FLIGHT CENTER
Huntsville, Alabama

Reporting Period
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THE EAGLE-PICHER COMPANY
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I. PURPOSE

The purpose of this contract is to generate design data making possible the construction of a reliable primary zinc-silver oxide battery of improved activated charge retention characteristics, greater voltage control, high energy density, increased temperature stability, and reduced gassing characteristics.

II. ABSTRACT

Studies conducted under the supervision of the National Aeronautics and Space Administration, Contract NAS 8-5493, have resulted in a primary zinc-silver oxide cell of improved design. Use of silver positive grid results in greater voltage control and increased activated cell life. Design factors for an improved cell design are presented. Reliable activated stand life of four days at 130°F and two weeks at 70°F are indicated..

III. FACTUAL DATA AND DISCUSSION

A. Curve-Fitting by Computer

An attempt has been made to determine an equation describing voltage and capacity responses for cells of varying design characteristics.* The equation is of the type $Y = \mu + a_i + B_1 b + B_2 b^2 + \gamma_1 c + \gamma_2 c^2 + d_j + \delta_1 e + \delta_2 e^2 + K_1 f + K_2{}^2 + g_k + h_e$.(1) The letters b, c, e and f refer to the variable level numbers employed in a certain cell. The terms a_i, d_j, g_k and h_e represent values calculated by computer to represent the effect of levels of the qualitative factors A, D, G and H. The terms μ, B_1, B_2, γ_1, γ_2, δ_1, δ_2, K_1, and K_2 were also determined by computer by the method of least squares.

Values were determined for all terms included in equation (1) to allow description of both capacity and voltage responses for stand periods of two hours, four days, six days, eight days and ten days at a temperature of 130°F. Table No. I reveals values used in calculating voltage responses.

In the experimental series, which yielded data for the determination of equation (1), actual responses were obtained from a maximum of eighteen of the more than five thousand included in the full factorial replicate set. It was anticipated that if effects of the test variables were consistent and included no important interactions, equation (1) might satisfactorily predict responses for any of the five thousand possible cell designs. This has proved to be impractical, however. For instance, after a stand period of eight days at 130°F, Cell Nos. 19 and 25 were internally shorted. Therefore, terms of the least squares equation were determined from sixteen, rather than eighteen responses. Table No. II

*See Progress Report No. 10, pp 12 and 13, NAS 8-5493 for a presentation of the construction variables associated with this series of experimental cells.

contains comparative data whereby the response deterioration characteristics were used to estimate closely responses which Cell Nos. 19 and 25 might have exhibited, had they not suffered premature electrical failure. Responses were also calculated by means of equaticn (1).

TABLE NO. I

Values Used in Calculating Voltage Response
By Use of Least Squares Equation (1)

TERM	2 Hr.	4 Days	6 Days	8 Days	10 Days
μ	91.103	76.866	84.841	72.325	80.733
a_o	-0.916	-5.975	-0.284	-5.770	-4.333
a_1	1.758	3.325	-1.598	5.209	3.000
a_2	0.577	5.958	-0.760	3.997	1.060
a_3	-1.419	-3.308	2.639	-3.437	0.267
B_1	0.187	-7.083	-1.202	-6.231	3.816
B_2	-0.477	1.983	-0.416	0.499	-3.116
γ_1	2.340	5.550	4.243	11.183	8.433
γ_2	-0.929	0.649	-1.846	-2.008	-3.766
d_o	-2.069	-4.649	-2.221	-0.685	-2.483
d_1	2.069	4.649	2.221	0.685	2.483
δ_1	-0.342	-2.350	5.327	-5.097	0.333
δ_2	-0.262	1.283	-2.510	3.289	-0.800
K_1	3.869	18.499	-5.852	15.088	2.383
K_2	-1.360	-7.633	3.259	-5.463	-0.083
g_o	0.331	2.200	1.343	2.779	-1.179
g_1	-0.562	-0.233	-2.090	-3.163	1.089
g_2	0.232	-1.966	0.747	0.384	0.090
h_1	-0.005	-0.099	0.368	0.079	0.084
h_2	0.005	0.0099	-0.368	-0.079	-0.084

TABLE NO. II

RESPONSES (voltage**)

Cell No.	2 Hr.	4 Da.	6 Da.	8 Da.	10 Da.
2	96.0	86.0	85.3	84.0	84.0
3	88.7	78.7	81.3	73.3	76.0
4	92.7	86.0	85.0*	84.0	84.7
6	94.7	89.3	86.0	80.7	82.7
7	96.0	92.0	88.0	85.3	88.7
8	90.7	79.3	82.0	78.7	83.3
10	96.0	92.0	92.0	88.0	89.3
12	90.7	76.0	76.0	74.0	79.3
13	90.7	84.7	85.3	82.0	86.0
14	94.7	95.3	92.0	89.3	89.3
17	87.3	77.3	82.0	73.3	82.0
18	93.3	85.3	85.3	74.7	77.3
19	90.7	88.0*	84.0	80.0*	77.3
20	91.3	84.0*	81.3	77.3	82.0
23	92.0	80.7	85.3	80.0	82.7
24	89.3	76.0	80.7	75.3	79.3
25	92.0	84.7	86.7	84.0*	82.0*
27	90.7	79.3	79.3	76.3	75.0*

*Responses for these cells (which failed to deliver usable capacity) were estimated from the response pattern.

**These responses are obtained by dividing the cell discharge voltage after 15 seconds by 1.50 volts. This artificial response facilitates handling of data.

These calculated responses are indicated by the points falling away from the response curves in Figure Nos. 1 and 2.

It is indicated that there may be interactions between several of the cell variables, since the effect of including a specific design factor is not predictably constant among a large number of cell design combinations. Such interactions would require a larger orthogonal fractional replicate test group for complete evaluation.

Data in Figure Nos. 1 and 2 also re-emphasize another basic fact. Direct comparison of data disclosed by these figures reveals that several cells representing maxima on the capacity response pattern correspond to minima on the voltage response pattern. Slopes of corresponding straight line segments represented by the two figures are frequently of opposite algebraic sign. This again confirms that common measures taken to improve capacity retention are deleterious to voltage control, and vice versa. This is a graphic indication of the difficulty encountered in producing an optimum "general purpose" cell design.

At the present state-of-the-art, it appears that it is impossible to incorporate maximum capacity retention and maximum voltage regulation in a single cell design.

Data of Figure Nos. 1 and 2 do, however, indicate that Cell Nos. 10 and 14, following eight days stand at 130 F, exhibit the greatest voltage responses, while their capacity responses are also well above the overall mean. Many features of these cell designs have been included in the design of the preprototype and prototype cells.

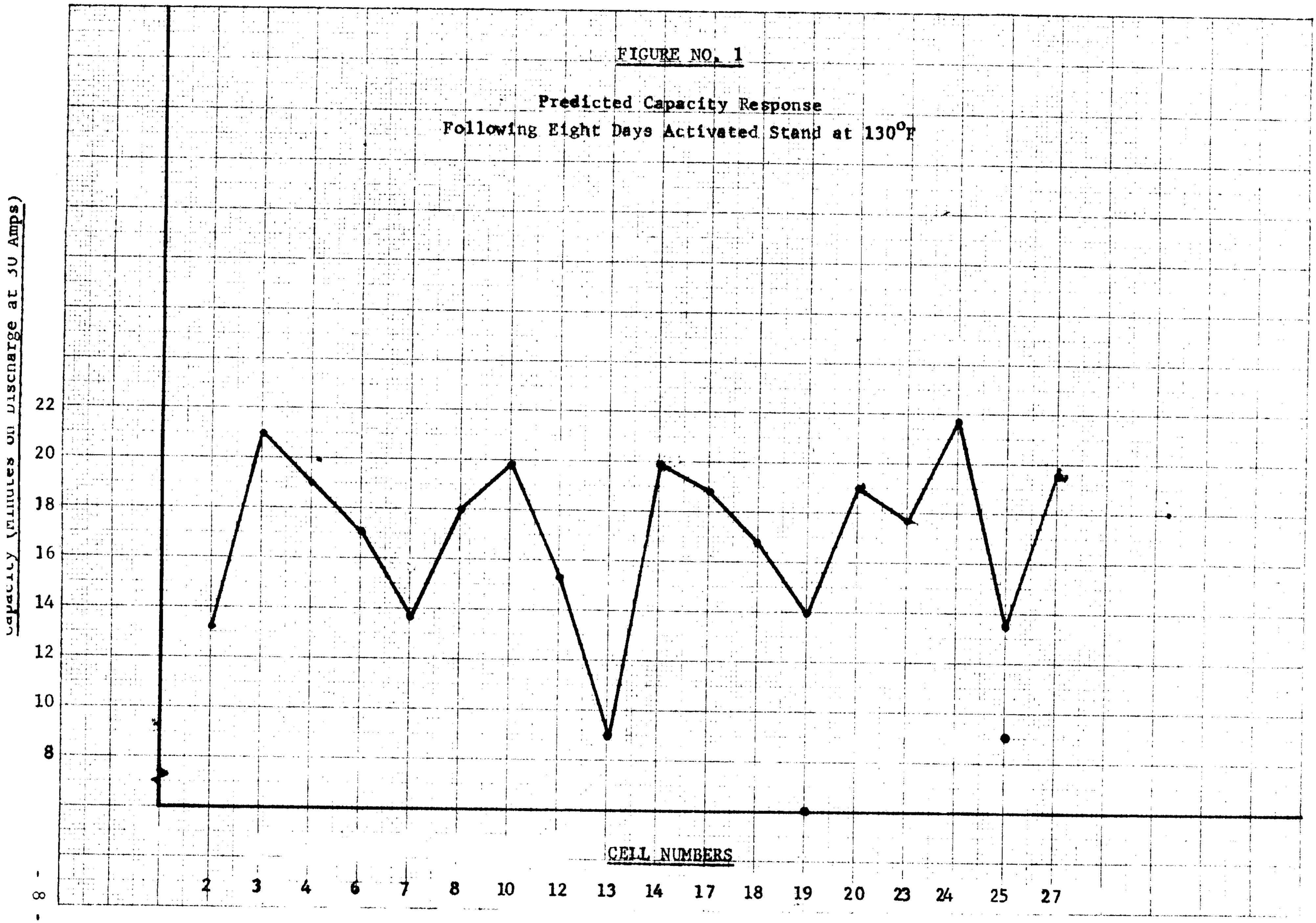
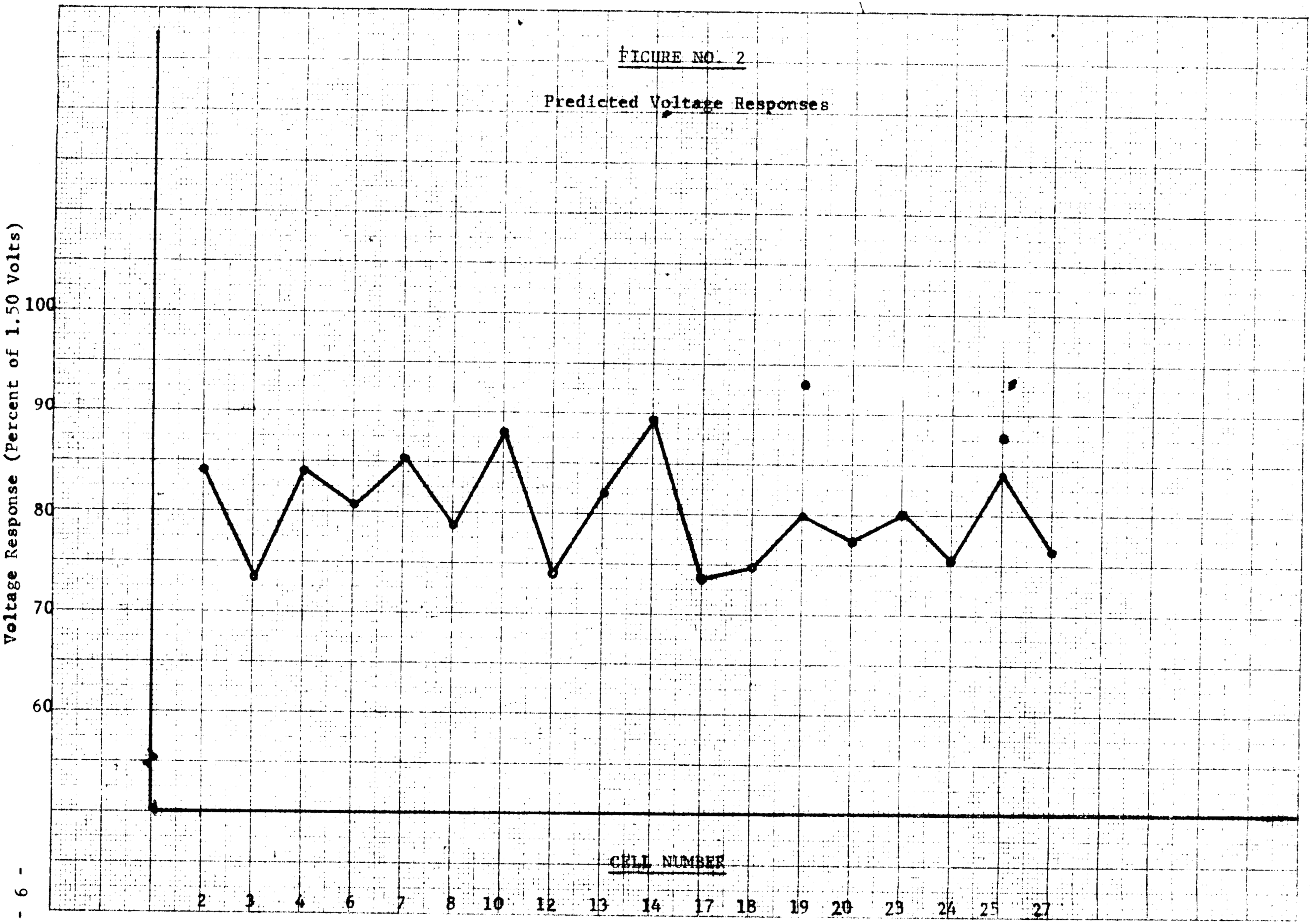


FIGURE NO. 1

Predicted Capacity Response
Following Eight Days Activated Stand at 130°F

FIGURE NO. 2

Predicted Voltage Responses



B. Preprototype and Prototype Cell Design

Prototype cells of improved design have been discharged at room temperature following stand periods, at +130°F, of three, five, seven, eleven and seventeen days. In addition, open circuit voltages of all cells were monitored and recorded daily while on stand at elevated temperatures. These voltages are displayed by Table Nos. III and IV. Certain cells were constructed with silver positive grid metal, while in others the active material was deposited nickel grid material. Discharge characteristics for cells on stand test are displayed by Figure Nos. 4 through 8. Data in Figure No. 3 reveals a significant variance between open-circuit voltage, retention-of-charge characteristics of the two experimental series of cells. Those cells having silver positive grid metal maintained higher open-circuit voltage. In addition, following seventeen days activated stand, none of the remaining five cells, having nickel positive grid, yielded useable capacity, while all cells having silver positive grid yielded only slightly decreased voltage. Increased open-circuit voltage exhibited by cells having silver positive grid metal is apparently reflected in the initial voltage during the first few minutes on discharge. Cells employing nickel positive grids display slightly greater ampere-hour efficiency initially. However, capacities of the two cell types converge with increased activated stand periods and cells employing nickel positive grid metal were first to suffer total failure, as disclosed by an inability to deliver capacity. Further studies would be necessary to determine which of the many commercial silver grid products may be most economically used without sacrificing cell voltage control during high rate discharges.

TABLE NO. III

OPEN-CIRCUIT VOLTAGES ON STAND
Preprototype Cell
Silver Positive Grid

Cell No.	DAYS ON STAND 3	4	5	6	7	10	12	17
2	1.85							
3	1.85	1.84						
4	1.85	1.84	1.84					
5	1.85	1.84	1.84					
6	1.85	1.84	1.84	1.84	1.84	1.84	1.83	
7	1.84	1.84	1.84	1.84	1.84	1.84	1.84	
8	1.84	1.84	1.84	1.84	1.84	1.84	1.84	1.83
9	1.85	1.84	1.84	1.84	1.84	1.84	1.84	1.68
10	1.85	1.84	1.84	1.84	1.84	1.84	1.84	1.74
11	1.85	1.84	1.84	1.84	1.84	1.84	1.78	1.82
Mean	1.85	1.84	1.84	1.84	1.84	1.84	1.83	1.77

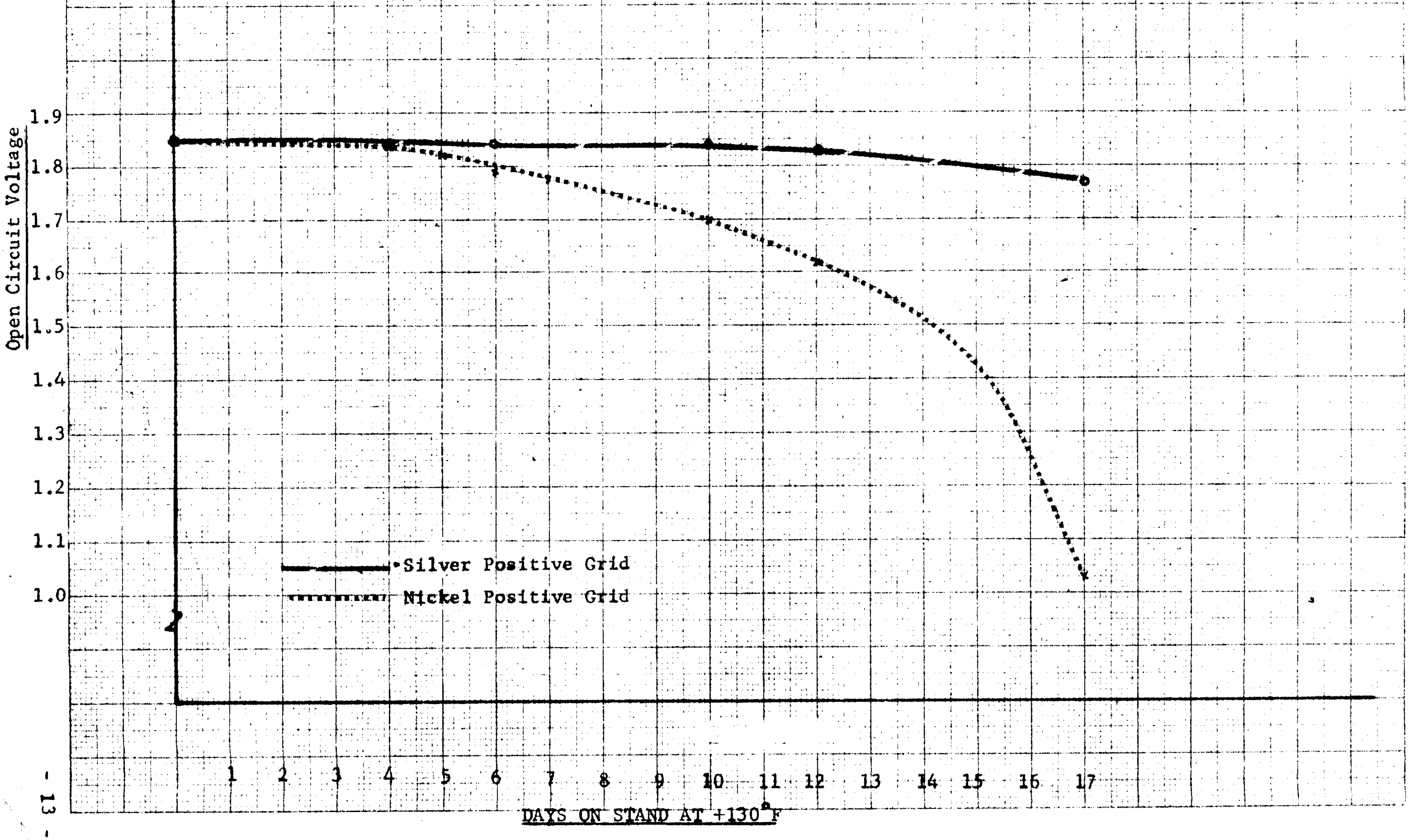
TABLE NO. IV

OPEN-CIRCUIT VOLTAGES ON STAND
PREPROTOTYPE CELL
NICKEL POSITIVE GRID

	DAYS ON STAND							
Cell No.	3	4	5	6	7	10	12	17
12	1.85							
13	1.85	1.85	1.84					
14	1.85	1.84	1.81	1.81	1.81			
15	1.84	1.82	1.80	1.80	1.80			
16	1.85	1.84	1.83	1.83	1.82	1.72	1.69	
17	1.84	1.84	1.81	1.81	1.81	1.74	1.65	
18	1.85	1.84	1.84	1.84	1.82	1.67	1.58	0.22
19	1.85	1.84	1.84	1.84	1.83	1.72	1.58	0.22
20	1.85	1.84	1.81	1.81	1.81	1.74	1.61	1.56
21	1.84	1.84	1.82	1.82	1.81	1.73	1.67	1.56
22	1.84	1.84	1.84	1.58	1.58	1.58	1.58	1.56
Mean	<1.85	1.84	1.82	>1.79	>1.78	1.70	1.62	1.03

FIGURE NO. 3

Open-Circuit Voltage Retention at 130°F
(Silver vs Nickel Positive Grid Metal)



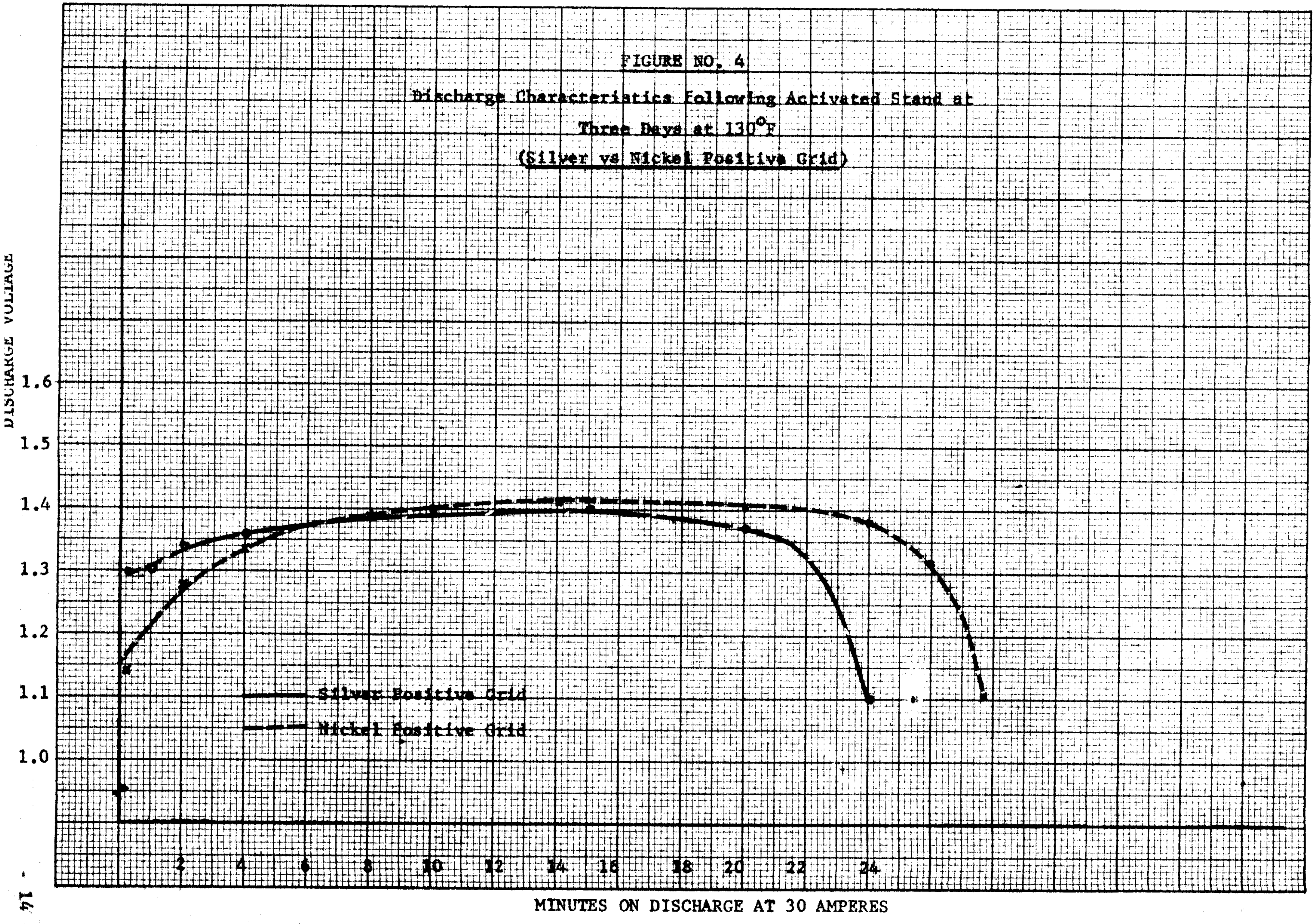


FIGURE NO. 4
Discharge Characteristics Following Activated Stand at
Three Days at 130°F
(Silver vs Nickel Positive Grid)
DISCHARGE VOLTAGE
1.6
1.5
1.4
1.3
1.2
1.1
1.0
Silver Positive Grid
Nickel Positive Grid
2
4
6
8
10
12
14
16
18
20
22
24
MINUTES ON DISCHARGE AT 30 AMPERES

were observed to have failed after a stand period of four days at +130°F. It is indicated that individual cells may be expected to perform reliably after a minimum of four days stand at +130°F. An activated life of two weeks appears obtainable at a stand temperature of 75°F. These improvements in overall cell performance result from changes in cell design and manufacturing processes as well as greater quality assurance measures. That is, the activated stand life of a primary cell has been significantly increased at no appreciable loss in energy density.

IV. SUMMARY

A. Phases of study, as outlined in the Master Schedule, are essentially complete. These studies were accomplished either directly, as in separator evaluations, or indirectly in a fractional factorial experimental series dealing with capacity retention and voltage regulation.

B. Under controlled conditions, individual cells may be expected to perform reliably following four days activated stand at 130°F or two weeks at 70°F. This represents an estimated minimum which might be increased as a result of detailed reliability studies. This increased reliable activated life results from experimental studies which yielded an improved cell design, as well as from continual improvement in the area of quality assurance as related to production procedures.

C. Studies to date indicate that very small fractional replicates may not be adequate to provide data needed to accurately predict responses for an extremely large number of individual cell designs. This apparently arises in part from interactions among design factors. For complete evaluation, these interactions could best be determined by a large fractional replicate or by several full factorials involving only a few carefully selected variables. Careful consideration will be given to this phase in outlining a master program in the extension of this work.

D. Use of silver positive grid metal and carefully prepared positive and negative active materials results in greater retention of open-circuit voltage as well as improved discharge voltage characteristics.

V. PROGRAM FOR THE NEXT INTERVAL

During the twelth contract month, extensive preparation will be directed toward the planning of enlarged studies to be conducted under the Modification to Contract No. NAS 8-5493. This will include reviews of patents, progress reports and other technical literature, as well as scheduling the various phases of study. All work, both fundamental and applied, will be directed towards improvement of performance characteristics of the primary zinc-silver oxide system, with emphasis on retention of capacity, voltage control, and high rate capabilities throughout long periods of activated stand. The statistical approach of investigation will be employed wherever applicable. Each of the two coming contract months will be shortened by the two-week plant vacation shut-down.

VI. PERSONNEL

The following totals of man-hours have been expended during the contract period:

Engineering	- 1500
Technical	- 2403
TOTAL	- 3903

A P P E N D I X

MASTER SCHEDULE

1 July 1963
P.O. DATE

PROGRAM PRIMARY ZINC-SILVER OXIDE BATTERY
CONTRACT NAS 8-5493
REFERENCE FA-242

PREPARED Bill R. Hawkins
APPROVED [illegible]
APPROVED [illegible]
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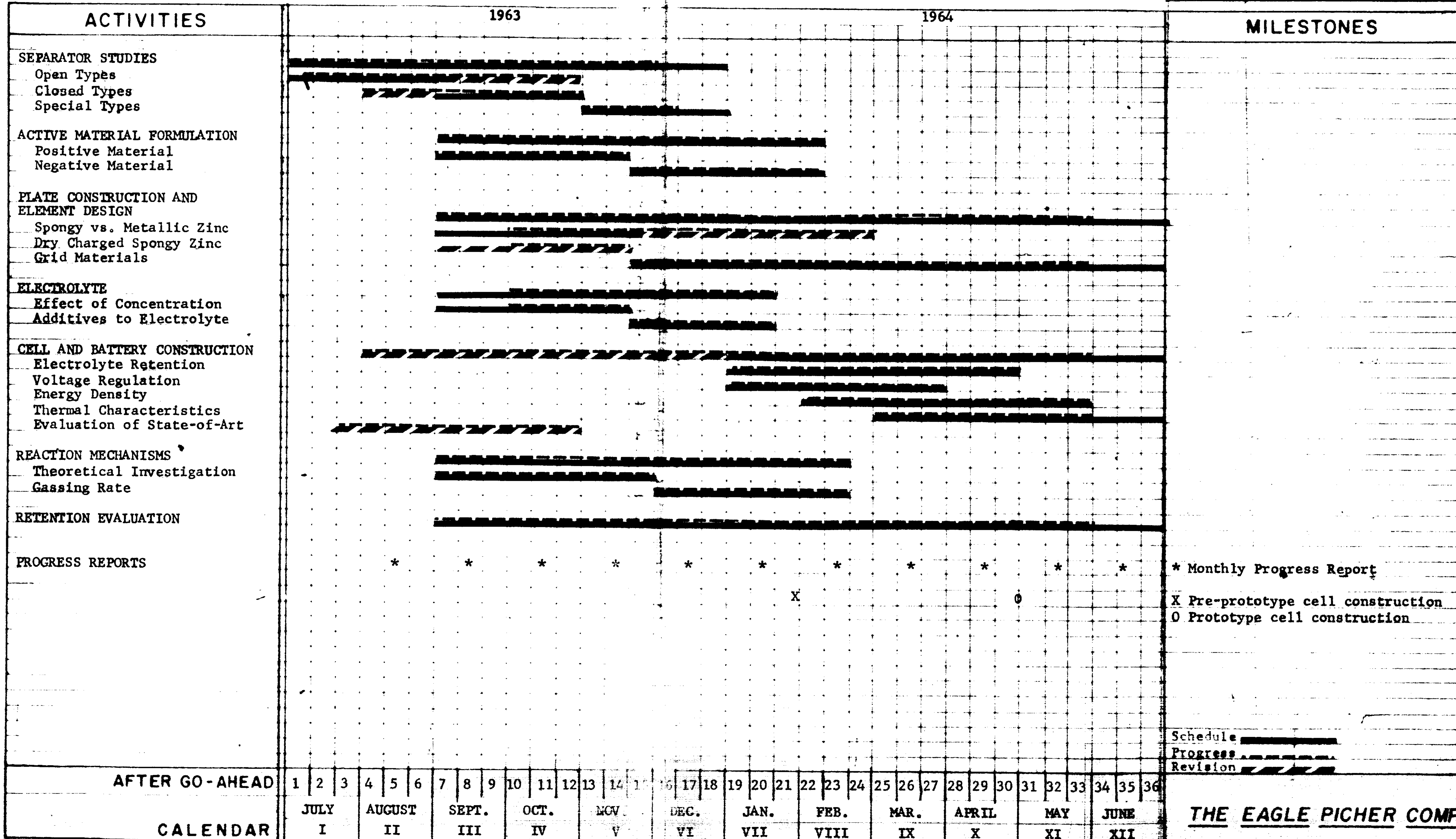

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