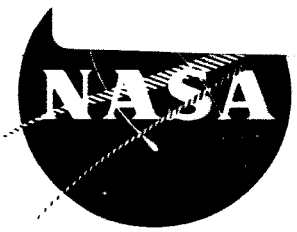

NASA CR-72084

FINAL REPORT

DEVELOPMENT OF IMPROVED CADMIUM ELECTRODES FOR SEALED SECONDARY BATTERIES

by

H. H. Kroger

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

17 August 1966

CONTRACT NAS 3-7636

NASA Lewis Research Center
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Mr. William A. Robertson

GENERAL ELECTRIC

Battery Business Section
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ABSTRACT

PHASE I of the program was extended to compare the electrochemical behavior of selected experimental fiber plaque materials with those of currently available nickel powder sinter plaques.

Specifically, the previously observed loss of active materials from the plaques was investigated as a function of plaque loading, depth of discharge, charge and discharge rates and separator designs, respectively.

No indications could be detected that the new experimental material plaques constitute a better material for the negative electrode of the nickel cadmium couple than the control material.

Consequently, it was recommended not to pursue this matter any further.

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1.0 SUMMARY

This second interim and final report contains the results of an extension of the first phase of a program planned to investigate the applicability of nickel fiber plaques for support of the negative electrode of the nickel cadmium couple.

Based upon the findings of our recent INTERIM REPORT #1, NASA CR-54,397, the number of different experimental materials was reduced from five to two. These were processed and tested simultaneously with General Electric control material.

The impregnation was conducted towards two different levels of plaque loading with active material, namely at four and eight complete impregnation cycles, respectively. During this process, the gains in weight obtained were closely monitored.

The subsequent electrochemical cleaning process and the aerospace formation were followed by a capacity test period of slightly longer than four weeks duration. In this time, 68 charge-discharge cycles at a depth of discharge of 120 percent and 93 cycles at a depth of 50 percent, respectively, were accomplished. In either depth of discharge group, two different separator designs were employed.

Under all combinations of test conditions applied, all electrodes lost active material. However, the losses encountered by the experimental materials were consistently greater by almost a factor of two than those of the control material electrodes under comparable conditions. An influence of the separator design on the magnitude of losses could only be detected in case of the lower depth of discharge of 50 percent.

As mentioned in the previous report, the reason for the unfavorably greater losses of the experimental plaques can be found in their considerably greater mean pore sizes.

In general, the tests conducted have shown that even the two specially selected experimental plaque materials, they were the better performers during the tests of PHASE I, are inferior to the currently available control materials. We have therefore recommended not to enter into PHASES II and III of the contract.

2.0 INTRODUCTION

2.1 General

The objectives of the extension of PHASE I of "Development of Improved Cadmium Electrodes for Sealed Secondary Batteries" were:

1. Impregnate selected experimental plaque materials at two levels of plaque loading and submit to a capacity testing under a variety of test conditions,
2. Investigate the influence of different separator materials and designs on the retention of the active material in the pores of the electrodes,
3. Compare the performance of the experimental plaques with a General Electric control material sample,
4. Make recommendations whether and under what circumstances the initially planned program should continue into its PHASES II and III.

2.2 Materials Studied

The experimental material was received from the Huyck Metals Company and originally consisted of five different items, namely:

ITEMS	HUYCK-DESIGNATION		TEST-DESIGNATION
1	AX1	10%	1-10
2	AX1,modified	10%	M-10
3	AX2	10% dense	2-10
4	AX1	20%	1-20
5	AX1,modified	20%	M-20

However, based upon the pertinent results of PHASE I, only the items 4 and 5, respectively, were found to have any potential at all for an application as negative battery electrodes.

Twenty-four so-called triple plaques (T.P.) of each of the two items were used in the extension of PHASE I. They were taken from the 36 T.P. being reserved for the remaining PHASES II and III of the program.

As control plaques, 24 General Electric triple plaques of the VO negative type were used.

2.3 Technical Meeting

During the extension of PHASE I, one technical meeting was held with Mr. W. A. Robertson of NASA-Lewis Research Center at Gainesville, Florida, on 6 July 1966.

Principal General Electric personnel attending were Drs. R. L. Hadley, D. L. Barney, and H. H. Kroger.

3.0 PHYSICAL PROPERTIES

3.1 General

For a description of the methods applied in determining the physical properties of the materials used in this part of the program we refer to the pertinent sections of our INTERIM REPORT #1, NASA CR-54, 395, pages 5 through 22.

4.0 IMPREGNATION AND ELECTROCHEMICAL CLEANING

4.1 General

As has been shown in our previous report, a continuation of the impregnation procedure beyond seven to eight impregnation cycles yielded only relatively small incremental gains both in weight and plate capacity.

Consequently, one half of all the plaques used for the present task received a maximum of eight impregnation cycles and were designated as heavily loaded (Program Code Letter: H), while the remaining half received only four impregnation cycles and was designated as lightly loaded (Program Code Letter: L).

A description of the pre-impregnation processing steps such as "Coining, Coding and Compressing" and of the plaque holder design employed can be found in our INTERIM REPORT #1, NASA CR-54,395, pages 23 through 25.

The sequence of plaques within said plaque holders was always the same and such that two General Electric control plaques occupied the outward positions. Thus, a safety feature against damages to the mechanically less stable experimental plaques was provided. Advanced test had shown that the gain in weight of a particular plaque was not related to its relative position in a holder.

4.2 Impregnation Procedure

As already outlined in our previous report, it was necessary to impregnate the plaques in the laboratory. However, a strict adherence to the factory processing conditions was observed.

In addition to the procedure reported, this time the weight of each plaque holder was determined and recorded after each completed impregnation cycle. Despite the fact that the six plaques per holder consisted of two plaques of each kind of material, the averaged gains in weight observed were a valuable means for monitoring the efficiency and completeness of the impregnation process.

It should be mentioned here that the experimental materials again became stiff and brittle in the initial portions of the process. First signs of this behavior appeared after the very first drying operation and the maximum state was reached after not more than three complete cycles. The materials then became so stiff that touching them with a nickel spatula produced a distinct metallic sound. In this state the experimental plates are prone to breakage.

4.3 Electrochemical Cleaning

The objectives of the electrochemical cleaning procedure have already been dealt with in our previous report. It might be mentioned here that the usual intensive brushing of the plates was replaced by a softer one in order to avoid possible damages to the experimental materials. To give all the plaques equal starting conditions, the brushing of the General Electric control plates was also restricted.

During the course of the electrochemical cleaning operation the holder assemblies encountered losses in weight which amounted from 0.5 to 1.0 grams per plate.

And again, it was observed that, at least partially, the initial flexibility of the experimental plates was restored.

4.4 Results

The impregnation procedure was conducted without any difficulties and all three materials developed only traces of external scaling. This was another reason to permit a less intensive brushing of the plates at the beginning of the electrochemical cleaning procedure.

The accumulated gains in weight were determined for each holder after each completed impregnation cycle. These numbers are given in Table 1 together with average values for holders and plates.

In Figure 1, the average values for the plates are plotted versus the number of impregnation cycles achieved. The first four points represent the average for all 72 plates which received at least four impregnation cycles. The points from five through eight cycles constitute the average of 36 plates processed to a higher level of plate loading.

The course of the curve is typical for the impregnation process and the absence of any break in its steadiness indicates that the process was conducted properly.

To indicate the uniformity of the plaque materials with respect to impregnation and cleaning procedures, in Table 2 the individually obtained gains in weight are given as observed after the electrochemical cleaning.

As can be seen, a treatment of the data for the plates as two groups only is warranted for the purpose of calculating the appropriate currents for the following sections of the program.

4.5 Conclusions

The following conclusions pertaining to this part fo the program can be drawn:

TABLE 1

ACCUMULATED GAINS IN WEIGHT (GRAMS) PER HOLDER ASSEMBLY OF 6 PLAQUES

(TWO PLAQUES OF EACH KIND; BEFORE ELECTROCHEMICAL CLEANING)

HOLDER	IMPREGNATION CYCLE							
	1	2	3	4	5	6	7	8
1	16.1	29.7	42.0	52.2	60.6	67.0	72.4	77.5
2	17.3	31.6	43.8	54.4	62.8	70.2	75.8	80.8
3	16.3	31.0	43.9	54.8	63.0	70.0	75.6	80.5
4	15.7	30.1	42.8	53.2	61.2	68.8	74.6	80.1
5	16.7	31.0	43.7	54.1	62.3	69.6	75.3	80.1
6	16.6	30.9	43.4	53.1	61.1	68.1	73.4	77.5
7	17.0	31.2	43.3	52.9	----	----	----	----
8	16.9	30.6	42.9	52.2	----	----	----	----
9	17.8	32.6	44.5	54.1	----	----	----	----
10	17.8	31.6	43.2	52.5	----	----	----	----
11	17.4	31.4	43.3	52.9	----	----	----	----
12	17.2	31.2	42.8	52.2	----	----	----	----
Average/ Holder	16.9	31.1	43.3	53.2	61.7	69.0	74.5	79.4
Average/ Plaque	2.82	5.18	7.22	8.87	10.29	11.50	12.42	13.24

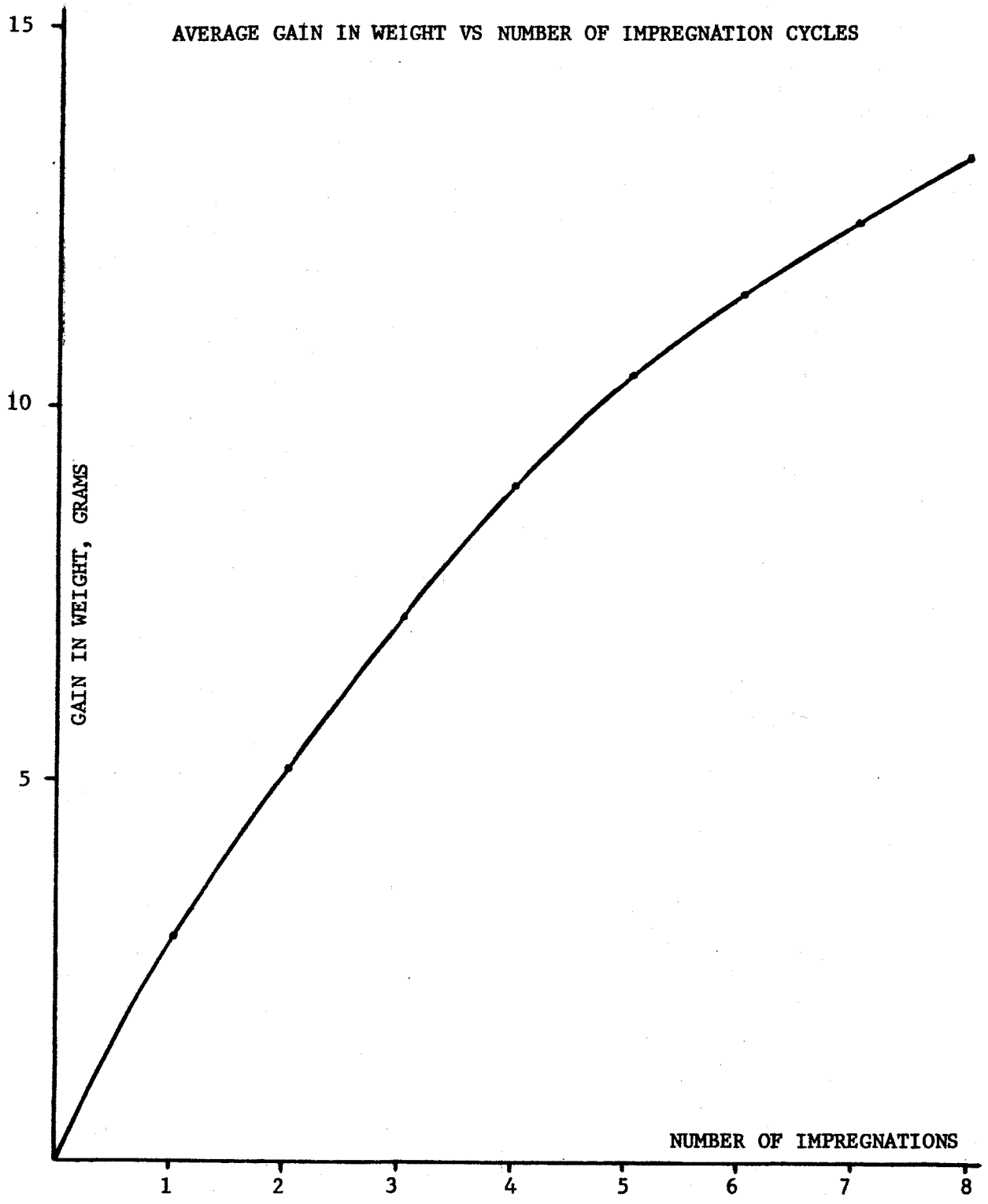
AVERAGE GAIN IN WEIGHT VS NUMBER OF IMPREGNATION CYCLES
15
10
5
GAIN IN WEIGHT, GRAMS
NUMBER OF IMPREGNATIONS
1
2
3
4
5
6
7
8

FIGURE 1

TABLE 2

FINAL GAINS IN WEIGHT OF INDIVIDUAL PLATES (GRAMS) AFTER ELECTROCHEMICAL CLEANING

PLATE NUMBER	1-20	M-20	CONTROL
1. 8 IMPREGNATIONS			
1	12.28	11.67	11.10
2	12.66	12.12	11.72
3	13.12	12.01	12.55
4	13.15	11.80	11.86
5	13.42	13.07	11.71
6	12.80	12.60	11.45
7	12.73	11.61	11.97
8	12.66	12.58	12.43
9	12.50	12.36	12.34
10	12.63	11.86	12.04
11	11.75	12.01	11.80
12	12.16	12.90	12.12
Average	12.66	12.22	11.92
Grand Average		12.27	
2. 4 IMPREGNATIONS			
13	8.42	8.24	8.33
14	8.72	8.34	8.26
15	8.74	8.04	8.14
16	8.69	8.07	8.33
17	8.63	8.53	8.29
18	8.82	8.44	7.93
19	8.40	8.11	8.20
20	8.48	8.19	8.23
21	8.51	8.24	8.27
22	8.70	8.12	8.35
23	8.68	8.04	8.47
24	8.64	7.82	8.02
Average	8.62	8.27	8.24
Grand Average		8.38	

1. The two experimental plaque materials again developed an extreme and permanent stiffness during the first impregnation cycles. The resulting brittleness made the handling of the plaques rather difficult and it took great care to avoid breakage.

2. As before, the electrochemical cleaning process partially restored the initial flexibility of the experimental materials.

3. Contrary to the respective findings of INTERIM REPORT #1, no differences in the impregnation behavior between the experimental and control materials could be detected. This is probably due to the fact that larger size samples have been used in obtaining the points of Figure 1.

4. Hence, the gains in weight observed for the different plaque materials differ only with respect to the number of impregnation cycles achieved.

5. The first four impregnation cycles resulted in an average of accumulated gains in weight of about nine grams. Four more cycles, i.e. an identical amount of labor, costs and time, yielded a further increase of only four and a half grams. Therefore, eight impregnation cycles can be considered to be the upper limit of economical feasibility.

5.0 AEROSPACE FORMATION

5.1 General

Upon completion of the impregnation and electrochemical cleaning sections, the plates were submitted to a special treatment referred to as Aerospace Formation Process.

Essentially, this treatment is an extended electrochemical cleaning performed as a batch process. The objectives of this process are:

1. To continue the cleaning of the active material,
2. To continue the formation of the active material,
3. To characterize the plate material for comparison with design requirements.

Specifically, the third point was of great importance for this program inasmuch as the initial calculation of charge and discharge rates heavily relies upon the capacity values obtained during this processing step.

5.2 Procedure

For a detailed description of the pertinent steps we refer to our INTERIM REPORT #1, NASA CR-54,395, pages 37 through 40.

5.3 Results

In Table 3, the results of the Aerospace Formation are given. The meaning of the column of the table and Table 4, respectively, is from left to right:

1. Electrode number
2. Theoretical capacity in A-hrs based upon the gains in weight in grams after the electrochemical cleaning and employing a conversion factor of .366.

TABLE 3

RESULTS OF AEROSPACE FORMATION PROCESS, PART ONE:

EXPERIMENTAL MATERIAL AX1 20 PERCENT DENSE = 1-20

ELECTRODE	THEORETICAL CAPACITY	UTILIZATION FACTORS FIRST DISCHARGE	SECOND DISCHARGE	THEORETICAL CAPACITY CORRECTED
1	4.490	82	73	4.320
2	4.630	79	74	4.490
3	4.800	23*	81	4.710
4	4.810	24*	81	4.620
5	4.910	79	73	4.510
6	4.680	82	74	4.450
7	4.660	81	73	4.520
8	4.630	80	73	4.450
9	4.580	81	74	4.390
10	4.620	80	73	4.390
11	4.300	82	74	4.130
12	4.450	80	73	4.270
Average	4.630	81	73	4.440
13	3.090	87	82	2.990
14	3.190	87	81	3.100
15	3.200	86	82	3.100
16	3.180	84	81	3.090
17	3.160	87	83	3.100
18	3.230	86	84	3.130
19	3.070	89	85	3.010
20	3.100	89	84	3.040
21	3.110	89	85	3.050
22	3.180	87	83	3.050
23	3.180	87	83	3.080
24	3.160	86	82	3.100
Average	3.150	87	83	3.070

* Not fully charged

TABLE 3

RESULTS OF AEROSPACE FORMATION PROCESS, PART TWO:

EXPERIMENTAL MATERIAL AX1-MODIFIED 20 PERCENT DENSE = M-20

ELECTRODE	THEORETICAL CAPACITY	UTILIZATION FACTORS FIRST DISCHARGE	SECOND DISCHARGE	THEORETICAL CAPACITY CORRECTED
1	4.270	82	64	4.100
2	4.440	80	75	4.300
3	4.440	82	73	4.220
4	4.320	82	73	4.100
5	4.780	81	73	4.540
6	4.610	82	74	4.420
7	4.250	83	75	4.120
8	4.600	70	62	4.470
9	4.520	71	71	4.210
10	4.340	83	73	4.170
11	4.400	82	75	4.260
12	4.720	39*	67	4.630
Average	4.470	80	71	4.300
13	3.020	90	82	2.920
14	3.050	89	81	2.990
15	2.940	90	81	2.830
16	2.950	94	87	2.900
17	3.120	87	82	3.030
18	3.090	87	83	3.000
19	2.970	90	84	2.910
20	3.000	89	83	2.940
21	3.020	90	82	2.920
22	2.970	91	84	2.880
23	2.940	90	82	2.880
24	2.860	93	82	2.800
Average	2.990	90	83	2.920

* Not fully charged

TABLE 3

RESULTS OF AEROSPACE FORMATION PROCESS, PART THREE:

CONTROL MATERIAL, GENERAL ELECTRIC VO NEGATIVE

ELECTRODE	THEORETICAL CAPACITY	UTILIZATION FACTORS FIRST DISCHARGE	SECOND DISCHARGE	THEORETICAL CAPACITY CORRECTED
1	4.060	84	75	4.020
2	4.290	83	77	4.270
3	4.590	78	74	4.500
4	4.340	82	73	4.300
5	4.290	84	76	4.240
6	4.190	84	74	4.150
7	4.380	84	75	4.340
8	4.550	85	74	4.500
9	4.520	85	76	4.420
10	4.410	85	78	4.360
11	4.320	86	79	4.320
12	4.440	--**	--**	4.420
Average	4.370	84	76	4.320
13	3.050	90	86	3.050
14	3.020	90	85	3.020
15	3.000	89	83	3.000
16	3.050	89	84	3.050
17	3.030	91	87	3.030
18	2.900	92	86	2.900
19	3.000	90	86	3.000
20	3.010	91	87	3.010
21	3.030	89	85	3.030
22	3.060	89	84	3.060
23	3.100	88	85	3.100
24	2.940	90	85	2.940
Average	3.020	90	85	3.020

** Cycled only, no potential monitoring

TABLE 4

RESULTS OF AEROSPACE FORMATION PROCESS:

COMPARISON OF AVERAGE VALUES

TYPE	THEORETICAL CAPACITY	UTILIZATION FACTORS FIRST DISCHARGE	SECOND DISCHARGE	THEORETICAL CAPACITY CORRECTED
HIGH-LOADING				
1-20	4.630	81	73	4.440
M-20	4.470	80	71	4.300
CONTROL	4.370	84	76	4.320
LIGHT-LOADING				
1-20	3.150	87	83	3.070
M-20	2.990	90	83	2.920
CONTROL	3.020	90	85	3.020

3. Utilization factor of the active material in percent, i.e. the ratio of capacity actually obtained to theoretical capacity, for the first formation cycle discharge.

4. Utilization factor in percent for the second formation cycle discharge.

5. Final theoretical capacity considering the respective losses of active material during the course of the formation process.

In Table 4, the average values of Table 3 have been compiled in order to facilitate comparisons and conclusions.

5.4 Conclusions

An evaluation of these data reveals:

1. Regardless of plate material and plate loading, the first formation cycle yielded better utilization factors than the second.

2. The decline in utilization is slightly less for the lighter loaded plates. This is in agreement with previous findings.

3. Regardless of the plate material, the lighter loaded plates exhibited a significantly better utilization than the higher loaded ones.

4. With the exception of the lighter loaded control plates, the plates encountered further, but slight losses of active material during the course of the formation process. This in turn resulted in an even more pronounced equalization of their theoretical capacities.

6.0 CAPACITY TESTING

6.1 General

The objective of this part of the program was to investigate the influence of repetitive cycling on the processed plaque materials under a variety of test conditions.

In addition to the already mentioned differences in plate loading, i.e. the two levels represented by the code letter H and L, respectively, we now have to introduce

1. Two different separator designs, namely:
   a. a single layer of non-woven nylon with a nominal thickness of 0.023 cm or 0.008 inch, respectively, (This separator received the code letter N)
   b. a three-layer composite consisting of woven nylon/cellophane/woven nylon with thicknesses of 0.0076/0.0051/0.0076 cm or 0.003/0.002/0.003 inch, respectively. (This separator design received the code letter C)

Both separator designs were of a bag type, i.e. they were sealed at three of their edges. They were used in lieu of the corrugated perforated PVC separators which are common use in the Aerospace Formation Process and which were also used in the capacity testing described in our Interim Report #1.

2. and furthermore two depths of discharge, namely:
   a. a depth of discharge of 50 percent of the practical capacity. (This group received the code letter P.)
   b. a depth of discharge of 120 percent of the practical capacity. (This group received the code letter T.)*

---

* Naturally, a depth of discharge of greater than 100 percent implies a reversal of the potential of the test electrodes.

These four new test conditions in addition to the two levels of plate loading brought the number of possible combinations to eight. Each of these eight combinations was represented in triplicate for each of the three plate materials studied.

6.2 Test Equipment

Basically, the experimental set-up consisted of three parts, namely:

1. the current circuitry
2. the potential monitoring system
3. the test cells proper

6.2.1 Current circuitry

The combination of two plate loadings with two depth of discharge, as just mentioned, required four separate test groups. Each of the equally sized groups of 18 cells had to be cycled independently with respect to currents and times involved. All cells of a group were electrically connected in series, and by means of timer controlled relays, were submitted to pre-determined charge and discharge periods.

Direct current for the charging and discharging of the cells was provided by rectifying the AC line and the currents were regulated by means of adjustable resistors. In essence, this system permitted a constant current operation. The monitoring of the discharge currents revealed that in case of the two 120 percent depth of discharge groups the currents dropped below their set nominal values during the final phases of the discharge

periods. This behavior was due to the fact that the internal resistance of cells of a group is increasing as soon as the particular cells were completely discharged and driven into reverse.

However, in all instances the calculation of the amount of charge removed was possible because the change of discharge currents as a function of the overall state of charge of the test group could be calibrated.

6.2.2 Potential Monitoring System

Two different systems were employed, namely:

1. In case of the 50 percent depth of discharge group, the voltage of those 36 cells were visually read and recorded at pre-determined suitable times. For this purpose each cell could be individually connected to a voltmeter by means of a manually operated selector switch. This kind of system proved to be satisfactory inasmuch as at a depth of discharge of 50 percent regime only small changes in cell voltages are to be expected during each charge or discharge period, respectively.
2. For the 120 percent depth of discharge groups a different system had to be selected. We employed a continuous monitoring of the cells' voltages during the significant portions of the charge and discharge periods.

For this purpose, 35 of the total 36 cells of the two groups were connected to a scanning

device in sub-groups of seven cells. A two minute scanning cycle had eight equal intervals of 15 seconds each of which seven were used for monitoring the cells while the eighth interval served to continuously calibrate the system.

The individual cell voltages were printed out on Rustrak recorders operating with a speed of paper transport of 12 inches per hour. The recorders were automatically turned on for that section of each discharge period during which the completed discharge of cells was anticipated. The recorders were again turned off after 15 minutes of the subsequent charge period had elapsed.

The evaluation of the recorded data revealed that an accuracy in determining the moment of completed discharge of any cell of about one minute could be achieved.

6.2.3 Test Cells

The test cells employed in this part of the program were the same as described in our Interim Report on pages 37 and 38, respectively. However, as mentioned above, the corrugated perforated PVC separators were replaced by either non-woven nylon or nylon/cellophane/nylon separators of a bag type design.

6.3 Test Procedure

6.3.1 Current and Time Requirements

The currents for charging and discharge the cells of the four test groups were calculated based upon the actually observed capacities of the cells at the second Aerospace Formation discharge. Furthermore, certain rate requirements pertaining to subsequent phases of the overall program were also considered.

The lengths of times for which these currents were applied were established by the following conditions:

1. At a constant charge current, a sufficient amount of charge had to be returned to the cells. The specified overcharge factor of 1.4 was based upon the amount of charge removed in case of the two 50 percent depth of discharge groups. Whereas in the case of the two 120 percent depth of discharge groups, 1.4 times of the initially obtained capacities were returned to the cells at each charge period.
2. The amount of charge removed from the cells of the four test groups had to be 50 percent or 120 percent, respectively, of the initially observed capacities.
3. The total length of time for charge and discharge was kept to a whole number of hours, and where possible, to a simple fraction of 24 hours. This was done in order to obtain reoccurence of events at easily predictable times.

The numerical values for currents and times are given in Table 5 with currents in mA and times in hours.

TABLE 5

CAPACITY TEST OPERATING CONDITIONS

TEST-GROUP	MODE	CHARGE CURRENT	CHARGE TIME	DISCHARGE CURRENT	DISCHARGE TIME
HIGH LOADING NYLON/CELLOPHANE TOTAL DISCHARGE	HIGH	1,050	4.4	1,100	3.6
	MEDIUM	960	4.8	550	7.2
	LOW	800	5.6	270	14.4
	HIGH	1,050	4.4	1,100 (1)	3.6
LOW LOADING NYLON/CELLOPHANE TOTAL DISCHARGE	HIGH	815	4.4	850	3.6
	MEDIUM	740 (2)	4.8	430 (3)	7.2
	LOW	570	5.6	190	14.4
	HIGH	810	4.4	850 (4)	3.6
HIGH LOADING NYLON/CELLOPHANE PARTIAL DISCHARGE	HIGH	500	4.5	1,080	1.5
	MEDIUM	380	6.0	540	3.0
	LOW	380	6.0	270	6.0
	HIGH	500	4.5	1,080	1.5
LOW LOADING NYLON/CELLOPHANE PARTIAL DISCHARGE	HIGH	400	4.5	850	1.5
	MEDIUM	300	6.0	425	3.0
	LOW	300	6.0	210	6.0
	HIGH	400	4.5	850	1.5

Due to the diminishing group capacities, the currents marked above were adjusted from the values shown to

(1) = 850 mA ; (2) = 670 mA ; (3) = 380 mA ; (4) = 570 mA

6.3.2 Number of Cycles

The cells were cycled at a given set of conditions for about one week. Depending on the different length of a cycle, this resulted in numbers of cycles achieved as given in Table 6.

6.3.3 Test Sequence

As can be seen from these two tables, the discharge currents were applied in the sequence: high, medium, low and high repeated.

6.4 Results

6.4.1 Capacities and Utilization of Active Material

6.4.1.1 120 Percent depth of discharge cells

Although the voltages of the cells of these groups were continuously monitored, the capacities removed were calculated only for about 40 percent of the cycles performed. These cycles were evenly distributed over the entire length of the test program, and as has been shown previously, such a mode and quota are more than sufficient to cover changes in performance as they occur as function of time and currents.

As done before in our INTERIM REPORT #1, we again selected to present utilization factors of the active materials rather than the experimentally observed capacities. The utilization factor is defined as the ratio of capacity being discharged to the calculated theoretical capacity based upon the weight of active material observed. The

TABLE 6

NUMBER OF CHARGE-DISCHARGE CYCLES

	MODE				
	HIGH	MEDIUM	LOW	HIGH	TOTAL
HIGH LOADING NYLON/CELLOPHANE TOTAL DISCHARGE	18	13	13	24	68
LOW LOADING NYLON/CELLOPHANE TOTAL DISCHARGE	18	13	13	24	68
HIGH LOADING NYLON/CELLOPHANE PARTIAL DISCHARGE	24	16*	22	31*	93
LOW LOADING NYLON/CELLOPHANE PARTIAL DISCHARGE	24	16*	22	31*	93

*) The last normal discharges to a depth of 50 percent in these two test periods were followed by a complete discharge.

advantage of this form of presentation is that it permits a direct comparison of different electrode materials and levels of loadings with active material.

A review of the course of the utilization factors of the individual cells over the whole length of the testing revealed the following facts:

1. The utilization factors of the three cells belonging to a group which received equal processing and cycling were always close together. These sub-groups can therefore be presented by the average value of the three cells.
2. Regardless of the electrode material, the cells fitted with the nylon/cellophane combination separator consistently displayed a better utilization by about two percentage points than those with the pure nylon separators.
3. The utilization factors of the cells with the two experimental plate materials were so similar as to warrant their presentation as one group.

Consequently, the numbers given in Tables 7 and 8, respectively, are average values of all those observations made. They are given for the beginning and the end of each test mode with intermediate points where necessary. The utilization factors are given in percent of the theoretical capacities of the electrodes as calculated upon completion of the Aerospace Formation process.

TABLE 7

UTILIZATION FACTORS IN PERCENT FOR TEST-GROUP: HIGH LOADING NYLON/CELLOPHANE TOTAL DISCHARGE

MODE	MATERIAL	CYCLE NUMBER 1	11	16	18
High	Experimental	76	72	67	66
	Control	76	69	64	60
		19	25	31	
Medium	Experimental	75	72	70	
	Control	75	72	70	
		32	36	44	
Low	Experimental	76	73	70	
	Control	76	73	70	
		45	50	56	
High	Experimental	65	61	58	
	Control	69	64	60	
		57	62	68	COR
	Experimental	62	60	58	71
	Control	62	60	58	68

TABLE 8

UTILIZATION FACTORS IN PERCENT FOR TEST-GROUP: LOW LOADING NYLON/CELLOPHANE TOTAL DISCHARGE

		CYCLE NUMBER			
MODE	MATERIAL	1	11	16	18
High	Experimental	86	73	68	65
	Control	86	73	68	65
		19	26	31	
Medium	Experimental	75	70	68	
	Control	79	74	72	
		32	38	44	
Low	Experimental	71	68	66	
	Control	76	73	71	
		45	51	56	
High	Experimental	64	58	54	
	Control	68	63	59	
		57	63	68	COR
	Experimental	58	55	54	69
	Control	64	60	59	70

The values presented were used for a graphical presentation in Figures 2 and 3, respectively.

As can be seen from both tables and figures,

1. The utilization of the active materials was steadily decreasing with increasing number of cycles accumulated within a given charge-discharge regime.
2. A decrease in the discharge rate was always followed by an immediate, but transient, recovery of the utilization factors. However, the downward trend was not broken by those recoveries.
3. When the testing was going to be concluded with the planned repetition of the initial high discharge currents, the utilization factcrs observed became so low that a reduction of discharge rates became necessary at cycle 67.
4. The control material generally displayed, i.e. with the exception of the first high rate cycles, utilization factors of some percentage pcints higher than the experimental materials.

Considering the loss of active material from the plates, the finally observed utilization factors had to be corrected. These values are shown in the tables and figures marked as "cor".

If one assumes that the loss of active material and hence the reduction in theoretical capacities was evenly distributed over the total length of the testing time, one

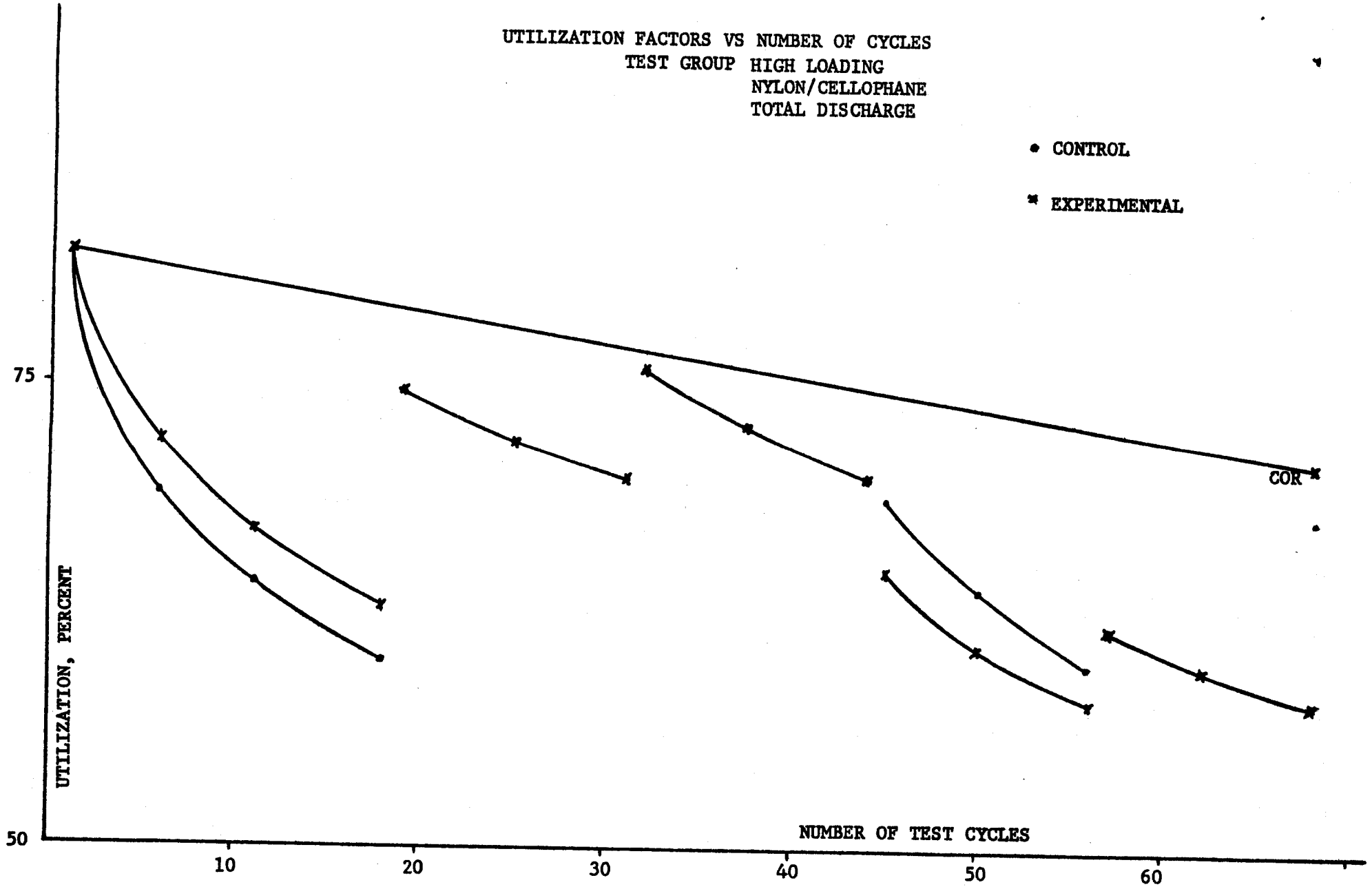
UTILIZATION FACTORS VS NUMBER OF CYCLES
TEST GROUP HIGH LOADING
NYLON/CELLOPHANE
TOTAL DISCHARGE
CONTROL
EXPERIMENTAL
COR
75
50
UTILIZATION, PERCENT
NUMBER OF TEST CYCLES
10
20
30
40
50
60

FIGURE 2

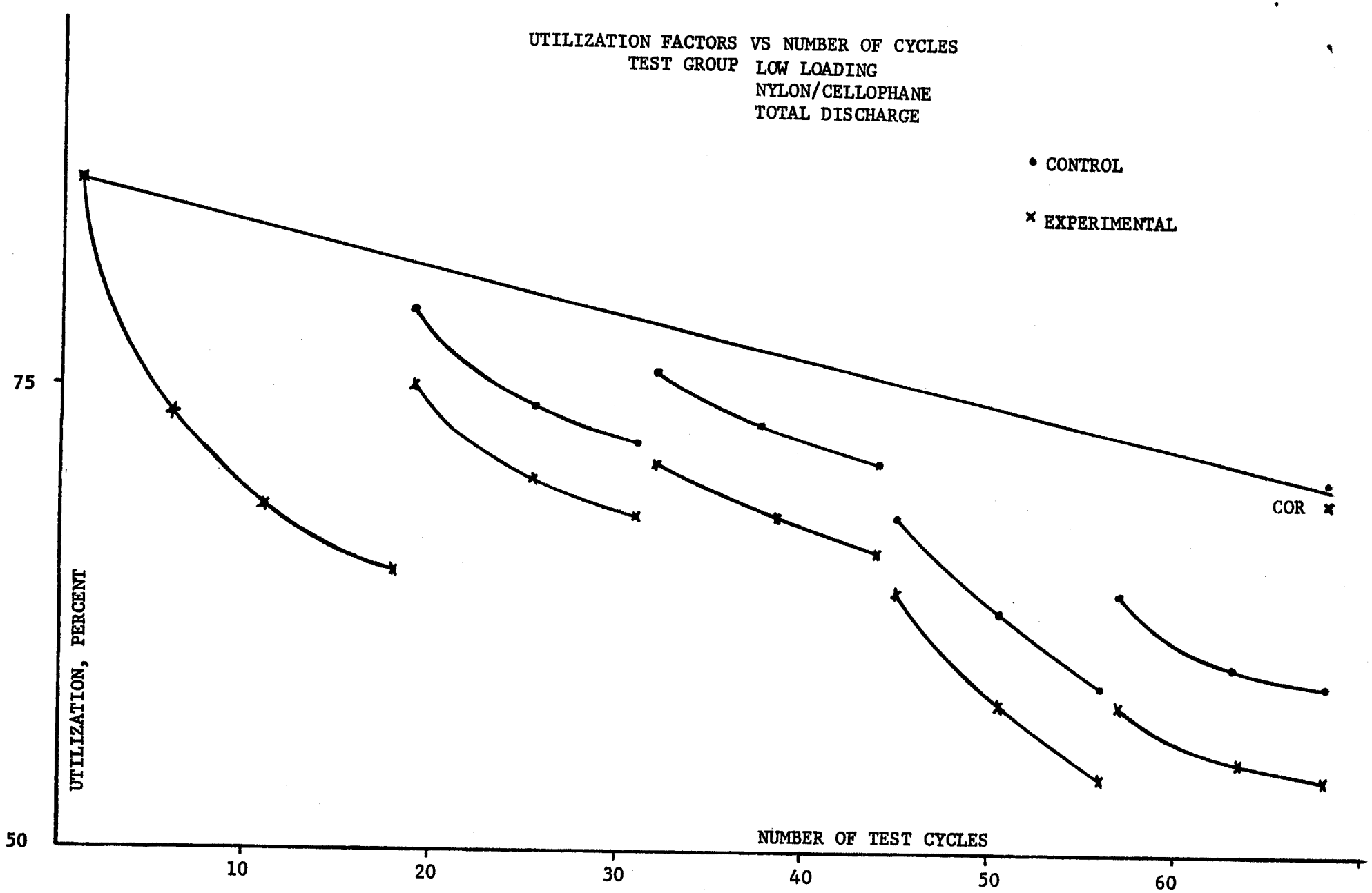
UTILIZATION FACTORS VS NUMBER OF CYCLES
TEST GROUP LOW LOADING
NYLON/CELLOPHANE
TOTAL DISCHARGE
• CONTROL
× EXPERIMENTAL
COR
75
50
UTILIZATION, PERCENT
NUMBER OF TEST CYCLES
10
20
30
40
50
60

FIGURE 3

can connect the initial and final corrected utilization factors by a straight line. Then the interesting observation can be made that none of the interim averaged utilization factors ever exceeded this boundary line.

From this fact it might be concluded that the separator designs employed were sufficient to suppress the development of high resistance short circuits inside the test cells. This was a phenomenon which dreadfully affected the capacity testing during PHASE I of the program.

During the whole course of the current testing, actually only three instances could be observed within the two test groups which pointed to the presence of high resistance shorts.

6.4.1.2 The 50 percent depth of discharge group

From the monitoring of the voltages of the cells of this group at pre-selected times during the course of the testing, no indications for the development of any high resistance short circuits could be obtained.

Upon completion of the regular discharge periods at cycles 2-16 and 4-31, respectively, the discharge of the cells was continued with the same currents as before until reversal of all cells was observed.

The capacities thus obtained were used to compute the utilization factors of the active materials in the usual manner. These numbers are given in percent of the initially observed capacity in Table 9. In addition to the

TABLE 9

AVERAGE UTILIZATION FACTORS FOR 50 PERCENT DEPTH OF DISCHARGE GROUPS

MATERIAL	GROUP	2-16	4-31	4-31(CORRECTED)
1-20	HIGH LOADING CELLOPHANE	99	87	100
	HIGH LOADING NYLON	101	92	96
	LOW LOADING CELLOPHANE	117	79	91
	LOW LOADING NYLON	118	82	88
M-20	HIGH LOADING CELLOPHANE	101	88	102
	HIGH LOADING NYLON	103	93	98
	LOW LOADING CELLOPHANE	118	75	91
	LOW LOADING NYLON	120	83	86
CONTROL	HIGH LOADING CELLOPHANE	103	89	92
	HIGH LOADING NYLON	104	91	92
	LOW LOADING CELLOPHANE	122	83	92
	LOW LOADING NYLON	124	80	87

values observed at the times indicated, a corrected value for the end of the test program is given which considers the losses of active material encountered by the cells.

The conclusions to be drawn are simple, namely:

1. At the end of the 16th cycle of the medium discharge rate period, i.e. at designation 2-16, all cells had developed internal short circuits. These were of the high resistance type as indicated by the abnormally high utilization factors.
2. At the end of the last cycle of the program, i.e. at cycle designation 4-31, the utilization factors observed are high again, but in many cases not too high as to indicate the presence of internal short circuits. However, when the losses of active materials from the plates are taken into consideration and the utilization factors are corrected accordingly, it can be seen that all cells exhibited internal shorts of the high resistance type.

6.4.2. Loss of Active Materials from the Plates

Upon completion of the test program, the cells were dismantled and the plates were intensively washed and dried. Then the final weight was determined for each plate and compared with the weight obtained after the completion of the Aerospace Formation process.

By definition, any difference between the two values was considered to be a loss of active material in the form of cadmium hydroxide. This loss was then calculated as percent of the weight present in the respective plates at the beginning of the capacity testing.

In Table 10 these numbers are given together with average values for the sub-groups of three identical cells. In Table 11, these average values are again presented in a rounded off fashion.

As can be seen from Tables 10 and 11, respectively:

1. Electrodes in the test groups with 120 percent depth of discharge (third letter T) consistently encountered heavier losses of active material than their counterparts in the 50 percent depth of discharge groups (third letter P).
2. When operated at a depth of discharge of 120 percent, the type of separator employed (second letter C or N) hardly influenced the amount of active material lost.
3. However, when operated at the lower depth of discharge of 50 percent, the three-layer separator exercised a far better retention of the active material than the single layer nylon separator.
4. Under identical conditions and test combinations, the two experimental plate materials showed the same losses of active material.

TABLE 10

LOSS OF ACTIVE MATERIAL IN PERCENT OF INITIAL WEIGHTS

TEST - GROUP	1-20	M-20	CONTROL
HIGH LOADING	17.2	15.7	11.5
CELLOPHANE	15.7	19.2	10.2
TOTAL DISCHARGE	15.3	13.1	11.0
	16.1	16.0	10.9
HIGH LOADING	6.2	6.0	1.2
CELLOPHANE	6.3	7.0	1.0
PARTIAL DISCHARGE	6.8	5.7	0.0
	6.4	6.2	0.7
HIGH LOADING	17.6	23.2	9.1
NYLON	16.8	17.7	11.7
TOTAL DISCHARGE	16.9	16.4	10.9
	17.1	20.0	10.6
HIGH LOADING	13.8	13.8	4.5
NYLON	12.8	10.6	6.0
PARTIAL DISCHARGE	13.8	10.8	3.1
	13.5	11.7	4.5
LOW LOADING	20.6	21.0	10.2
CELLOPHANE	22.6	21.7	9.0
TOTAL DISCHARGE	20.8	22.5	13.1
	21.3	21.7	10.8
LOW LOADING	8.5	5.6	6.9
CELLOPHANE	8.4	9.2	7.6
PARTIAL DISCHARGE	7.8	10.7	7.5
	8.2	8.5	7.3
LOW LOADING	21.1	20.9	11.3
NYLON	21.9	26.4	11.9
TOTAL DISCHARGE	21.9	20.9	13.2
	21.6	22.7	12.1
LOW LOADING	15.4	9.9	10.1
NYLON	13.2	12.8	8.1
PARTIAL DISCHARGE	12.8	13.1	13.6
	13.8	11.9	10.6

TABLE 11

LOSS OF ACTIVE MATERIAL IN PERCENT OF INITIAL WEIGHTS

ROUNDED OFF AVERAGE TEST GROUP VALUES

TEST - GROUP	1-20	M-20	CONTROL
HIGH LOADING CELLOPHANE TOTAL DISCHARGE	16	16	11
HIGH LOADING CELLOPHANE PARTIAL DISCHARGE	6	6	1
HIGH LOADING NYLON TOTAL DISCHARGE	17	20	11
HIGH LOADING NYLON PARTIAL DISCHARGE	14	12	5
LOW LOADING CELLOPHANE TOTAL DISCHARGE	21	22	11
LOW LOADING CELLOPHANE PARTIAL DISCHARGE	8	9	7
LOW LOADING NYLON TOTAL DISCHARGE	22	23	12
LOW LOADING NYLON PARTIAL DISCHARGE	14	12	11

5. Under the same identical conditions and test combinations, the losses of active material from the General Electric control material were always the smallest by almost a factor of two.
6. Only in test group L C P, i.e. with low plate loading, cellophane combination separator and 50 percent depth of discharge, the losses were about the same for all three plate types.
7. In the high loading group as a whole, the losses encountered by the experimental plates were two times greater than those of the controls.
8. In the low loading group as a whole, the losses of the experimental plates exceeded those of the controls by more than 50 percent.

7.0 CONCLUSIONS

Summarizing the observations and results of the extension of PHASE I, the following conclusions can be drawn:

1. As detected previously, the experimental plaque materials became extremely stiff and brittle in the course of the impregnation process. The initial flexibility was partially restored in the electrochemical cleaning process.
2. With the exception of the cycles of the initial high rate discharge regime of the heavily loaded plates, the General Electric control material displayed utilization factors for its active material which were equal or better by some percentage points than those of the selected experimental plates.
3. In the case of the 120 percent depth of discharge groups, the application of the two new separator designs resulted in the elimination of the development of internal high resistance short circuits.
4. In case of the 50 percent depth of discharge groups, all cells had developed or still showed, respectively, internal short circuits at the two instances tested for residual capacities.
5. The new separator designs did not prevent the loss of active material from the plates. Under identical circumstances, the loss was always greater for the experimental plates than for the control plates.
6. The separator designs employed, were partially successful in suppressing the adverse consequences of cadmium migration. However, as just mentioned, they could not eliminate the sources of said migration.

7. Based upon these and previous findings, one can safely declare that the experimental materials investigated anew did not show any sign of superiority to the currently available control material.

8.0 RECOMMENDATIONS

The objective of the contract "Development of Improved Cadmium Electrodes for Sealed Secondary Batteries" cannot be met with the existing experimental plaque material.

We therefore strongly recommend not to commence with PHASES II and III, but to terminate this project at this stage.