FOURTH QUARTERLY REPORT

On

ALKALINE BATTERY SEPARATOR CHARACTERIZATION STUDIES

(23 March 1968 - 23 June 1968)

J. J. Kelley and J. Szymborski

For

GODDARD SPACE FLIGHT CENTER

CONTRACT NAS 5-10418

Contracting Officer: John Comstock
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Prepared by
ESB INC. RESEARCH CENTER
Yardley, Pennsylvania 19067

For

GODDARD SPACE FLIGHT CENTER
Greenbelt, Maryland 20771

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ALKALINE BATTERY SEPARATOR CHARACTERIZATION STUDIES

by

J. J. KELLEY

ABSTRACT

During the fourth quarter of the contract period, completion of the cell testing of the candidate membranes was emphasized. Seventeen membrane type separators and eight of the absorber variety were tested. Completed results are reported on twelve membranes and all absorbers.

Three membrane separators have been chosen on the basis of screening test data for testing in 12-ampere hour batteries. These are Permions 1770C and 2290, and Borden 574-151F.

Cell performance of $Ca(OH)_2$ coated positive electrodes was encouraging in that although the cycle life obtained was short of the specified goal, failure in each cell was localized at the coating edges.

Results are not, as yet, completed on those separators which required modification of the cell construction to obtain reliable data on cell performance.

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PROJECT PERSONNEL

The experimental work presented herein has been performed at the Central Research Laboratory of ESB Incorporated, by the following personnel:

1) Analytical Determinations

Mr. Howard Wilson, Section Head, Analytical Chemistry

Mr. Harry Canning, Scientist, Analytical Chemistry

Mr. Reginald Merrell, Scientist, Analytical Chemistry

2) Silver Diffusion and Reactivity

Dr. Wm. P. Sholette, Section Head, Physics Section

Mr. Joseph Szymborski, Scientist, Radioactive Chem. Lab.

3) Battery Assembly and Testing, Physical Testing

Mr. Joseph Carpino, Senior Technician, Polymeric Materials Laboratory

Mr. Edward Woytko, Senior Technician, Polymeric Materials Laboratory

Mr. Walter Zamerovsky, Technician, Polymeric Materials Laboratory

1.0 INTRODUCTION

Work has continued during the fourth quarter with the cycling of silver-cadmium oxide and nickel-zinc oxide cells, constructed utilizing the various separator systems under examination. In order to provide an up-to-date listing, those semi-permeable type separator materials which have been received for testing are listed in Table 1, and the absorbers in Table 2.

The bench screening tests have been finished on all samples listed,and only completion of the cell cycling regimes remains of the characterization studies. A standardized cell assembly was used in constructing the test cells. This involved wrapping the cathode in two layers of membrane separator, where the physical characteristics of the separator permitted. With several samples, lack of sufficient flexibility precluded wrapping of the electrode, and these are being tested in a three-compartment, split cell design in which the membrane being examined serves to separate the elements of the cell. This cell is adapted from a design used at NASA - Goddard Space Flight Center to test rigid separators. Polymethylmethacrylate blocks milled out to hold the electrodes,serve as end elements and the center section is a u-shaped member of the same material. Through bolts are used to secure the assembly and each section is gasketed to prevent leakage.

Table 1

Separator Samples Under Test - Membrane Type

	Material	Composition	Supplier	Status
1.	PUDO 300	regenerated cellulose	DuPont de Nemours	Testing completed
2.	SWRI GX 110	radiation grafted polyethylene	The Jet Propulsion Laboratory	Testing completed
3.	Borden 5-9107-C1	10% PVME-MA 90% Methyl Cellulose (MC)	Monomer-Polymer Lab. Borden Chemical Co.	Testing completed
4.	Borden 5-9107-21	MC + 9% KOH	Borden Chemical Co.	Testing completed
5.	Borden 5-9107-29	Polyvinyl Alcohol	Borden Chemical Co.	Testing completed
6.	Borden 574-151F	Methyl Cellulose	Borden Chemical Co.	Testing completed
7.	ESB 1021G	Heterogeneous Ion exchange membrane	ESB Incorporated	Cell testing incomplete
8.	Permion 110	radiation grafted polyethylene	RAI Research Corp.	Testing completed
9.	Permion 116	radiation grafted polyethylene	RAI Research Corp.	Testing completed
10.	Permion 1770C	chemically grafted polyethylene	RAI Research Corp.	Testing completed

Table 1 (contd)

Separator Samples Under Test - Membrane Type

	Material	Composition	Supplier	Status
11.	Narmco	Not revealed	The Jet Propulsion Laboratory	Cell testing incomplete
12.	Douglas	Not revealed	removed from cells supplied by NASA - Goddard Space Flight Center	Cell testing incomplete
13.	Dewey and Almy E-5114	Not revealed	W. R. Grace Co.	Testing completed
14.	DuPont 7Q109A1	Ion exchange membrane based on Fluorine containing monomers	DuPont de Nemours	Cell testing incomplete
15.	Permion 2290	chemically grafted polyethylene	RAI Research Corp.	Cell testing incomplete
16.	Calcium hydroxide coated silver and nickel electrodes	-	ESB Inc. electrodes coated by General Electric Research	Cell testing incomplete
17.	Polyimidazopyrrolone (Pyrrone) films	-	NASA - Langley Research Center	Cell testing incomplete

Table 2

Separator Samples Under Test - Absorbers

	Material	Composition	Supplier	Status
1.	Pellon 2505 K	Non-woven polyamide	Pellon Corporation	Testing completed
2.	Pellon T15045	2505K, washed 3X with organic wetting agent added	Pellon Corporation	Testing completed
3.	Pellon T15046	2505K - washed with 0.7% HCl organic wetting agent added	Pellon Corporation	Testing completed
4.	Pellon T15047	2505K - washed with 0.7% KOH organic wetting agent added	Pellon Corporation	Testing completed
5.	Pellon T15048	2505K - 3X washed cellulose treated	Pellon Corporation	Testing completed
6.	Pellon T15049	2505K - 0.7% HCl washed - cellulose treated	Pellon Corporation	Testing completed
7.	Pellon T15050	2505K - 0.7% KOH washed cellulose treated	Pellon Corporation	Testing completed
8.	Chem-Sorb KS-900	Non-woven polyamide	Chem-Sorb Inc.	Testing completed

In cells of this type, the Narmco, ESB-1021G, and DuPont No. 7Q109A1 films, as well as the Douglas material, are currently being tested. The first three materials and the Douglas separator were found to be sufficiently brittle even when electrolyte saturated to require this form of construction. The DuPont film, although quite flexible, was included because the quantity on hand was not sufficient to wrap electrodes.

2.0 SEPARATOR SCREENING METHODS

2.1 New Materials

Two additional membrane materials were received during this quarter and their properties measured in the bench screening tests. The data obtained in these tests is listed in Table 3. Permion P2290 is reported to be a polyolefin film to which is grafted polyacrylic or methacrylic acid side chains. The grafting is reportedly achieved by chemical activation, rather than radiochemically, as is the case with Permions 110 and 116. Permion P2290 and Permion 1770C then, are both examples of chemically grafted polyolefins, and contrast with Permions 110 and 116. The differences among the samples such as method and degree of cross linking and differing structural characteristics of the base polyolefin have not been revealed. Both chemically

Table 3

Membrane Materials - Properties

	RAI-2290	Pyrrone
Electrolyte absorption g/cc	0.731	3.44
Electrolyte retention g/cc	0.663	3.21
Dimensional changes %		
length	+4	+7.8
width	+5	+7.5
thickness	+10	+72
Sample thickness		
dry cm x 10^3	3.1	2.5
in 40% KOH cm x 10^3	3.4	4.4
Separator Expansion Factor		
wet thickness ÷ dry thickness	1.1	1.76
Electrical Resistance A.C.		
Ω-cm^2	0.27	0.22
Ω-cm	80	48
Tensile Strength		
dry-psi	2060	Film very brittle
in 40% KOH-psi	755	These tests not run
Oxidation and Hydrolytic Resistance		
% tensile strength retained at 168 hrs.	100	These tests not run
336 hrs.	100	
Pore Size - pore diameter Å	7-13	Samples split
Tortuosity Factor	5.3	
Porosity in 40% KOH - cc/cc	.52	.51
Silver Permeability		
moles Ag/cm^2 sec x 10^{10}		no detectable Ag at 120 h

Table 3 (contd)

Membrane Materials - Properties

	RAI-2290	Pyrrone
Zinc Diffusion		
moles Zn/cm^2 sec x 10^7	0.04	0.05
Silver Adsorption		
g $Ag/in^2/hr$ x 10^6	0.65	72.6
Zinc Penetration Value		
time-hours	2.11	5.2 - > 25
hours/cm x 10^{-2}	6.2	11.8 - > 56
Zinc Adsorption		
K-value (at 1 mole ZnO/liter 40% KOH)	0.73	0.79

grafted membranes give higher resistivities and lower permeation values than the radiation grafted specimens. The results of cell testing agree with this general trend, in that the chemically grafted films give greater cycle life in both silver-cadmium oxide and nickel-zinc oxide cells, than was found with Permion 110 or 116. Both Permion 1770C and Permion P2290 are recommended for additional testing in silver-zinc batteries.

The pyrrone film (polyimidazopyrrolone) was submitted by NASA - Langley Research Center. The polymer is prepared by condensation of pyromellitic dianhydride and 3, 3'-diamino benzidine, and forms transparent, amber films which are quite brittle when dry, but are somewhat more flexible after immersion in 40 percent KOH. Although plasticized by KOH, the pyrrone films were still too brittle to measure many of the required properties. Attempts to construct cells by wrapping the electrodes was the principle problem encountered. Cell testing of the film is underway using the split cell design previously described.

2.0 SEPARATOR SCREENING METHODS (contd)

2.2 Low Temperature Equilibration of Methyl Cellulose Film

Good results were found in both bench and cell testing for pre-swollen Borden 574-151F. This has been reported to be mainly methyl cellulose. The pre-swelling technique, while effective, offers some disadvantage where the activation of full size batteries is contemplated. Hence, an alternate scheme for increasing the electrolyte absorption of this film was of interest. Immersion in 30 percent KOH, or lower concentrations, at sub-ambient temperatures has been reported to substantially increase the electrolytic conductivity of methyl cellulose films; so this was explored. Film strips were immersed in 30 percent KOH overnight at ambient temperature, and the temperature then lowered and maintained at various temperatures from -30 to -60°C. After four hours equilibration at the lower temperature, the solution was allowed to come to room temperature and the resistance of the film measured in 31 percent KOH. Film resistance was found to decrease with decreasing temperature; but was still 4.7 Ω-cm^2 after equilibration at -60°C. Without the low temperature equilibration, the resistivity was 21 Ω-cm^2; while using pre-equilibration with dilute KOH solution, it was possible to reduce resistivity to 0.2 Ω-cm^2. Table 4 shows the effect of various equilibrating temperatures on the Borden 574-151F film.

Table 4

Low Temperature Equilibration of
Methyl Cellulose Films
(Borden 574-151F)

Equilibrating Temperature °C	Film Thickness cm x 10^3	Resistivity Ω-cm^2
+21	4.0	21
-30	3.8	13.5
-40	3.8	8.5
-50	4.0	5.8
-60	4.0	4.7

The freezing point of 31 percent KOH limits the equilibrating to about -65°C. Thus, it did not appear useful to pursue this scheme further with 31 percent KOH. Lower concentrations of KOH or modified methyl cellulose films would be expected to yield lower resistance values and both approaches will be examined. One other experiment was performed to discover the effect of several temperature cycles on the film resistivity. As many as three cycles between +21°C and -60°C do not appreciably lessen the resistivity of the film. Low temperature storage to induce electrolyte absorption of methyl cellulose films does not, on this evidence, provide a feasible alternative to pre-swelling, and it is recommended that batteries built containing the Borden 574-151F film be activated first with 20 percent KOH, and the concentration then be increased to the final desired value.

2.0 SEPARATOR SCREENING METHODS (contd)

2.3 Coated Electrodes

In previous investigations, General Electric Company personnel investigated a process for electrodepositing $Ca(OH)_2$ films onto electrodes. Both silver and nickel electrodes were used as substrates. As a part of this separator study, a number of silver and nickel electrodes were supplied to the General Electric Research and Development Center and coated by the same personnel responsible for the initial process development. The coating solutions contained 150 g/l of calcium acetate buffered with either one or four to five g/l calcium hydroxide. Coating current density was 100 ma/cm^2 and thickness of coating was controlled by monitoring voltage rise during the process and terminating within a specified voltage range. The coatings obtained were between 2.0 and 5.0 mils on the silver electrodes and 1.0 and 5.0 on the nickel electrodes. Weight gain ranged from 0.32 to 1.16 grams. Each electrode chosen for cell testing (see Tables 5 and 6), was examined under low magnification so that flaws and inhomogeneities in the coating could be detected, and where such was found, the electrode was discarded. In all, 12 coated nickel electrodes and 6 coated silver electrodes were tested, in the appropriate three-plate cell, under the same conditions used for the other separator materials. In each case, a single layer of cellophane was used to supplement the electrode coating.

Table 5

General Electric Coated Electrodes
Nickel Electrodes

Electrode	Coating Thickness mils/side	Weight Gain (grams)
1	1.0	0.3902
2	1.0	0.3203
9	1.5	0.2948
10	2.5	0.3097
14	2.0	0.3702
15	2.0	0.3629
11	4.5	0.6839
12	4.5	0.6780
6	5.0	0.9120
7	4.5	0.9399
23	2.5	0.4726
24	3.0	0.5257

Table 6

General Electric Coated Electrodes
Silver Electrodes

Electrode	Coating Thickness mils/side	Weight Gain (grams)
3	4.0	0.9762
4	3.0	0.9639
6	4.0	0.7312
8	2.5	0.6315
10	2.5	0.7330
17	3.5	0.7044

Using as a failure point a loss of 50 percent of original capacity, the coated silver electrodes gave 20-23 cycles while the nickel-zinc cells built with coated nickel electrodes gave 16-28 cycles to the same end point. A summary of cycle capacity is given in Table 7. In each instance, tear down analysis of the cells indicated failure stemming from the extreme edges of the coating. This is undoubtedly due to the "edge effect" commonly encountered in plating operations. Were this overcome, it appears likely that sufficient protection could be obtained from as little as 2.0 mil coatings. Neither silver staining, nor zinc penetration of the cellophane layer were extensive compared to control cells containing only cellophane as separator material. No meaningful correlation of cycle life and coating thickness was observed in these tests and at the rates used, no significant effect of thickness on voltage was observed.

Table 7

Electrical Cycling Performance
Coated Electrodes

	Ni-ZnO Cell Capacity A-Hrs			Ag-CdO Cell Capacity A-Hrs		
Cycle	Coating Thickness 1.0 mils	Coating Thickness 2.0 mils	Coating Thickness 3.0 mils	Coating Thickness 4.0 mils	Coating Thickness 4.0 mils	Coating Thickness 2.5 mils
1	0.97	0.95	0.95	1.49	1.97	1.96
5	1.37	1.37	1.33	1.52	2.40	2.47
10	0.88	0.94	1.04	1.88	2.44	2.34
15	0.99	0.67	0.80	1.63	1.98	1.50
20	0.92	0.35	0.33	1.50	1.50	1.18
25	0.70	-	0.43	0.38	0.82	-
30	0.20	-	0.41			

3.0 CELL TESTING

3.1 Film Type

The cycling regime has been completed on all separators except the Narmco, Douglas, DuPont, and NASA-Langley materials. These four required special handling and are being tested as a group. Of the completed group, three gave better capacity retention on cycling; Permions 1770C and P2290, and Borden 574-151F, in both systems tested. Borden's 5-9107-29 film met the cycling goal in the Ag-CdO cell test but did not in the Ni-ZnO test. The reverse was found with the Dewey and Almy separator which performed well in the zinc system but not in the silver system. A combination of these two separators might be beneficial in maintaining capacity in the silver-zinc battery system. Table 8 lists the results obtained in the cycling tests for each of the membrane separators.

Table 8

Separator Performance - Cycling Tests

Ag-CdO System Cycles to 50% Original Capacity	Original* Capacity Amp-Hrs	Separator	Ni-ZnO System Cycles to 50% Original Capacity	Original* Capacity Amp-Hrs
>30, > 30	1.46	methyl cellulose	>30, 26	1.48
>30, > 30	2.36	Permion 1770C	> 30, > 30	1.46
> 30, > 30	1.84	Permion P2290	28, > 30	1.26
14, 25	1.51	Dewey and Almy E-5114	> 27, 28	1.51
> 30, > 30	1.85	Borden 5-9107-29	15, 16	1.07
18, 22	2.27	PUDO 300	11, 11	1.30
26, 27	2.11	SWRI GX 110	14, 15	1.13
9, 11	1.77	Borden 5-9107-C1	14, 15	1.33
18, 24	1.81	Borden 5-9107-21	15, 15	1.17
30, 27	2.18	Permion 116	15, 17	1.51
21, 27	1.51	Permion 110	15, 12	1.51
23, 23, 30	2.15	G.E. coated electrodes	28, 18, 18	1.17

*average of first four cycles

3.0 CELL TESTING (contd)

3.2 Absorber Type

The cell testing has been completed also on the various absorber materials. In each instance, cellophane PUDO 300 was used as the primary separator. Cycle life to one-half original capacity was not appreciably different among the absorbers examined, varying from 15 to 24 for the Ni-ZnO cells, and 22 to in excess of 30 for the Ag-CdO cells. In these cells, Viscon retainers were used on the zinc negatives.

In the Ag/CdO cell testing, best capacity over cycle life was obtained with Pellons T15045, T15046, and T15047, although Samples T15048 - T15050 gave slightly less capacity/cycle; capacity varied by only about 30 percent out to 30 cycles. Little difference among the absorbers could be noted in the Ni-ZnO testing. Since the cells were operated in the flooded condition and with rather low rates, differences in wetting rates, absorption and wicking evidently did not play an important part in determining performance.

4.0 FUTURE WORK

4.1 Examine in cell testing, the performance of the Narmco, Douglas, DuPont, ESB Incorporated, and NASA-Langley separators.

4.2 Seek correlation between cell performance and bench test results.

4.3 Evaluate the newly received Permion P2291.