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FIFTH QUARTERLY REPORT

On

ALKALINE BATTERY SEPARATOR CHARACTERIZATION STUDIES

(23 June 1968 - 23 September 1968)

J. J. KELLEY

For

GODDARD SPACE FLIGHT CENTER

CONTRACT NAS 5-10418

TECHNICAL MONITOR: THOMAS H. HENNIGAN

Prepared by
ESB INCORPORATED
RESEARCH CENTER
Yardley, Pennsylvania

For

GODDARD SPACE FLIGHT CENTER
Greenbelt, Maryland

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ALKALINE BATTERY SEPARATOR
CHARACTERIZATION STUDIES

by

J. J. KELLEY

ABSTRACT

The results of additional separator and characterization tests on PERMION 2291 membranes and non-woven absorbers, PELLON 2530, and KENDALL EM 476, are reported. PERMION 2291 gave satisfactory performance in the cell cycling testing of Ag-CdO and Ni-Zinc cells and is to be further tested.

Cell testing of the polybenzimidazole, and pyrrone films and the inorganic separators was completed but with inconclusive results. In all but the case of the pyrrone film, cracking of the separator appears to have contributed to the failure. With the pyrrone film, silver penetration in very localized areas was the cause of failure.

Electrolyte absorbant separators, such as PELLON Lots 14,000, 15126 and 16015, were investigated to determine physical properties and wetting characteristics.

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PROJECT PERSONNEL

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

1. Project Leader - J. J. Kelley

2. Analytical Determinations - Materials Analysis and Structure Section

   Mr. Anthony Monteleone, Scientist

   Mr. Harry Canning, Scientist

   Mr. Reginald Merrell, Scientist

3. Silver Diffusion and Reactivity

   Dr. Wm. P. Sholette, Section Head, Physics Section
   Mr. Joseph Szymborski, Scientist, Radioactive Chem. Lab.

4. Battery Assembly and Testing, Physical Testing

   Mr. Joseph Carpino, Senior Technician, Polymeric Materials Lab.

   Mr. Edward Woytko, Senior Technician, Polymeric Materials Lab.

   Mr. Walter Zamerovsky, Technician, Polymeric Materials Laboratory

1.0 INTRODUCTION

The objective of this work was the examination of available separators for alkaline silver cells by the use of previously proposed screening procedures. The use of these screening methods permitted the comparison of performance of the various separators in bench tests designed to measure those parameters considered important in separator functioning. Absolute values are, of course, not to be expected from these screening methods (described in detail in the Second Quarterly Report of this contract, August - November 1967) since they are, for the most part, conducted under idealized conditions which simulate only a portion of the total battery environment. This poses the familiar problem of correlation of the results of screening methods with actual performance and the examination of this latter area was a further purpose of this study. The correlations found make up a later portion of this report.

The receipt of an additional membrane type separator, PERMION 2291, brings the total of such films examined to eighteen (including $Ca(OH)_2$ coated electrodes). PERMION 2291 is a highly cross-linked, polyethylene based, weak acid cation exchange resin. Cross linking is accomplished by electron irradiation. The polyethylene which is used in this membrane is stated to have a narrow molecular weight distribution which leads to efficient cross linking.

With two additional absorber separators evaluated in this Quarter, ten absorber samples have been examined in both the bench screening and preliminary battery screening methods.

2.0 SEPARATOR SCREENING METHODS

2.1 New Materials

A newly developed separator film, PERMION 2291, was purchased from RAI Research and examined in the test program. The results of the testing are given in Table I which also lists for comparative purposes, the values obtained on similarily prepared films, which were tested earlier in the contract. It is indicated that in moving from left to right across the table, the separator becomes a greater barrier to ionic transport. Permeability to zincate and silver ion decreases as does conductivity.

In the three-plate cell testing, PERMION 2291 performed adequately, completing the stipulated thirty cycles with no indication of shorting through the membrane. In the silver-cadmium oxide cells, silver had penetrated one of the two layers used. Similar behavior was found for zinc penetration in the nickel-zinc oxide cells. The successful completion of the cycling tests makes PERMION 2291 a candidate for further battery testing in silver-zinc oxide cells and it is recommended that it be included in the battery assembly phase of this program.

Table 1

Grafted Polyethylene Separators

Screening Test Results

	SWRI GX	P110	P116	P1770C	P2290	P2291
1) Electrolyte Absorption g/cc	1.14	0.86	0.81	- *	0.73	0.5
2) Dimensional Changes (40% KOH) %						
Length	+5.9	+10	+6.6	+13	+4	+3
Width	+7.2	+ 9	+8.8	+12	+5	+3
Thickness	+19	-15	-16	- *	+10	+10
3) Sample Thickness dry (cm x 10^3)	3.0	5.4	6.3	-	3.1	3.0
4) Electrical Resistance A-C Ω-cm^2	0.095	0.14	0.16	0.21	0.27	0.69
5) Tensile Strength psi						
dry	1880	1790	1700	-	2060	1850
in 40% KOH	990	850	990	-	755	1350
6) Silver Permeability Moles Ag/cm^2 sec x 10^{10}	121	80	57	47	34	4.8
7) Silver Adsorption g Ag/in^2 hr x 10^6	1.1	0.8	0.8	0.65	0.65	0.73

*The puckered surface of this film made thickness measurements of doubtful validity.

Table 1 (contd)

Grafted Polyethylene Separators

Screening Test Results

	SWRI GX	P110	P116	P1770C	P2290	P2291
8) Zinc Diffusion moles Zn/cm^2 sec x 10^7	26	10	10	8	0.04	0.08
9) Zinc Penetration Value hrs/cm x 10^{-2}	1.4	1.9	1.4	3.8	6.2	10.7
10) Zinc Adsorption K-value (at 1 mole ZnO/1 40% KOH)	0.77	0.87	0.76	0.86	0.73	0.84
11) Pore Size - pore diameter Å	5/9	19/27	10	17	7/13	10/25

12) Oxidation and Hydrolytic Resistance
% tensile strength retained at 336 hrs. No change in strength during test.

2.0 SEPARATOR SCREENING METHODS (contd)

2.1.1 On the basis of the battery screening results, it had been previously recommended that a film obtained from the Monomer-Polymer Laboratories of The Borden Chemical Company, BORDEN 574-151F, be tested in silver-zinc cells. This was one of four films obtained from this source and tested under the contract. The Borden Chemical Company would not, however, agree to supply the quantity required for the test to be run. Attempts to procure similar films from commercial sources have not been successful, and the planned use of BORDEN 574-151F has been cancelled.

2.2 Absorber Materials

Properties were measured on three additional non-woven separator fabrics; a polyamide from Pellon Corp. (PELLON Style No. 2530, Lot 14019), a polypropylene (EM 476), and a dynel (EM 309), from the Kendall Company. All were treated to enhance electrolyte absorption and the testing was performed on the as-received material. Table 2 lists the results of tests for air permeability, wetting times with electrolyte, and the electrolyte wicking behavior of the fabrics. Electrolyte absorption and electrical resistance data on the polyamide and polypropylene samples are given in Table 3. PELLON 2530, as received, wets out more rapidly, absorbs a greater total quantity of electrolyte and, consequently, is lower in resistance than EM 376 which, however, is considerably better in wicking ability.

Table 2

Absorber-Screening Test Results

		EM 309	EM 476	PELLON 2530
Air Permeability seconds to pass 300cc		2.7	20	1.3
Wettability spreading time seconds	40% KOH	36.5	1850	3490
	30% KOH	7.5	321	102
	20% KOH	2.5	62	0.5
Wicking - 40% KOH hgt cm at	5 min	0	1.0	0
	15 min	0	3.0	0
	30 min	0	4.0	0.2
Wettability minutes to minimum resistance in 40% KOH		0.5	51.	1.2

Table 3

Absorber Separator Characteristics

	PELLON 2530	EM 476
Thickness cm dry	0.0283	0.029
in 40% KOH	0.0285	
Electrolyte Absorption %	450	220
Electrical Resistance Ω-cm^2	0.056	0.389

2.0 SEPARATOR SCREENING METHODS (contd)

As an additional facet of this work, several polyamide absorber materials were submitted by the Contracting Officer for characterization testing. Information as to the effect of addition agents added either during manufacturing operations or subsequently, which affected the wetting properties was desired. The test data accumulated on the samples submitted is shown in Table 4. The materials were then solvent washed using either methylene chloride or 95% ethanol. The extracted material was weighed to obtain the value for extractables, and the properties of the extracted material reexamined. The data on the extracted samples is given in Table 5. Wicking ability is the most seriously affected property. The extraction procedure used was that recommended by Hummel, [D. Hummel, "Identification and Analysis of Surface Active Agents," Vol. 1, Interscience, New York, 1962.].

1. the sample is dried in a vacuum oven at 60°C for 2 hours
2. extraction is carried out in a Soxhlet extraction apparatus using 95% ethanol at the boiling point for 2 hours.

Table 4

Absorber Characteristics - Pellon Samples

Test Data

	Lot No. / Style No.	14000 2505ML	15126 2505ML	16015A 2505ML	16015B 2505ML	12777 2505K
Thickness	cm dry	0.042	0.039	0.041	0.042	0.040
	in 34% KOH	0.078	0.090	0.088	0.095	0.092
Electrical Resistance 34% KOH Ω-cm^2		0.059	0.058	0.060	0.069	0.092
Air Permeability seconds to pass 300cc		2.3	2.5	2.5	2.5	9.3
Wicking - 34% KOH hgt mm at	5 min	7.5	5	0	0	2.5
	15 min	32	29	2.5	2	15
	30 min	73	40	5.5	7	37
Wettability seconds to minimum resistance		14	10	66	80	47
Ethanol Extraction % wgt loss		9.5	8.4	0.6	0.8	*
Ethanol Chloride Extraction % wgt loss		5.0	6.9	2.0	1.2	1.4

*data not taken

Table 5

Absorber Wetting Characteristics - Extracted Samples

		Wicking height cm (34% KOH Avg. 5 san								
	Minutes	0	0	5	10	15	20	25	30	45
Lot No.	Style No.									
12777	2505K*	0	0	0	0	0	.3	.4	.5	.6
14000	2505ML**	0	0	.4	.5	.5	.6	.7	.8	1.0
15126	2505ML**	0	0	0	0	0	0	0	0	0
16015A	2505ML**	0	0	0	0	0	0	0	0	0
16015B	2505ML**	0	0	0	0	0	0	0	0	0

Wet-Out Time and Resist. (Avg. 3 samples)

Lot No.	Style No.	Wet-Out Time	Resist. (Ω-cm^2) 34% KOH
12777	2505K	17.1 sec	.138
14000	2505ML	18.9 sec	.227
15126	2505ML	12.3 sec	.077
16015A	2505ML	73.2 sec	.161
16015B	2505ML	85.9	.153

*K - hot calendered

**ML - maximum loss

2.0 SEPARATOR SCREENING METHODS (contd)

3. the ethanol solution is removed by distillation and final evaporation and the residue examined if identification is desired

4. The weight change in the alcohol insoluble material gives the extractable content

5. to test for relatively hydrophobic agents, a further extraction with methylene chloride or chloroform is effective in removing these.

6. Hummel notes in his description that the presence of carboxymethyl cellulose can be detected by charring a portion of the alcohol insoluble fraction and noting the smell of charred sugar.

Because of the vast number of surface active agents available and the diversity of functionality built into them, it is certainly possible that the scheme outlined would not be effective with some fraction of those. Thus the solvent choice must be modified to accomodate what is known about both the substrate and the surface active material.

3.0 CELL TESTING

The three-plate cell testing of PERMION 2291, PELLON 2530, and EM 476 was completed with the results given in Table 6.

Table 6

Separator Performance-Cycling Tests
(Average of two cells)

Ag-CdO System Cycles* to 50% Original Capacity	Original Capacity A-Hrs	Separator	Ni-ZnO System Cycles to 50% Original Capacity	Orig Cap A-
>30	2.2	Permion 2291	30	1.
24	1.9	Pellon 2530/PUDO 193	19	1.
30, 19	1.9	EM-476/PUDO 193	20	1.

*Cycling regime

Silver-cadmium cells	charge 0.07 amp to 1.25 x AH previous disch. discharge 0.50 amp to 1.30 v
Nickel-zinc cells	charge 0.10 amp to 1.25 x AH previous disch. discharge 0.25 amp to 1.30v

3.0 CELL TESTING (contd)

Four of the separators could not be tested in the same cell construction as the remainder of the group. The alternative construction adopted involved edge gasketing in a split cell design, rather than wrap-around construction. In this particular program, the following separators were examined with the noted results:

3.1 NARMCO - A film made from a modified polybenzimidazole polymer-supplied equilibrated with caustic. The film was rather brittle and cracked at the bend when an electrode wrap was attempted. In the split cell, low capacity was obtained in the silver-cadmium oxide cell tests due principally to excessive voltage drop. Satisfactory capacity maintenance with cycling was shown by both cells in the Ag-CdO test. The nickel-zinc oxide tests were rather short lived with dendrite penetration after 8 cycles and 13 cycles. This is quite disappointing in view of the excellent zinc penetration value obtained in the bench screening tests(2100-7000 hrs/cm Second Quarterly Report). A microscopic examination of the failure area indicated microcracking in that region but it was not possible to determine whether this was cause or effect. Unused separator material and that removed from the silver-cadmium cells examined the same way did not show this cracking. Insufficient material remains at this point to examine this further.

3.0 CELL TESTING (contd)

3.2 DOUGLAS Inorganic Separator - The separators tested were removed from 5 A-Hr cells. In the cells, the separator sheets formed a box around the negative plate. Since the separators were quite inflexible, the edges of the box were closed by use of plastic composition which adhered to the separator. In order to free a separator for testing, the box was cut open, the negative plate removed, the adhesive scrapped from the surface, and the slab soaked in excess 40% KOH, prior to assembly into the split cell. A number of the separators were split in attempting to remove them, so that only six were finally obtained for cell testing. Cell performance was maintained for 25 cycles before dropping below 50% of original capacity with the Ag-CdO couple, and for only 11 and 19 cycles with Ni-ZnO. Failure was by shorting in both couples. Microscopic investigation indicated separator cracking at the edges, where the separator is clamped to effect a seal. Although not visually evident, failure may well have occurred at these spots.

3.0 CELL TESTING (contd)

3.3 PYRRONE - The Pyrrone film, chemically polyimidazopyrrolone, was supplied by the Langley AFB Research Center. It was quite brittle, cracking easily on bending. Cracking in the cell remained a problem until all pressure points were removed. Cell performance in Ag-CdO cells was 19 and 24 cycles to failure while in the nickel-zinc testing, equipment failure led to excessive overcharging and premature failure so that no data is available since insufficient sample remained to re-test. It is possibly worth noting that film removed from the silver-cadmium cells were only very spottily penetrated by silver.

3.4 Du PONT 7AQ-1094-1 - Sufficient film was on hand to build only one cell. This was a Ag-CdO cell which cycled for 20 cycles before capacity loss reached 50% of original. Cell voltage was considerably reduced on discharge (mid voltage 0.85 vs 1.01 Pyrrone, 0.96 Douglas, 0.93 Narmco) so that the cut-off voltage was reduced to 0.60 volt.

3.0 CELL TESTING (contd)

3.5 Screening Test - Performance Correlation

The membrane separators (PERMIONS 2290, 2291, 1770C, BORDEN 574-151F), which gave satisfactory performance in the battery cycling tests will appear to function as diffusion barriers with resistivities three or more times that of cellophane. Zinc penetration values are greater by factors of 2-15, while silver ion and zincate diffusion are reduced.

The superior performance by the group of films which have given best cell cycle life is achieved mainly by reducing the total amount of electrolyte absorbed by the film. Other films of those tested were even more efficient in controlling diffusion or zinc penetration by failed to meet cycling requirements in the cell testing due either to being so brittle and inflexible that normal stresses in operation caused rupture or to low conductivity which raised the internal resistance of the cell to such an extent that use in a practical system would be precluded.