

SIXTH QUARTERLY REPORT

On

ALKALINE BATTERY SEPARATORS
CHARACTERIZATION STUDIES

J. J. Kelley

For

GODDARD SPACE FLIGHT CENTER

CONTRACT NAS 5-10418

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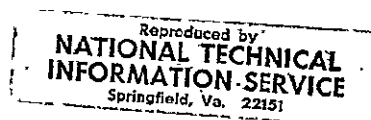
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For

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TERMATREX DESCRIPTORS

ABSORBERS

ALKALINE BATTERIES

CHARACTERIZATION

NAS 5-10418

SEPARATORS

SEPARATOR TEST METHODS

TESTING

ALKALINE BATTERY SEPARATOR CHARACTERIZATION STUDIES

by

J. J. Kelley

ABSTRACT

PERMION 1770C, 2290 and 2291 have shown the best overall balance of properties in bench characterization testing of separator materials for silver-zinc batteries. Both non-battery and three-plate cell data were evaluated for fifteen film type separators. Based on this test program, the following characteristics were used to choose the above films for battery testing:

- 1) Electrical Resistance in 40 percent KOH
less than $1.0 \Omega\text{-cm}^2$
- 2) Zinc diffusion rates through the film, less
than 1×10^{-8} moles Zn/cm² sec
- 3) Zinc penetration value greater than 3
- 4) A minimum of 30 cycles in silver-cadmium and
nickel-zinc laboratory cell tests
- 5) No loss in physical properties on exposure
to 40 percent KOH saturated with Ag₂O and ZnO.

Absorbent type separators were also examined for physical and chemical properties relevant to use in silver zinc batteries. Significant variation in wetting properties exist among the absorbers but the effect of this variation was not evinced in the cell testing where flooded conditions were used.

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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 :

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Mr. Harry Canning, Scientist

3. Silver Diffusion and Reactivity

Dr. Wm. P. Sholette, Senior Scientist

Mr. Joseph Szymborski, Scientist

Mr. Sanford Orenstein, Scientist

4. Battery Assembly and Testing, Physical Testing

Mr. Joseph Carpino, Advanced Technician

Mr. Edward Woytko, Advanced Technician

Mr. Walter Zamerovsky, Technician

1.0 INTRODUCTION

The objective of this study was to characterize the available separator materials proposed as improvements over the commonly used cellulose; cellophane and fibrous sausage casing. A similar characterization study of cellulosic materials was conducted under NASA Contract No. NAS 5-2860. The work statement to which this investigation is responsive, calls for bench screening tests of separators to measure:

- 1) dimensional changes on exposure to electrolyte,
- 2) electrolyte absorption,
- 3) electrical resistivity,
- 4) rate of permeation of dissolved silver oxide through
the separator,
- 5) zincate permeability through the separator,
- 6) pore size and tortuosity,
- 7) tensile strength,
- 8) resistance to oxidation and hydrolysis,
- 9) reactivity with silver oxides dissolved in the electrolyte,
- 10) separator wettability with electrolyte,
- 11) wicking properties and air permeability of absorber
type separators,
- 12) zinc penetration value, and
- 13) performance in three-plate nickel zinc and silver
cadmium cells.

The tests applied were adapted from those appearing in the Aero Propulsion Laboratory Handbook, edited by J. E. Cooper and A. Fleischer, entitled "Battery Screening Methods"(AD 447301)"¹, from the previous study done under Contract NAS 5-2860², or were developed in the present work.

The detailed procedures used in the separator bench screening phase of the investigation are reported in Appendix I.

The separators examined fall into two distinct categories. One group consists of continuous films of relatively thin gauge. This class can be loosely designated as semi-permeable and they are akin to the films used in ion exchange membrane applications e.g., reverse osmosis and electrodialysis. Their distinguishing feature is small pore size, comparable to the diameter of the ions in the electrolyte. In the case of true membranes, interaction occurs between the fixed ions in the membrane structure and diffusing ions in the electrolyte. At high concentrations of fixed ions relative to ionic concentration in solution, the membrane will exclude ions of similar charge to its fixed ions, and is termed permselective. At high solution concentration, permselectivity approaches zero as a limit and the membrane is non-selective.

The second type of separator is "wide pored" and consists of a skeleton structure through which run liquid filled pores. The separators act merely as geometric boundary, with transport processes in the separator identical to those in the free electrolyte.

The separators considered in this study are listed in Table I.

TABLE 1
SEPARATOR MATERIALS INVESTIGATED

Film Type Separators

	<u>Material</u>	<u>Film Composition</u>	<u>Supplier</u>
1.	PUDO 193	regenerated cellulose	Du Pont
2.	SWRI GX 110	radiation grafted polyethylene	The Jet Propulsion Laboratory
3.	Borden 5-9107-C-1	10% copolyvinylmethylether- maleic-anhydride 90% methylcellulose	Monomer-Polymer Lab. The Borden Chemical Co.
4.	Borden 5-9107-21	methylcellulose + 90% KOH	The Borden Chemical Co.
5.	Borden 5-9107-29	polyvinylalcohol (42-88)	The Borden Chemical Co.
6.	Borden 574-151F	methylcellulose	The Borden Chemical Co.
7.	ESB 1021G	heterogeneous ion exchange membrane	ESB Incorporated
8.	Permion 110	radiation grafted polyethylene	RAI Research Corp.
9.	Permion 116	radiation grafted polyethylene	RAI Research Corp.
10.	Permion 1770C	chemically grafted polyethylene	RAI Research Corp.
11.	Narmco	not revealed	The Jet Propulsion Laboratory
12.	Douglas	not revealed	removed from cells supplied by Goddard Space Flight Ctr.
13.	Dewey and Almy E-5114	not revealed	W. R. Grace Co.
14.	DuPont 7Q109A1	ion exchange membrane based on fluorine containing monomers	DuPont de Nemours

TABLE 1 (contd)
SEPARATOR MATERIALS INVESTIGATED

Film Type Separators

	<u>Material</u>	<u>Film Composition</u>	<u>Supplier</u>
15.	Permion 2290	chemically grafted polyethylene	RAI Research Corp.
16.	Calcium hydroxide		ESB Inc. electrodes coated by General Electric Research
17.	Polyimidazopyrrolone (Pyrrone) films		NASA - Langley Research Center
18.	Pellon 2505KW	non-woven polyamide	Pellon Corporation
19.	Pellon T15045	2505K - 3 times washed + org. wetting agent	Pellon Corporation
20.	Pellon T15046	2505K - HCl washed + org. wetting agent	Pellon Corporation
21.	Pellon T15047	2505K - KOH washed + org. wetting agent	Pellon Corporation
22.	Pellon T15048	2505K - 3 times washed cellulose treated	Pellon Corporation
23.	Pellon T15049	2505K - HCl washed cellulose treated	Pellon Corporation
24.	Pellon T15050	2505K - KOH washed cellulose treated	Pellon Corporation
25.	Chem-Sorb KS-900	non-woven polyamide	Chemsorb, Inc.
26.	Permion 2291	radiation grafted polyethylene	RAI Research Corp.

2.0 BENCH SCREENING TESTS

2.1 Film Type Separators

2.1.1 Electrolyte Absorption

In membranes, the absorption of liquid is the first step in the solution process. Solvent molecules can easily enter the concentrated polymer phase, since only the movement of chain segments is required. Such movements are relatively unrestricted due to the flexibility of most polymer chains. Since only portions of the chain must move to permit solvent diffusion, swelling is a rapid process compared to solution (or dispersion) of the polymer where many segmental diffusional movements are required to disentangle individual chains from their neighbors. The extent to which swelling and absorption occur varies with the nature of both polymer and solvent. Swelling is more pronounced with polymers of high molecular weight and is a reflection of the osmotic pressure difference between the absorbed liquid and the external solution.

With crystalline polymers, swelling occurs by solvent penetration into amorphous regions, with the crystalline regions serving as effective cross links and preventing solution. The cellulose, modified polyethylenes, and polyvinyl alcohol polymers among others, are crystalline polymers in which the extent of crystallization affects the solubility and swelling of the polymer in solvents. Modification of these by inclusion of polar groups can significantly alter swelling or solubility, if the polymer-solvent interaction is strengthened. In general, the more polar groups contained in the membrane,

the greater the absorption of polar liquids. It is, however, interesting to note, that increased solvation does not always lead to solution.

Cellulose is soluble in 10 percent NaOH, where the crystalline lattice is weakened sufficiently to permit solubilization. At NaOH concentrations greater than 10 percent, conversion to the highly crystalline alkali cellulose occurs and the cellulose is again not soluble.

In Table 2 are listed the weight of 40 percent KOH absorbed on a unit weight and volume basis by each of the homogeneous film type separators examined in the present study. Measured values range from 3.5 g/cc of dry separator for cellophane to 0.2 - 0.35 g/cc for the least absorbent materials.

High electrolyte absorption is critical to the use of a separator in a battery since the electrical resistance, the diffusion of zincate and of dissolved silver species, zinc penetration, dimensional changes in the electrolyte and loss of tensile strength all depend to some extent on the volume of electrolyte taken up by the separator.

The variation in quantity of electrolyte absorbed by the various films correlates well with the electrical resistance measurements on these same films in 40 percent KOH except for the NARMCO and pyrrone films which had lower than expected conductivity despite rather high electrolyte pick-up. A description of the preparation of pyrrone polymers has recently been published³ and the electrochemical properties of the NARMCO type film reported.⁴ The electrolyte (40 percent KOH) pick-up of these modified polybenzimidazole

TABLE 2

ELECTROLYTE ABSORPTION AND RETENTION

Sample	Electrolyte Absorption (40% KOH)		Electrolyte Retention (g/cc)
	(g/cc)	(g/g)	
PUDO 193	3.46	2.36	3.02
SWRI GX110	1.14	0.95	1.01
Borden 5-9107-C-1	0.592	0.44	0.535
Borden 5-9107-21	0.568	0.49	0.503
Borden 5-9107-29	1.64	1.28	1.57
Borden 574-151F	0.328	0.26	0.303
ESB 1021G	0.198	0.13	0.185
Permion 110	0.86	1.32	0.65
Permion 116	0.81	1.15	0.71
Permion 1770C	0.48	1.65	0.41
Permion 2290	0.73	0.76	0.70
Permion 2291	0.52	0.72	0.50
Narmco	1.40	3.34	1.20
Douglas.	0.309	0.12	0.270
Dewey and Almy E-5114	0.800		0.749

TABLE 2 (contd)

ELECTROLYTE ABSORPTION AND RETENTION

Sample	Electrolyte Absorption (40% KOH)		Electrolyte Retention (g/cc)
	(g/cc)	(g/g)	
DuPont 7Q109A1	0.603	0.52	0.486
Calcium hydroxide	-		-
Polimidazopyrrolone (Pyrrone films)	3.4	1.30	3.2
Pellon 2505KW	0.87	2.86	0.84
Pellon T15045	0.96	2.30	0.69
Pellon T15046	0.83	2.92	0.80
Pellon T15047	0.79	2.71	0.77
Pellon T15048	0.72	2.05	0.70
Pellon T15049	0.79	2.15	0.75
Pellon T15050	0.79	2.02	0.76
Chem-Sorb KS-900	1.02	3.70	0.96

films reportedly could be varied from 15-260 percent based on the dry weight of the film. The resistivity of the more absorbent film was reported as being $90 \text{ } \Omega\text{-cm}$. Based on the thickness of film examined in this work, this works out to be $8.7 \text{ } \Omega\text{-cm}^2$ considerably in excess of the $1.46 \text{ } \Omega\text{-cm}^2$ here measured. The electrolyte absorption figures vary in similar fashion - 260 percent compared to 430 percent. By comparison, cellophane absorbs 340 percent of its original dry weight of 40 percent KOH in achieving an electrical resistivity of $8.7 \text{ } \Omega\text{-cm}$.

2.1.2 Electrical Resistance

Values of the increase in electrical resistance caused by the introduction of a separator into a battery are probably the most directly applicable measurement made of separator properties. As previously stated, the measured value is the result of a number of physical and chemical properties of the material and gives a direct measure of the energy losses in the battery attributable to the separator. Two methods of measurement have been advocated and both were employed in this work. The methods vary in the manner in which the current is passed through the cell. The ac method utilizes a high frequency alternating current (1590 Hz) which is imposed on high surface area inert electrodes. A voltage drop is measured across the separator clamped between two halves of a conductance cell by use of a four terminal conductance bridge capable of isolating resistive, inductive and capacitive impedances. In the dc method, a constant current is imposed across a cell divided by the separator, and the voltage drop across

the separator measured using reference electrodes in Luggin capillaries. Comparison of values obtained using the two methods indicates a somewhat lower resistivity reading is obtained by the dc method. Especially was this true for the higher resistance films. The ac method is, however, more quickly run and has a much higher reproducibility on a day-to-day basis. Hence, the bulk of the resistance measurements reported were made using ac method and a Wayne-Kerr Bridge fitted with a low impedance adaptor.

In Table 3, the resistance measurements are given for the film type separators examined. The values range over two orders of magnitude but only those which fall below $1.00 \mu\text{-cm}^2$ have shown useful performance in cell testing. Cellophane has the lowest resistance found which accords with its high electrolyte absorption. It is followed by the polyvinyl alcohol film, BORDEN 59107-29, and the polycarboxylic acid-polyethylene graft copolymers.

2.1.3 Dimensional Changes

Table 4 lists the dimensional changes which result from the interaction of the separator films and 40 percent KOH. In an isotropic film, the volume expansion which occurs upon absorbing the electrolyte would result in equal dimensional changes in all of the separator dimensions. That these are not isotropic films is evident from the data in Table 4, where, in the majority of the examples, the change in film thickness is the predominant effect and the factor which must be considered in the design of cells wherein these are to be used. Several of the samples appear to contract in thickness in the equilibration but the observed differences are small enough to be accounted for by surface irregularities and measurement precision. As might be expected,

ELECTRICAL RESISTANCE AND SAMPLE THICKNESS

Sample	Electrical Resistance (AC)		Sample Thickness (cm x 10 ³)	
	Ω -cm ²	Ω -cm	dry	in 40% KOH
PUDO 193	0.065	8.7	2.5	7.5
SWRI GX110	0.095	27	3.0	3.5
18% KOH pre-equil. Borden 5-9107-C1	0.052	7.2	3.6	7.2
Borden 5-9107-21	1.33	317	3.5	4.2
Borden 5-9107-29	0.145	15	4.0	9.8
18% pre-equil. Borden 574-151F	0.328	33.6	3.8	5.8
ESB 1021G - treated	0.198	124.3	9.6	10.7
Permion 110	0.157	34	5.4	4.6
Permion 116	0.300	57.7	6.3	5.2
Permion 1770C	0.207	39.8	- 1	5.2
Permion 2290	0.27	79.4	3.1	3.4
Permion 2291	0.69	215.6	3.0	3.2
Narmco	1.46	150.5	- 2	9.7

TABLE #3 (contd)

ELECTRICAL RESISTANCE AND SAMPLE THICKNESS

Sample	Electrical Resistance (AC)		Sample Thickness (cm x 10 ³)	
	Ω -cm ²	Ω -cm	dry	in 40% KOH
Douglas	1.21	20.2	60	60
Dewey and Almy E-5114	0.242	26	9.6	10.3
DuPont 7Q109A1	29.5	3500	8.9	8.5
Calcium hydroxide			5-25	
Polimidazopyrrolone (Pyrrone films)	0.222	50.5	2.5	4.4
Pellon 2505KW	0.083	4.0	20.6	20.8
Pellon T15045	0.094	4.7	30.3	20.1
Pellon T15046	0.091	4.1	22.4	23.0
Pellon T15047	0.091	4.6	22.4	22.0
Pellon T15048	0.091	4.4	20.6	20.7
Pellon T15049	0.098	4.8	20.2	20.4
Pellon T15050	0.115	5.7	20.4	20.4
Chem-Sorb KS-900	0.054	2.3	20.6	23.6

¹ - Thickness measurement not reliable because dry material is badly wrinkled.

² - Received wet. After washing and drying thickness is 8.2×10^{-3} cm

TABLE 4

DIMENSIONAL CHANGES (%)

Sample	Length	Width	Thickness	Volume Swell Factor
PUDO	+ 6.0	- 3.0	+300	3.08
SWRI GX110	+ 5.9	+ 7.2	+ 16.7	1.32
Borden 5-9107-C1	+ 0.6	+ 0.9	+ 200	2.03
Borden 5-9107-21	+ 0.8	+ 0.5	+ 20	1.22
Borden 5-9107-29	- 4.0	- 4.4	+225	2.25
Borden 574-151F	0	+ 0.2	+ 52.6	1.53
ESB 1021G	+ 0.7	+ 1.4	+ 11.5	1.14
Permion 110	+10.4	+ 9	- 15	1.02
Permion 116	+ 6.6	+ 8.8	- 17.5	0.96
Permion 1770C	+13	+12	- 10 ¹	1.39
Permion 2290	+ 4	+ 5	+ 9.7	1.20
Permion 2291	+ 3	3	+ 6.7	1.13

estimated

TABLE 4 (contd)

DIMENSIONAL CHANGES (%)

Sample	Length	Width	Thickness	
Narmco	+ 6.6	+ 6.0	+ 18	1.33
Douglas	0.0	.0.0	.0.0	0.00
Dewey and Almy E-5114	-<1	+ 2	+ 7.3	1.10
DuPont 7Q109A1	-<1	- 7.5	-<1	0.93
Polimidazopyrrolone (Pyrrone films)	+ 7.8	+ 7.5	+ 76	2.04

high electrolyte pick-up and greater comparable dimensional changes are linked together. Cellophane PUDO 193 increases in volume by 300 percent, BORDEN 59107-29 by 215 percent, and the polyethylene graft by 90-130 percent.

2.1.4 Tensile Strength

The tensile strength of the dry separator is an important property in the utilization of the film in constructing silver zinc batteries where multi wraps are required. Since the folding of the separator around the plate edges can impose considerable strain, both strength and elasticity are required. The fact that anisotropic dimensional changes of considerable magnitude occur in the film when equilibrated with electrolyte makes it even more important that the film be physically strong enough to withstand the stresses of assembly and battery activation. Care must be exercised in the manner in which the separator is placed in the battery so that the changes which occur on addition of electrolyte do not exceed the mechanical strength of the separator. It is well documented that with polar polymers, the absorption of water causes a diminution in physical strength. It is expected, and has been observed, that the absorption of KOH electrolyte causes a loss in physical strength of film-type separators and that the greater the quantity absorbed, the greater the strength loss. Anisotropic behaviour of tensile strength is also observed and is illustrated by measurement of tensile strength in the directions perpendicular to one another.

The data accumulated on the film separators is given in Table 5. Each sample was equilibrated for 24 hours at $70 \pm 2^\circ\text{F}$, at a relative humidity of 50 ± 5 percent for the dry measurement, and for 24 hours, in 40 percent KOH, at $70 \pm 2^\circ\text{F}$. for the wet measurement. A marked difference is apparent in the strength of the cellulose based samples which have tensile strengths at break of 10,000 - 20,000 psi and which lose 50-75 percent of this strength upon absorption of KOH; and the polyethylene copolymers which are in the 1700 to 2200 psi range in the dry state, drop to 800 to 1000 psi tensile strength upon equilibration. The equilibrated polyvinyl alcohol film, BORDEN 59107-29, has a tensile strength of only 400 psi on equilibration. Since each of these materials has been successfully used in battery construction without failure due to physical limitations, it can be assumed that tensile strength as low as 400 psi in the KOH equilibrated film is sufficient.

2.1.5 Oxidation and Hydrolytic Resistance

Granted the properties required for an ideal separator, the retention of these properties under the conditions imposed on a separator in a silver-zinc battery is a matter of some importance. In order to test for property retention, one must consider at least the changes that can occur due to the highly oxidizing environment of the silver oxide electrode and its soluble species and the degrading effect of the KOH electrolyte. Tensile specimens cut from each of the separator films were used. These were immersed in 40 percent KOH which was saturated with both zinc oxide and

argentous oxide. Solid argentous oxide was included in each test vessel to maintain saturation throughout the test. The test consisted of immersion of the tensile specimens at 45 °C for 168 and 336 hours. Changes in tensile strength were indicative of changing structure caused by components of the battery environment.

Examination of the last column of Table 5 shows that only cellophane and polyvinyl alcohol were appreciably degraded by the electrolyte. In the oxidation test, each of the samples was discolored by silver pick-up but only cellophane PUDO 193 and the polyvinyl alcohol films were seriously degraded.

2.1.6 Pore Size and Tortuosity

The approach used in determining pore size in membrane separators requires adoption of the pore model of membrane structure and assumes the applicability of Poiseuille's Law which relates the diameter of a tube with the time rate of flow of a liquid through the tube. Averaging over the surface tested gives a measure of the mean size of the pore through which the flow occurs. The method used, the measured values and necessary equations are given in the Appendix. The values of mean pore diameter obtained on the test samples are listed in Table 6. These vary from a low of 3 Å for BORDEN C-1 to a high of 5000 Å for the sample separator removed from the DOUGLAS cells. The value obtained for cellophane (24 Å) is markedly different from that previously reported (300 Å)(2). This latter value was found to be due to an error in calculation.

TABLE 5

TENSILE STRENGTH MEASUREMENTS (psi)

Sample	dry cross direction		in 40% KOH
PUDO 193	22,930 Machine Direction 12,210 Cross Direction		4100
SWRI GX110	1880	1265	990
Borden 5-9107-C1	10,340	11,280	-
Borden 5-9107-21	6,200	6110	2880
Borden 5-9107-29	4,310	4040	426
Borden 574-151F	10,490	10,310	5630
ESB 1021G	660	620	420
Permion 110	2,275	1790	850
Permion 116	1,750		910
Permion 1770C	-		(puckered surface)
Permion 2290	2,060		755
Permion 2291	1,850		1350

TABLE 5 (contd)

TENSILE STRENGTH MEASUREMENTS (psi)

Sample	dry	in 40% KOH
NARMCO	Brittle Material	Data not taken
Douglas	insufficient sample	insufficient sample
Dewey and Almy E-5114	840	840
DuPont 7Q109A1	2800	4200
Polimidazopyrrolone (Pyrrone) films	Brittle Material	Data not taken
Pellon 2505KW	860	640
Pellon T15045	700	830
Pellon T15046	700	600
Pellon T15047	700	994
Pellon T15048	715	566
Pellon T15049	1330	1145
Pellon T15050	1150	1290
Chem-Sorb KS-900	425	370

TABLE 6
POROSITY AND TORTUOSITY

Sample	Porosity - P (cc/cc)	Tortuosity	Pore Diameter
PUDO 193	0.804	2.0	24
SWRI GX110 18% KOH pre-equil.	.617	3.0	9
BORDEN 5-9107-C1	.209	0.91	9
BORDEN 5-9107-21	.335	7.6	22
BORDEN 5-9107-29 . 18% KOH pre-equil.	.523	2.1	24
BORDEN 574-151F treated	.154	1.7	9
ESB 1021G	.125	2.9	35-170
PERMION 110	.603	3.4	25
PERMION 116	.607	4.4	10
PERMION 1770C	.222	2.2	17
PERMION 2290	.436	4.4	13
PERMION 2291	.317	6.1	10-25
NARMCO	.755	7.9	84
DOUGLAS	.222	1.6	5,000
DEWEY AND ALMY E-5114	.524	2.6	324
DuPONT 7Q109A1	.60	2.7	66
Polimidazopyrrolone (Pyrrone) films	.51	3.8	13

Samples were run in duplicate and repeated where large differences were found. Where reproducible results were not obtained, the range of the values is reported in this Table.

The tortuosity parameter, also given in Table 6, is an effort to correct for obvious defects in the chosen capillary model. It is the ratio of the mean effective pore length to the measured thickness of the sample. The tortuosity figures calculated using this approach are given in Table 6. These vary from 0.91 to 7.9.

2.1.7 Zinc Diffusion

The rate of diffusion of zincate dissolved in KOH through the film separators was measured using a two-compartment cell separated by the film. The zincate concentration was one molar in zincate on one side and 10^{-4} molar on the other. The zincate flux, J, is given by

$$J = D \text{ grad.}$$

where D is diffusion coefficient of zincate in the solution. For well stirred solutions, as in this case, grad C is approximated by $\Delta C/l$ where l is the diffusion layer thickness, and ΔC the change in concentration on the dilute side. Since $C_1 \ll C_2$, ΔC is small and to a first approximation can be considered constant. The rate of zincate transfer through the membrane can then be written

$$\frac{\Delta M}{\Delta t A} = \frac{\Delta C}{\Delta t} \frac{V}{A} = K$$

Where V is the volume of the dilute compartment, A exposed membrane area, Δt time interval of measurement, and ΔM the molar change in zincate concentration in the dilute compartment. The fluxes measured using the procedure recommended by Lander (1) are shown in Table 7. These vary over three orders of magnitude from 26×10^{-8} to 0.04×10^{-8} (which latter value exceeds the detectability limits of the method and hence can be read as essentially no transport in the time limit of measurement).

In considering the results of battery testing and the times obtained for the various separators in the zinc penetration test, the indication is that the lower the zincate permeation rate, the more resistant is the film in cells to zinc shorting. Correlation is also obtained, for the most useful separators, between electrical resistance and zinc penetration, so that the same limits can probably be applied; a resistivity greater than $1.0 \mu\text{-cm}^2$ would not be useful, the zincate permeation corresponding to the resistance (roughly $> 0.1 \times 10^{-8}$) would, by present indications, be adequate to control zinc dendrite growth. In cell testing utilizing the nickel-zinc couple failure by zinc shorting was not observed with films showing zincate permeation rates which ranged from 0.4×10^{-8} to 0.04×10^{-8} moles $\text{Zn}/\text{cm}^2\text{sec}$. The SWRI film had the highest measured flux rate but performed on a par with films of substantially lower zincate permeation rates (26×10^{-8} to 0.2×10^{-8}) all failing after 11 to 15 cycles. Acceptable cycle performance was set at 30 cycles.

TABLE 7

PERMEABILITY MEASUREMENTS

Sample	Silver Diffusion (moles Ag/cm ² sec x 10 ¹⁰)	Zinc Diffusion (moles Zn/cm ² sec 10 ⁸)
PUDO 193	35.5	2.7
SWRI GX110	121.1	26.0
Borden 5-9107-C1	6.7	0.2
Borden 5-9107-21	25.1	0.2
Borden 5-9107-29	38.6	1.2
Borden 574-151F	4.3	6.8
ESB 1021G	6.3	1.8
Permion 110	79.9	0.32
Permion 116	57.2	0.61
Permion 1770C	46.6	0.35
Permion 2290	34	0.04
Permion 2291	4.8	0.08
Narmco	4.3	1.8 - 18
Douglas	23.2	5 - 77
Dewey and Almy E-5114	83.0	2.1
DuPont 7Q109A1	2.6	0.2
Polimidazopyrrolone (Pyrrone) films	(no detectable silver at 120 hrs)	0.05

2.1.8 Silver Permeability and Reactivity

The method used measures the rate of self-diffusion of Ag^{110} tracer ions through the equilibrated films. The details of the procedure are given in the Appendix together with a description of the apparatus and the methods of calculation. The values obtained are given in Table 7. Noteworthy in this data is the fact that cellophane PUDO 193 and the polyvinyl alcohol film, both of which react with the dissolved silver oxide species, retard silver migration as effectively as PERMION 2290 which has a resistance higher by almost an order of magnitude. This effect is further illustrated in Table 8 where the values listed represent the amount of silver pick-up by a one inch piece of separator immersed in 40 percent KOH saturated with ZnO and Ag_2O . The most reactive films are cellophane, polyvinyl alcohol and ESB 1021 G. The most unreactive are the methyl cellulose films of Borden and the grafted polyethylenes.

2.1.9 Zinc Penetration

The apparatus and procedure used in this determination are described in Appendix I. The test measures the time required to penetrate a separator clamped in contact with a zinc electrode on which zinc is being plated. Transport of zincate is through the separator and hence the rate of this transport controls the deposition. The time is measured for dendrite growth to occur through the body of the separator and penetration is detected by monitoring the potential between a platinum indicating electrode on one face of the separator and connected with the zinc

TABLE 8

SILVER REACTIVITY AND RATE OF SILVER ADSORPTION

Sample	Silver Adsorption (g Ag/in ² /hr x 10 ³) (sample mounted in cell dry)
PUDO 300	62.7
SWRI GX110	1.09
Borden 5-9107-C1	1.5
Borden 5-9107-21	3.85
Borden 5-9107-29	13.9
Borden 574-151F	1.33
ESB 1021G	62.9
Permion 110	0.8
Permion 116	0.78
Permion 1770C	0.65
Permion 2290	0.65
Permion 2291	0.73
Narmco	9.9
Douglas	
Dewey and Almy E-5114	11.3
DuPont 7Q109A1	0.27
Polimidazopyrrolone (Pyrrone) films	72.6

cathode on the other face. Penetration times are recorded in Table 9, where times to failure are shown, as well as a zinc penetration value - the time to penetration for a unit thickness of the various films.

Those films with zinc penetration values exceeding 3.0 gave best cycle life in the nickel-zinc cell testing with a single exception. Separator E 5114 performed well in the cell testing (28 cycles to failure) despite a low zinc penetration value. Attempts to follow up on this material were thwarted when it became unavailable.

2.1.10 Zinc Oxide Adsorption

The measurement involves comparison of zincate concentration in the pore liquid of the film with that in the bulk equilibrating electrolyte. It has been proposed that separator films which exclude zincate have increased resistance to zinc shorting. The distribution coefficients measured for the four films yielding the best results in the zinc penetration and cell testing are:

BORDEN 59107-151 F	0.24
PERMION 2290	0.73
PERMION 2291	0.84
DEWEY-ALMY E-5114	0.86

and for the four separators giving shortest cycle life

BORDEN 59107-29	0.82
PUDO 193	0.87
SWRI GX 110	0.68
PERMION 110	0.68

No obvious correlation was found between the zincate distribution and the other screening test results.

ZINC PENETRATION

Sample	Time to Penetrate	
	Hours	Hrs/cm x 10 ²
PUDO 193	1.5	2.0
SWRI GX110	0.70	1.37
Borden 5-9107-C1	1.29	1.70
Borden 5-9107-21	3.01	7.14
Borden 5-9107-29	0.31	0.32
Borden 574-151F	3.23	5.6
ESB 1021G	20.2	18.9
Permion 110	0.89	1.9
Permion 116	0.72	1.4
Permion 1770C	2.07	3.76
Permion 2290	2.11	6.2
Permion 2291	-	10.7
Narmco	7.3 - > 24	21 - > 70
Douglas	2.4	1.21
Dewey and Almy E-5114	1.4	1.4
Polimidazopyrrolone (Pyrone) films	5.2 - > 25	11.8 - > 56

2.2 Absorbers

In addition to the film type separators which are used principally to control the diffusion of soluble electrode species, open pored, fibrous structures are used as components of the total separator system. These absorbent separators are usually non-woven synthetic polymer mats made from dynel, polyamide, or polypropylene fibers, but may also be of inorganic fibers. These materials serve as electrolyte reservoirs for the electrodes during charge and discharge of the battery. The open structure gives high liquid absorption, low resistivity and reduces diffusional problems immediately adjacent to the electrodes. An additional benefit derived from the use of absorbers is the spacing of the membrane separators from contact with the electrodes, thus delaying failure modes attributable to such contact. Measured electrolyte absorptions range from 0.70 to 1.0 g/cc of dry separator. The wetting properties of the absorbent separator is of great importance in achieving the low electrical resistivity required for optimum battery performance. Fast initial wetting is usually obtained by use of a wetting agent added either deliberately, or present as a result of other operations in the formation of the fiber or mat. Polyamides, polypropylene, and dynel (a copolymer of vinyl chloride and acrylonitrile) are hydrophobic polymers having contact angles (wetting angle) with water of $< 60^\circ$. The use of wetting agents absorbed onto the polymer fiber lowers the contact angle and promotes rapid wet out. The non-woven mats usually used as absorbent separators, can be viewed as an assemblage of randomly oriented capillaries. The extent to which wetting and wicking up the separator occurs depends on the contact angle between the liquid and fiber and the distance between adjacent fibers.

In order to test the usefulness of various electrolyte absorbent mats as separators, many of the same tests used to measure film separators were used. Measurements were made of electrolyte absorption, electrical resistance, dimensional changes, tensile strength and the changes in physical properties occurring due to exposure to the cell environment. This data is presented in Table 10 for the absorber materials considered in this work.

For these absorbent separators, the speed and manner in which the electrolyte absorption occurs is of prime importance in the initial activation and continuing functioning of the cells in which they are used. To gain some insight into the differences in wetting behavior of these separators, several other test methods were adopted from those in use in the textile industry. Measurement was made of

- 1) the time required for a drop of electrolyte placed on the mat to be absorbed into the mat,
- 2) the height to which electrolyte would wick up the fibrous structure and the time required for this wicking to occur,
- 3) the permeability of the various materials to air - a measure of the porosity of the mat,
- 4) the time required to achieve minimum electrical resistance with the absorber completely immersed in electrolyte and finally,
- 5) cell testing in silver-cadmium and nickel-zinc cells.

Table 10

Absorber Samples - Property Data

	Electrolyte Absorption % w/w	Electrolyte Retention %	Electrical Resistance $\Omega\text{-cm}^2$	Wicking Height mm at 30 minutes	Thickness cm		Tensile Strength (psi) in 40% KOH	Tensile Strength (psi) after electrolyte exposure	Air Permeability secs/30 cc	Minutes to Minimum Resistance	% Ethanol Extractables
					dry	wet					
Pellon 2505K	390	94	0.08	75	0.020	0.021	640	540	6.8	<1	5.2
T15045	320	71	0.09	52	0.020	0.020	830	650	6.5	30	-
15046	390	96	0.09	52	0.022	0.023	600	570	5.2	30	-
15047	380	97	0.09	80	0.022	0.022	990	980	5.7	20	-
15048	315	97	0.09	18	0.021	0.021	560	550	9.5	< 1	-
15049	315	95	0.098	1	0.020	0.020	1140	910	9.0	20	-
15050	300	96	0.115	0	0.020	0.020	1290	900	13.2	30	-
2530	450	93	0.14	0.2	0.028	0.028			1.3	1	3.7
Chem Sorb KS900	370	94	0.05	3	0.021	0.024	370	340	1.3	< 1	1.8
Kendall EM309	-	-	0.07	0	0.0037	0.0037	-	-	2.7	< 1	-
EM476	220	92	0.15	4	0.011	0.011			2.0	5	1.4

Since the fibers used to make the non-woven separators are essentially non-wetting to the battery electrolyte, various agents are added to provide adequate wet-out. These agents are incorporated on the fibers. Various manufacturers, of course, use different addition agents to provide this rapid and complete wetting. In order to determine the amount of such addition agents and to examine the types of agents used (since some of the possible surfactants are known to affect electrode performance) an extraction procedure was adopted to remove the surfactants from the fibers. This consisted of extraction of the fibers in a Soxhlet extraction apparatus using 95 percent ethanol at the boiling point for two hours.

The detailed methods for the extraction procedure as well as for the wetting tests are given in Appendix I. Table 11 examines the changes in wet-out properties as a result of extracting the wetting aids.

The most seriously affected property is wicking of the electrolyte up the separator. Changes in the electrolyte wicking properties, of the separator would considerably affect the performance of sealed cells containing limited electrolyte. The ability to wick electrolyte is also the most significant variation among the samples listed in the table of absorber properties varying from essentially zero to 7.5 cm in 30 minutes. In the cell testing performed in three-plate cells, the effect of the variability in wetting characteristics was not a controlling factor in cell performance since the cells were not run utilizing limited electrolyte. Rather, discrimination among the samples was sought in the electrical performance and the maintenance of this performance through the

Table 11

Comparison Wetting Characteristics of Solvent
(E)' Extracted vs "As Received" Absorbers (μ)

	Pellon 12,777		14000		15126		16015	
	E	U	E	U	E	U	E	U
Wicking hgt in cm @ 30 mins	0.5	3.7	0.8	7.3	0.0	4.0	0.0	5.5
Wet Out Time (seconds)	47	17	19	14	12	10	73	66
Electrical Resistance Ω -cm ²	0.138	0.092	0.227	0.059	0.077	0.058	0.161	0.060

cycle regime. Such differentiation as did result could not be considered significant. Additional cell testing is required in cells containing limited electrolyte in order to meaningfully examine wetting characteristics of the separator as a function of the electrical performance of the cell.

2.3 Cell Screening Tests

To supplement the non-battery screening tests, each separator was examined in three-plate cells to provide at least qualitative confirmation of the significance of property variations observed in the bench tests on battery performance. Two electrochemical couples were chosen so that a separate measure of the effects of the silver and zinc electrode could be obtained.

Two layers of primary separator and a single layer of absorbent separator were used in constructing the cells. A standard pack tightness based on the expansion of the separator in 40 percent KOH compared to original thickness was used. Cells were shimmed with polysulfone spacers to achieve the calculated pack dimension. Electrode dimensions and other pertinent details of cell construction and the cycling regime are given in Table 12.

As originally conceived, fifteen cycles using the nominal five-hour rate were considered a minimum performance level for further consideration of the particular separator. This was increased to thirty cycles so as to provide better discrimination among the test materials. The cells were vented and flooded with electrolyte, levels adjusted to plate top height with the cell fully

Table 12

Electrode Data

	Silver	Cadmium	Nickel	Zinc
Dimensions	1.75x1.875x0.028	1.75x1.875x0.050	1.75x1.875x0.028	1.75x1.875x0.041
Grid	2/0 Ag	2/0 Ag	Nickel Screen	2/0 Ag
Electrode Type	Sintered	Pressed Powder	Sintered	Pressed Powder
Theor. Capacity A.H.	3.12	2.30	-	3.45
Capacity @ 5 Hr-Rate A.H.	1.73	1.75	0.75	2.3
Manufacturer	ESB	ESB	ABL	ESB

Cycling Regime

Silver-Cadmium

- 1) discharge $I = 0.50 \text{ A}$ to 0.80 V
- 2) recharge constant current $I = 0.10 \text{ A}$ to replace 125% of preceding discharge capacity

Nickel-Zinc

- 1) discharge $I = 0.25 \text{ A}$ to 1.30 V
- 2) recharge constant current $I = 0.07$ to replace 125% of preceding discharge capacity

charged. In those tests in which the film separator was examined, a standard absorber, PELLON 2505 KW, was used as the retainer on the negative electrode. Where the absorber was the variable, two layers of cellophane were used as the standard film separator.

In Table 13 are grouped the results of the cycling testing of all the film separator materials examined. For the absorbers, cycle life to one-half original capacity was not appreciably different among those tested, varying from 15 to 24 for the nickel-zinc testing and from 22 to 30 for the silver-cadmium cell results.

2.4 Coated Electrodes

G. E. has previously investigated electrodeposited films of Ca(OH)_2 as separators in alkaline silver cells⁵. In order to obtain comparative data on these coatings, the silver and nickel electrodes were supplied to G. E. Research and Development Center to be coated with Ca(OH)_2 . The coating solutions contained 150 g/l calcium acetate, buffered with 4 or 5 g/l Ca(OH)_2 . Coating current density was 100 mA/cm² and coating thickness was monitored by terminating the deposition at a specified voltage. The coating thickness was between 2.0 and 5.0 mils for the silver electrodes and from 1.0 to 5.0 for the nickel electrodes. Weight gain ranged from 0.32 to 1.16 grams.

Each electrode chosen for cell testing was examined under a low power microscope to detect flaws and inhomogeneities in the coating. Where flaws or inclusions were found, these electrodes were discarded. In all, 12 coated nickel electrodes (Table 14) and six coated silver electrodes

Table 13

Separator Performance - Electrical Cycling Tests

Ag-CdO Cycle to 50% Original Capacity	Original Capacity AH	Separator	Ni-ZnO Cycle to 50% Original Capacity	Original Capacity AH
> 30, > 30	2.27	PUDO 300	11, 11	1.30
26, 27	2.11	SWRI GX110	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, > 30	1.85	Borden 5-9107-29	15, 16	1.17
> 30, > 30	1.46	Borden 574-151F*	> 30, 26	1.48
9, 12	1.24	ESB 1021 G	11, 11	1.13
30, 27	2.18	Permion 116	15, 17	1.51
21, 27	1.51	Permion 110	15, 12	1.51
> 30, > 30	2.36	Permion 1770C	> 30, > 30	1.46
> 30, > 30	1.84	Permion 2290	28, > 30	1.26
> 30, > 30	2.20	Permion 2291	30, 30	1.10
> 30 > 30	1.15	Narmco	8, 13	1.10
25	1.21	Douglas	11, 19	1.14
19, 24	1.63	Pyrrone	-	-
14, 25	1.51	Dewey Almy E5114	27, 28	1.51
20	1.72	DuPont 7Q109A1	-	-
23, 23, 30	2.15	Ca(OH) ₂ Coating	28, 18, 18	1.17

TABLE 14

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 15) were tested under the same conditions used for the other separators. A single layer of PUDO 193 was used to supplement the Ca(OH)_2 coating in every case.

Considering cell failure to be loss of 50 percent of original capacity, the coated silver electrodes gave 20-23 cycles operated against cadmium electrodes while the Ca(OH)_2 coated nickel electrodes gave 16-28 cycles to the same end point when operated against zinc. The cell cycling data is summarized in Table 16. In each case, tear down analysis of the cell after failure indicated that failure occurred at the electrode edges. This is probably related to the "edge effect" encountered in plating operations, and if overcome, a two mil coating appears to offer sufficient protection to meet the requirements of this test program. Neither silver staining, nor zinc penetration of the single cellophane layer were extensive compared to controls containing only cellophane. No meaningful correlation of coating thickness with cycle life or voltage was observed.

2.5 Silver-Zinc Cell Construction

Based on the combined bench screening and three-plate cell testing, PERMION 2290, PERMION 2291, and PERMION 1770 C were selected for testing in 12 Ahr silver-zinc cells. The following criteria were used in the selection:

- 1) electrical resistivity $< 1.0 \mu\text{-cm}^2$
- 2) greater than 30 cycles in the three-plate cell testing in both silver-cadmium and nickel-zinc cells

TABLE 15

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

TABLE 16

ELECTRICAL CYCLING PERFORMANCE

Coated Electrodes

Cycle	Ni-ZnO Cell Capacity A-Hrs			Ag-CdO Cell Capacity A-Hrs		
	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) zinc penetration value > 3.0
- 4) zinc permeation rate $< 1 \times 10^{-8}$ moles Zn/cm² sec
- 5) silver permeation rate $< 0.5 \times 10^{-8}$ moles/cm² sec
- 6) no significant loss in strength after 168 hours exposure to 40 percent KOH saturated with Ag₂O and ZnO.

The Ca(OH)₂ coated electrodes also appeared very promising candidates provided the coating at the edges could be controlled more closely. This was thought to be controllable so that the coated electrodes were included in the recommended group for testing in silver-zinc cells to be constructed by the Exide Missile and Electronics Division of ESB Incorporated. Fifteen designs in all, with eighteen cells in each design were proposed and built. The individual cell groups are listed in Table I of Appendix II (Separator Systems for Test Cells). Sufficient Ca(OH)₂ coated electrodes were obtained from both General Electric and Hughes to build two groups of eighteen cells from each coating source. Cellophane PUDO 193 was included as the control separator for film type separators and PELLON 2505 K as the control for absorbant separators.

The cell design and details of construction and initial testing are given in Appendix II.

3.0 LITERATURE CITED

- (1) Cooper, J. E. and Fleischer, A., ed., "Characteristics of Separators for Alkaline Silver-Oxide Secondary Batteries," AD447301, AFAPL 9/64.
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- (3) Bell, V. L. and Jewell, R. A., "Synthesis and Properties of Polyimidazopyrrolones," J. Polymer Sci., A-1, Vol. 5, pp. 3043-3060 (1967).
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APPENDIX I

SEPARATOR TEST PROCEDURES

- References - 1) Battery Separator Screening Methods
Ed., Cooper, J. E., Fleischer, A. - AD 447301
- 2) NASA Contract 5-2860, Report 2-8, (1964),
Oberholzer, C., Kelley, J., Salkind, A., and
Weiss, E.

1.0 Electrolyte Absorption, Dimensional Changes, Electrolyte Retention and Porosity (NAS 5-2860, Reports 2 and 3)

Six samples of each material are cut (in the roll direction) to 6.50cm by 2.50cm and individually measured using a steel rule marked off in 0.5mm divisions. The thickness of each sample is measured using an Ames platform dial micrometer with a 0.5" foot dia. and a pressure of 103 gms/cm². The dial is graduated in 0.001mm. Each sample is weighed to the nearest tenth mg. on an Analytical Balance, and then immersed in approximately 100cc 40% KOH in stainless steel containers fitted with tightly fitting lids. Dimensional changes are measured at 24 hour intervals until no further changes occur. The equilibrated samples are wiped across a Lucite plate until no droplets of electrolyte are left on the plate (see Cooper & Fleischer Handbook, p. 23).

Electrolyte retention, designed primarily for screening of absorber materials, is measured on the same samples, after draining for 15 minutes on a Lucite plate positioned at 45° angle. The samples are then re-weighed. This test does not have great significance for membrane materials where little electrolyte is lost in the drain period. The precision of the weight loss for this type material is decreased because the possible absorption of CO₂ from the air, etc., cannot be considered insignificant compared to the weight of the electrolyte drained.

1.1 Calculations

1.1.1 Electrolyte absorption is the difference between the wet equilibrated and the dry sample weights. This is reported as grams absorbed per dry sample volume in cc or alternatively as grams absorbed per square inch of dry film.

1.1.2 Electrolyte retention involves the same calculations as above, using the wet sample weight obtained in the retention part of the experiment to obtain an absorption value g/cc. Percent retention is calculated by

$$\% \text{ Retention} = \frac{W_r/V_d}{W_a/V_d} \times 100$$

W_r = grams electrolyte retained

W_a = grams electrolyte absorbed

V_d = dry Sample Volume cc

1.1.3 Dimensional Changes Due to Electrolyte Absorption.

Dimensional changes are calculated from the above data from the relations

$$\% \text{ Change} = \frac{(\text{wet dimension}) - (\text{dry dimension})}{\text{dry dimension}} \times 100$$

Report the mean of three determinations.

1.1.4 Porosity (cc/cc) or internal void volume is calculated by:

$$\frac{W_w - W_d}{V_w \rho} \times 100 = \text{Porosity}$$

where

W_w = wet weight of separator-grams

W_d = dry weight of separator-grams

V_w = wet volume of separator-cc

ρ = density of absorbed liquid gm/cc

the density of the absorbed liquid is taken to be the same as the density of the equilibrating electrolyte.

2.0 Electrical Resistance

2.1 A.C. Method (Cooper-Fleischer Handbook, Chapter 6b, Kelley and Salkind)

The separator sample is cut to give a piece at least 6 cm². Larger samples permit the measurement to be made at different areas of the sample. The separator is equilibrated in 40% KOH for a minimum

of twenty-four hours prior to measurement. A drawing of the test cell is attached as Figure 1.

Measurements are made by placing the fully equilibrated sample between the two cell halves, filling with electrolyte, and balancing the bridge circuit. The method employs a Wayne-Kerr bridge which permits isolation of resistive and capacitive impedance. The resistance cell contains separate current (platinum screen) and voltage electrodes (platinum wire) with the voltage electrodes positioned as close as was practical to the membrane surface.

A blank is determined on the cell without separator. The difference between the two readings represents the separator resistance.

2.2 Calculations

2.2.1 Separator Resistance ohm-cm²

$$R' = \text{Separator Resistance ohm-cm}^2$$

$$R' = (R_s - R_o)A$$

$$R_s = \text{Cell Resistance with Separator - ohms}$$

$$R_o = \text{Cell Resistance-blank - ohms}$$

$$A = \text{Area Membrane Measured - cm}^2$$

2.2.2 Separator Specific Resistivity ohm-cm²

$$\rho = \frac{R'}{t_w}$$

$$t_w = \text{Wet Separator Thickness - cm}$$

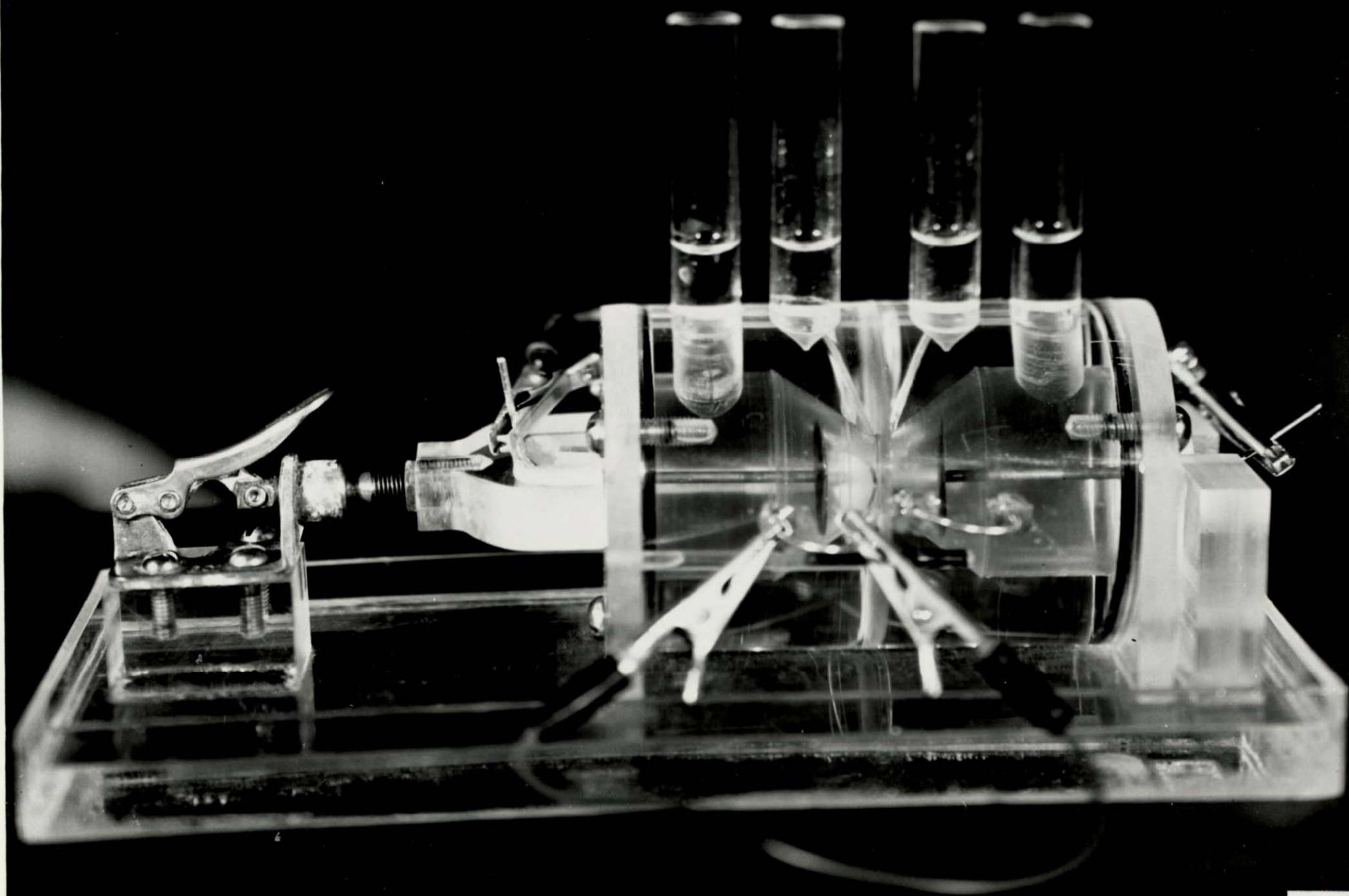


Fig. 1

2.3 Separator Resistance - DC Method

This method is essentially that described by Lander in Chapter 6a of the Cooper-Fleischer Handbook.

The cell is a modification of that used in the AC method. The platinized platinum current electrodes are replaced by disc cadmium electrodes (capacity 0.7A-hr) which are maintained in a partially discharged state. The voltage drop across the membrane is measured using two Hg/HgO reference electrodes which fit into ports in either cell half. The bottom of each port is connected by a diagonally drilled capillary to the membrane surface.

Equilibration technique and sample size are the same as in the AC method. The sample is introduced between the cell halves and the cell promptly filled with electrolyte and the reference electrodes placed. Current is passed by means of a constant current source to give 50 ma/cm². The voltage drop is measured between the two reference electrodes using either an electrometer or a potentiometer. A blank determination is made and subtracted from the cell resistance with the membrane in the path.

2.3.1 Calculations

Separator Resistance

$$R'' = \frac{E_r - E_b}{I} \quad A$$

2.3.1 Calculations (contd)

R'' = separator resistance ohm-cm²

E_r = voltage drop between Hg/HgO electrodes
with separator in path - volts

E_b = voltage drop between Hg/HgO electrodes
with separator out of path - volts

I = current - amperes

A = separator area exposed cm²

2.3.2 Separator Specific Resistivity

$$\rho'' = \frac{R''}{t_w}$$

ρ'' = separator specific resistivity ohm-cm

R'' = separator resistance ohm-cm²

t_w = equilibrated separator thickness cm

3.0 Separator Wettability

Separator wettability is measured by placing the dry separator sample in the resistivity cell, filling the cell with electrolyte, and recording the time required to attain a stable reference.

4.0 Tensile Strength at Break

Separator tensile strength measurements are made on die cut specimens 12.7cm by 2.5cm, cut in the roll direction, each of which must be carefully examined for flaws. Samples containing cracks,

nicks or inclusions must be discarded. At least five samples of each material are run and the mean value reported. The tensile strength at break is measured on samples which are conditioned both at $72 \pm 2^\circ\text{F}$, $50 \pm 5\%$ relative humidity for 24 hours, and after the 24 hour immersion in 40% KOH. A cross head speed of 2 inches per minute is used and the specimens are positioned in the rubber faced jaws so that the grip separation is 3 inches. Elongation measurements can be obtained by measuring the grip separation as the test progresses using the value at break to calculate % elongation. For the tensile measurement, the load in pounds is measured at the breaking point. Samples breaking outside the area between the jaws are not included.

The testing is carried out at $72 \pm 2^\circ\text{F}$, $50 \pm 5\%$ R.H.

4.1 Calculations

$$\text{Tensile Strength at Break} = \frac{\text{Breaking Load lbs.}}{\text{C.S.A.}}$$

C.S.A. - sample cross sectional area

$$\% \text{ Elongation} = \frac{L - L_o}{L_o} \times 100$$

L = sample length break

L_o = original length

5.0 Oxidation Resistance

This test gives a measure of the effect of electrolyte, and electrolyte soluble electrode species on the physical properties of separator materials. Tensile specimens cut in the roll direction 12.7cm by 2.5cm are immersed in 100 mls of electrolyte saturated with both zinc oxide and Ag_2O . The solution and specimens are placed in stoppered test tubes and maintained at $45 \pm 1^\circ\text{C}$ for 7 or 14 days, in a constant temperature bath. Excess solid silver oxide (Ag_2O) is maintained in each tube to prevent depletion by reaction of the dissolved specie. At 7, and again at 14 days, the samples are removed, measured, and the tensile strength at break determined as described in 2.4. A minimum of 5 specimens is measured and the mean reported. Degradation is revealed by decreases in the breaking strength of the material with immersion time in the electrolyte solution.

6.0 Pore Size

The test cell used in this determination is that pictured in Chapter 5a. of the Cooper-Fleischer Handbook. The method used is a combination of that described there by Cooke and Lander, and that of Chapter 5b by Kelley and Salkind. The permeating liquid is 40% KOH rather than water. The membrane area exposed is 20.3 cm^2 with a head of 90cm of 40% KOH in a capillary of 0.05 cm^2 across sectional area. The cell is immersed in a beaker containing 900cc of 40% KOH

assuring that the height and volume are essentially constant during the run. The rate of flow of electrolyte through the membrane is determined by the fall of liquid in the capillary and from this data, the approximate pore diameter calculated.

Sample size is 5.0" by 5.0" in which holes are cut to permit passage of through bolts which seal the cell. The dry sample weight to the nearest 0.1mg is recorded. The sample is placed dry in the test cell and placed into the beaker of electrolyte with the capillary vertical and the separator is allowed to equilibrate for 24 hours before being clamped into place in the cell. The capillary is filled to a height of 90.0cm and timing started at this point. Readings are made at hourly intervals of liquid height in the capillary and time. The test is run for 24-48 hours.

Remove the separator from the cell, allow to drain in a vertical position for 5 minutes, blotting the accumulation at the lower edge on a glass plate and weigh to the nearest 0.1mg. Immediately after recording the wet weight, measure the wet thickness of the separator.

6.1 Calculate:

$B = \text{Pore Volume per unit area cc/cm}^2$

$$B = \frac{(\text{Wet Wgt. gms}) - (\text{Dry Wgt. gms})}{(\text{Electrolyte Density gms/cc} \times (\text{Wet Area cm}^2))}$$

Measure a minimum of two samples.

6.0 Pore Size (contd)

6.2 Calculation Mean Pore Diameter

Plot a curve of log height (cm) vs. time t (hrs) and obtain the slope of the curve M (hr^{-1}).

$$D = 2 \left(\frac{(2.303)(8) \eta}{3600 g d} \frac{a}{A} \frac{ML^2}{B} \right)^{\frac{1}{2}}$$

η - electrolyte viscosity gm/cm-sec

g - gravitational constant 980cm/sec²

d - electrolyte density gm/cc

$\frac{a}{A}$ - ratio of cross sectional area of capillary to exposed membrane area.

M - slope of diffusion plot in hr^{-1}

L - wet thickness of membrane cm

B - pore volume of membrane in cc/cm²

7.0 Tortuosity

Tortuosity is a correction applied to the measured diffusion path through a separator to account for the geometric interference due to the separator structure. The effective path length through the separator is increased. Tortuosity is the ratio of the mean effective path length to the measured thickness.

7.1 Calculation

$$\text{Tortuosity } T = \left(\frac{\rho_s}{\rho_e} \times P \right)^{\frac{1}{2}}$$

7.0 Tortuosity (cont)

ρ_s = separator specific resistivity ohm-cm

ρ_e = electrolyte specific resistivity ohm-cm

P = separator porosity cc/cc

8.0 Silver Permeability

The method used is that described by T. Dirkse in the Cooper-Fleischer Handbook, Chapter 10. The test cell is pictured in Figure 2. Approximately 70cc of 40% KOH is contained in each compartment. One compartment A is filled with 40% KOH saturated with zinc oxide and silver oxide tagged with $\text{Ag}^{110\text{m}}$, the other B with 40% KOH saturated with zinc oxide. One cc samples are withdrawn from both compartments after 1, 2, 4, 8, and 24 hours, and counted, using a Baird-Atomics Model 530 Spectrometer and a Baird-Atomics Model 810 NaI (thallium activated) scintillation detector. The loss of activity in compartment A and the gain in B are measured, and finally, the silver content of the separator is determined by dissolving a measured area of the separator from the cell in HNO_3 and counting the activity in the solution. The rate of absorption is reported as $\text{gms. Ag}_2\text{O/cm}^2 \text{ sec.}$ The ratio of counts per minute and the amount of silver in solution is determined by an analytical determination of silver concentration per unit volume.

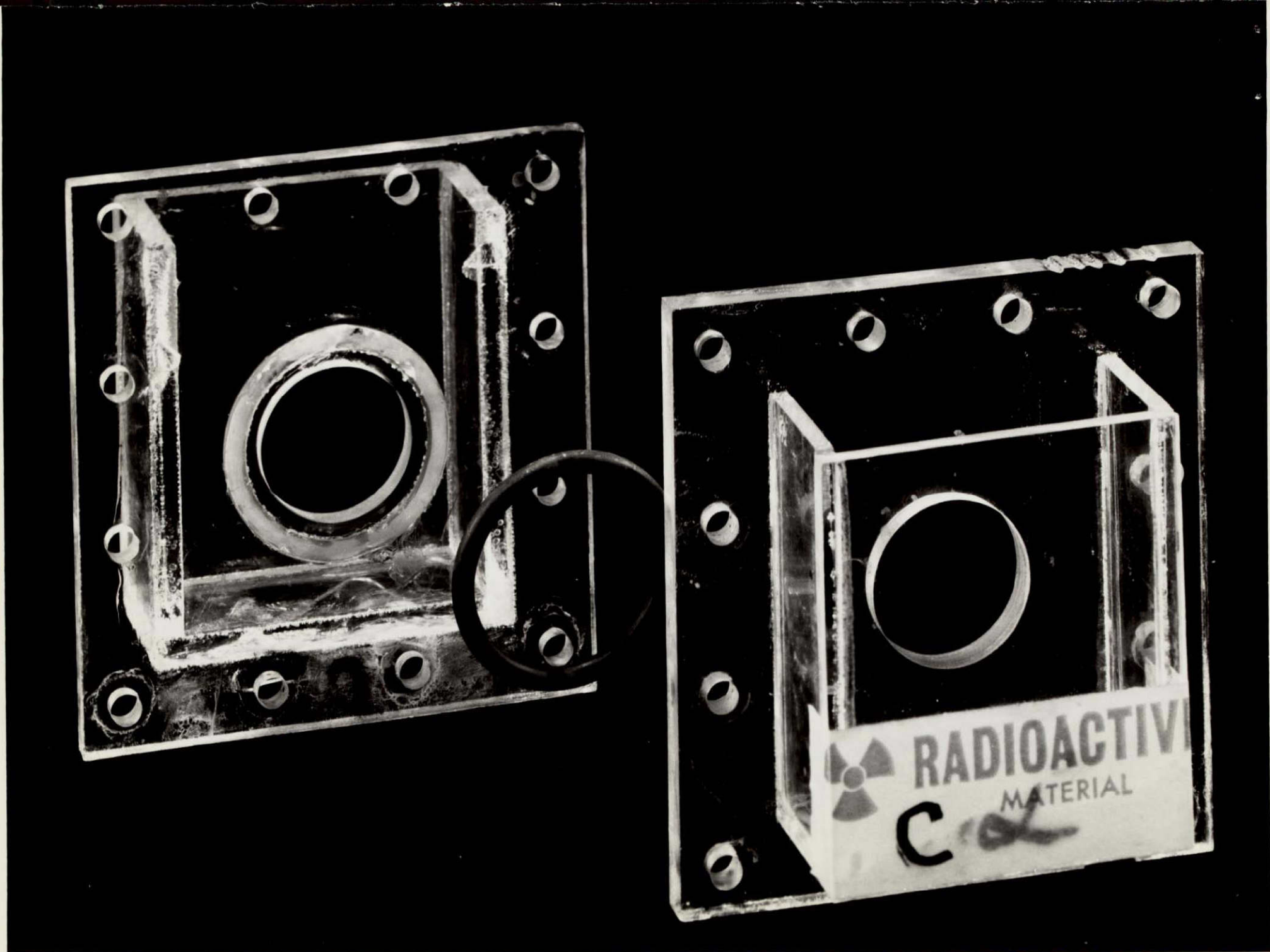


FIGURE 2

8.0 Silver Permeability (concluded)

and by counting a measured volume of the tagged solution.

The diffusion rate is calculated from:

$$\text{Counts in B at 24 hours} \quad \text{Conc. Ag g/cc} \times \frac{65\text{cc}}{\text{Area (in}^2\text{)}} \times \frac{1}{M_0}$$

M_0 = molar concentration initially in A. This gives the rate of diffusion in $\text{g hr}^{-1} \text{ in.}^{-2}$ which can be converted to $\text{moles/cm}^2 \text{ sec}$ by multiplying by the factor 1.86×10^{-7} .

9.0 Silver Reactivity

A 1 in^2 sample is suspended by silver wires in a beaker containing 50cc of a 40% KOH solution saturated with ZnO and Ag_2O . The Ag_2O is tagged with a radioactive $\text{Ag}^{110\text{m}}$. The samples are pre-equilibrated in ZnO saturated 40% KOH for 24 hours prior to testing. During the test, the solution is stirred using a synchronous drive magnetic stirrer. Samples of the electrolyte are withdrawn and counted at regular intervals. Percent silver loss from the electrolyte after 24 hours is calculated from this data. At the conclusion of the test, a fixed area of the separator is cut, washed with dilute HNO_3 , and the solution counted to obtain rate of silver absorption by the separator in $\text{g Ag/in}^2/\text{hr}$.

10.0 Zinc Diffusion

The method is that described in the Cooper-Fleischer Handbook, Chapter 11, by J. J. Lander.

The diffusion cell consists of two chambers of approximately 275cc capacity. Each side contains a well which will accommodate a magnetic stirring bar, permitting controlled agitation during the diffusion run. The separator sample is cut to 5.0cm by 5.0cm. and equilibrated in zinc oxide saturated 45% KOH for a minimum of 24 hours. It is then clamped between the two halves of the diffusion cell. Side A is filled with 45% KOH, 10^{-4} molar in ZnO. Side B is filled with 45% KOH one molar in ZnO. A Hg/HgO electrode and an amalgamated zinc electrode are introduced into one of the ports in Side A and the voltage between them recorded over a period of 115 minutes after it begins to change. Oxygen is excluded by bubbling Nitrogen through the solution and across the zinc electrode. Since the potential between the two electrodes at constant KOH concentration changes by 0.0295 volts per ten fold change in zincate concentration, the concentration in Side A at 115 minutes can be obtained by reference to a calibration curve relating zincate concentration and the potential between the two reference electrodes.

The flux of zincate through the separator is given by:

$$K \text{ (moles/cm}^2\text{-sec)} = (C_2 - C_1) V_a / t \times A$$

C_1 = initial zincate concentration Side A moles ZnO/l

C_2 = final zincate concentration Side A moles/ZnO/l

V_a = Volume Side A in liters

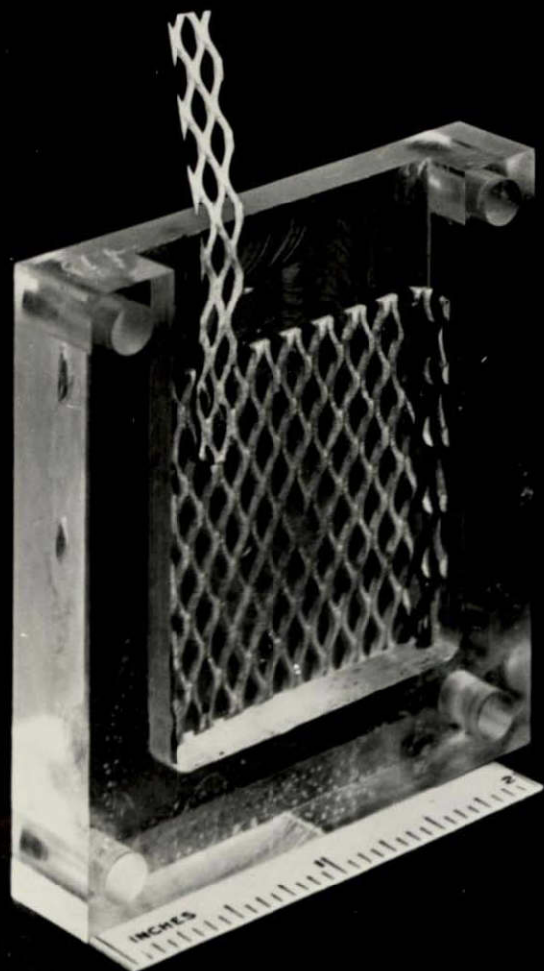
t = time-seconds

A = orifice area - cm^2

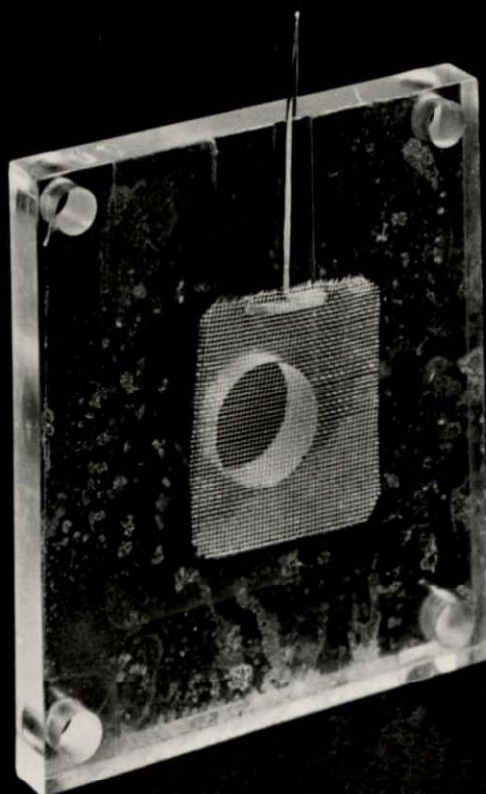
11.0 Zinc Penetration Test

The zinc penetration test is similar to that described in NASA Contract 5-2860, Report No. 7, and to the detailed write-up by Dalin and Solomon in the Cooper-Fleischer Handbook.

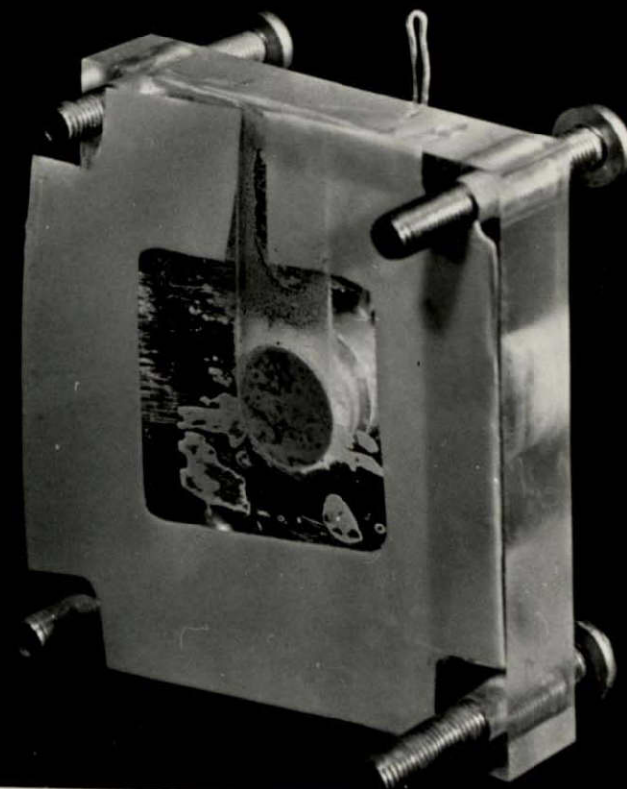
The method utilizes the Lucite test cell pictured in Photograph 3. The positive electrode is a zinc screen and the negative a 1/2" diameter zinc rod fitted into one wall of the cell. Between the two electrodes is placed a 1/4" Lucite plate containing a 1/2" diameter hole which is aligned with the negative electrode. Against the negative electrode is placed a sheet of pre-wetted absorber material (Viskon .005") followed by the separator under test, then a flat, platinum wire gauge sensing electrode. The separator is pre-equilibrated for 24 hours prior to test. The electrolyte used is 40% KOH saturated with ZnO. The cell, after filling with electrolyte, is charged at a current density of 10 ma/cm² using the two zinc electrodes.



FRONT CELL WALL
with POSITIVE ELECTRODE



PLEXIGLASS SPACER
with REFERENCE ELECTRODE



REAR CELL WALL
with NEGATIVE ELECTRODE,
CELLOPHANE SEPARATOR
and TEFLON SPACER

Fig. 3

11.0 Zinc Penetration Test (concluded)

The voltage between the platinum electrode and the cathode is recorded. When zinc penetrates the separator and reaches the platinum electrode, a sharp drop in voltage occurs. This time is recorded. The time required for penetration to occur is reported together with the time per unit wet thickness obtained by dividing the penetration time in hours by the wet thickness in cm.

12.0 Zincate Adsorption

The method measures the distribution of zincate ion between the electrolyte absorbed by the separator and free electrolyte. The method has been proposed and studied by Stachurski and McBreen (Study to Investigate and Improve the Zinc Electrode for Spacecraft Electrochemical Cells, NASA 5-10231, First Quarterly Report, June 1967).

12.1 Sample Preparation

Twelve pieces of each material are cut using a steel rule die to 7.60 by 5.10cm. Each sample is measured and weighed to the nearest 0.1mg and these values recorded. Paired samples are immersed in solutions of 40% KOH containing 0.1, 0.2, 0.3, 0.5, 0.75, and 1.0 mole ZnO/liter. Approximately 100cc of solution is used per pair. The containers are tightly stoppered

12.1 Sample Preparation (concluded)

and the samples equilibrated for 72 hours at 72°F. After equilibration, the separator pieces are measured for dimensional changes and re-weighed after allowing to drain in a vertical position for 5 minutes. Individual samples are next dissolved in dilute HNO_3 and the zinc content determined. This may be done polarographically by dissolving in 50cc of a solution of 1M NH_3 and 1M NH_4Cl , the residue obtained on evaporating the HNO_3 solution to dryness. This solution is analyzed. Alternatively, the zinc determination can be made by an EDTA titration using xylenol orange indicator in an ammonium acetate buffer, or by atomic absorption

12.2 Calculations

The zincate concentration (moles/liter adsorbed electrolyte) is calculated assuming no concentration difference between the adsorbed and equilibrating electrolyte. A plot of zincate concentration in the pore liquid vs. that in the external electrolyte has given a straight line for several separators. The slope of this line is the zincate distribution coefficient K . It represents the ratio of internal to external zincate concentration.

13.0 Absorber Testing

The screening tests for absorber materials previously reported have been supplemented by measurements of wicking, wet out time, and air permeability.

- 13.1 Wet Out Time - A disc of absorber material 2" dia. is die cut. A drop of 40 percent KOH is applied to the center of the disc and the time for the drop to spread is measured.
- 13.2 Wicking - Samples 5" by 1" are die cut, placed in a beaker so that 10 mm is immersed in 40 percent KOH., and the height attained by the electrolyte measured with time.
- 13.3 Air Permeability - Using a Gurley Densometer, the time required for passage of 300 ml air is measured. The sample is 0.1 in² in diameter and the effective pressure 1.22 H₂O.
- 13.4 Wet Out Time
- The electrical resistance is measured until a stable value is reached. The time to reach this value is recorded.

14.0 Procedure for Extracting Absorber Materials

1. Place 1 x 0.15 meter samples which have been weighed (rolled) in Soxhlet apparatus (do not use a thimble).
2. Place 150 cc of AR methylene chloride in round bottom flasks. Add about 10 glass beads.
3. Assemble the Soxhlet extractors in a water bath.
4. Extract for 4 hours at the boiling point of the solvent.
5. Take extractors apart. Pour any liquid in the upper section into the round bottom flask. Label and stopper the flasks.
6. Place absorbers into a vacuum oven IMMEDIATELY.
DO NOT allow material to air dry. Dry samples in vacuum at room temperature for one hour. (Use a cold trap between the pump and oven).
7. Evaporate extracts to about 10 cc. Transfer to a watch glass (or crystalizing dish), along with three 10 cc CH_2Cl_2 washes. Place watch glass over water bath and evaporate CH_2Cl_2 .
8. Dry watch glasses in a vacuum at 30-40° C for 1 hour.
9. Cool and store in a dessicator.
10. Weigh the extracted materials and calculate the percent Organic Extractable.

APPENDIX II

PREPARED BY

ESB INCORPORATED
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FOR USE ON

GODDARD SPACE FLIGHT CENTER CONTRACT
NAS 5-10418

APPENDIX II

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1. CELL DESIGN

Basically, the cell design is that of the standard line EMED S-12 secondary silver-zinc cell. Some adjustment in the plates was made, as will be discussed in Section 2. The S-12 cell, which uses the same jar as the S-15 and S-20, has polystyrene sheet shims between the cell pack and the jar wall. It was by varying the thickness of these shims that variations in cell pack thickness, caused by differences in separator thickness and degree of separator expansion when activated, could be accommodated. Figure 1 illustrates the basic cell design, Table II presents a typical calculation used to compute the thickness of shims. Separator dry and wet thicknesses were taken from the Central Research reports and were measured with an Ames platform dial micrometer with a 0.5 inch foot diameter and a pressure of 40 gm/cm².

2. PLATES

The only significant departure from the standard line S-12 plates used for the separator test cells was an increase in zinc active material (by increasing negative plate thickness). The uncharged active material ratio, based on 49.20 grams of zinc oxide per cell and 49.08 grams of silver per cell is approximately 1 to 1. On the basis of theoretical ampere-hours, this ratio is about 1.65 to 1.

The plates required to make all the shippable and test cells were made in one lot. A weight lot plot for the positive (capacity limiting) plates is shown in Figure 2. It will be seen that only 0.7 percent of the plates made were unusable for weight deviation.

3. DRAWINGS

A set of drawings was made, tabulated to describe the 15-cell design involved on the contract to date. The latest additions, including the specification of electrolyte volume for each design, are being made concurrently with the writing of this report. These amended drawings will completely describe the 15 designs.

4. CELL FABRICATION

The cells for the contract were built in three groups by the Engineering Pilot Plant. Group A involved three cell designs, SK-9211-1, -2 and -3. Group B contained eight designs, a repeat of SK-9211-1 plus types SK-9211-4, -5, -6, -7, -8, -9 and --. Group C was composed of the remaining cell types, SK-9211-10, -12, -13, -14 and -15. For each cell type, 18 cells were built - 15 for shipment to NAD-Crane, Indiana, and 3 for test at EMED. Table III shows the serial numbers of all the cells built, relating these to the cell design and listing the 3 cells taken for testing by ESB.

5. CELL SHIPMENTS

The following shipments of cells were made to NAD-Crane :

45 cells - Group A	December 16, 1968
120 cells - Group B	June 27, 1969
75 cells - Group C	July 31, 1969.

Copies of the shipping papers were sent to Messrs. Hennigan and Kelley.

6. ELECTROLYTE VOLUME

Due to difference in separator systems and shimming, the amount of electrolyte required by the different cell types varies. The correct amount of electrolyte was determined from the three cells of each type used for ESB tests. Following the formation charge, let-down discharge and operational charge, the electrolyte level was adjusted to the top of each cell's plates. The volume required was determined and checked by weight difference. Applicable volumes of 40 percent KOH are related to cell types in Table IV. A premeasured, marked bottle is sent with each cell shipped to NAD-Crane.

7. ESB TESTS ON CONTRACT

A series of tests were set up, to which the three cells of each design retained by ESB were subjected. These tests are described in Table V and agree with the first three cycles of testing to be conducted at NAD-Crane, as outlined in the NASA Statement of Work. The purpose of these tests was to compare initial performance obtained here with that obtained at Crane. Capacity data on the ESB tests are summarized in Table VI and voltage data in Table VII.

As the data obtained are mainly for comparative purpose, no detailed discussion of the results will be undertaken here. However, a few general observations will be made.

First, it will be seen from Table VI that cell S/N 55 has no recorded capacity on third cycle discharge. At some time during testing, the clamp which restrains the broad cell was overtightened on the cell group of which S/N 55 was the end cell, cracking the jar. Through electrolyte leakage and evaporation, the cell dried out and could not support the discharge load beyond 2 minutes on third cycle.

In general, discharge capacities averaged about 18 ampere-hours from fully charged cells at the 5-hour (nominal) rate. This represents about 50 percent over nominal capacity (which is based on the 1-hour rate) or about 0.38 ampere-hours per gram of silver. Obviously, those cells limited to 23 hours charging at a maximum of 0.5 ampere were not fully charged which was reflected in both capacity output and initial load voltage.

Plateau voltages at the 5-hour rate was not adversely affected beyond about 50 millivolts with any of the film separators or with the G.E. coating, as compared to 1 layer of PELLON 2505 K and 5 layers of cellophane. However, the voltage drop was closer to 100 millivolts with the HUGHES coating. This may indicate a more integral or uniform coating; whether this will increase cell life remains to be seen.

8. ESB TESTS AT EMED EXPENSE

Following the generation of data for comparison to initial performance at Crane, which ended the testing quoted to Central Research on the contract, it was decided to continue testing at EMED expense to gather further information

about the separator systems. As Crane is collecting cycling data, EMED will collect charged stand data. Accordingly, the test plan outlined in Table VIII was implemented. All information obtained from this testing will be presented in a future report.

TABLE I

SEPARATOR SYSTEMS FOR TEST CELLS

Cell Type SK-9211	Absorber Material (1 layer)	Positive Plate Coating	Separator No. 1		Separator No. 2	
			Material	Layers	Material	Layers
-1	Pellon 2505K	None	193 PUDO	5	None	
-2	Pellon 2505K	None	Permion 1770C	5	None	
-3	Pellon 2505K	None	Permion 2290	5	None	
-4	Pellon 2505K	None	Permion 2291	5	None	
-5	Pellon 2505K-T-15050	None	Permion 2291	5	None	
-6	Kendall EM-476	None	193 PUDO	5	None	
-7	Kendall EM-476	None	Permion 2291	5	None	
-8	Nylon Taffeta	None	Permion 2291	5	None	
-9	Pellon 2505K	None	Permion 2291	3	Permion 116	2
-10	Pellon 2505K	None	Permion 2291	3	Permion 2290	2
-11	None	None	Permion 2291	5	None	
-12	Pellon 2505K	.002" Ca(OH) ₂ G.E. Process	Permion 2291	5	None	
-13	Pellon 2505K	.002" Ca(OH) ₂ G.E. Process	193 PUDO	5	None	
-14	Pellon 2505K	.002" Ca(OH) ₂ Hughes Process	Permion 2291	5	None	
-15	Pellon 2505K	.002" Ca(OH) ₂ Hughes Process	193 PUDO	5	None	

Pellon 2505K

- non-woven polyamide

Pellon 2505K-T-15050

- non-woven polyamide, KOH washed, cellulose treated

Kendall EM-476

- polypropylene

193 PUDO

- Cellophane

Permion 116 and 2291

- radiation grafted polyethylene

Permion 1770C and 2290

- chemically grafted polyethylene

TABLE II

TYPICAL CALCULATIONS OF CELL PACK THICKNESS

The following calculations are for cell type SK-9211-12, which is $\text{Ca}(\text{OH})_2$ coated plates, 2505K absorber and 5 layers of PERMION 2291 separator. Other cell pack thicknesses were calculated similarly. Separator length and width were calculated on general secondary cell design principles.

	<u>Inches</u>	<u>Inches</u>
<u>Cell Jar (Bottom) Length:</u>		0.664
<u>Elements Common to All Cell Types:</u>		
4 positive plates at .028 in.	0.112	
5 negative plates at .048 in.	0.240	
2 cement joints for shims at .009 in.	<u>0.018</u>	<u>0.370</u>
<u>Remaining Space:</u>		0.294
<u>Special Elements For This Design:</u>		
$\text{Ca}(\text{OH})_2$ coating .002 in. x 2 sides x 4 plates	0.016	
2505 absorber* .008 in. x 2 sides x 4 plates	0.064	
2291 separator** .00145 x 11 layers x 4 plates	<u>0.064</u>	<u>0.144</u>
<u>Remaining Space:</u>		<u>0.150</u>

Use shims 0.075" thick (Part No. SK-9216-6)

- (*) Absorber is U-wrapped around each positive plate, therefore, no overlap allowance is required.
- (**) Separator is wrapped 5 layers to a side around the positive plates - with an overlap, this amounts to 11 layers. Wet thickness of RAI-2291 per Central Research data is 0.00132 inch. Separator allowances for all designs is 10 percent over wet thickness (based on Cellophane .0009 in. dry, .0030 in. wet = factor of 3.3. To allow a SEF of 3.6, allow .0033 in. wet thickness = 10 percent over wet thickness). For RAI 2291, this is $0.00132 \times 1.1 = 0.00145$.

TABLE III

ALLOCATION OF CELL SERIAL NUMBERS

<u>S/N's Assigned</u>	<u>Cell Type</u>	<u>Shipping Group</u>	<u>ESB Test Cell S/N's (3)</u>		
1-18	SK-9211-2	A	1	6	13
19-36	SK-9211-3	A	20	21	36
37-54	SK-9211-1	A	44	47	49
55-72	SK-9211-1	B	55	56	57
73-90	SK-9211-5	B	73	74	75
91-108	SK-9211-4	B	91	92	104
109-126	SK-9211-6	B	109	110	111
127-144	SK-9211-7	B	127	128	129
145-162	SK-9211-11	B	145	146	147
163-180	SK-9211-8	B	163	164	165
181-198	SK-9211-9	B	181	182	183
199-216	SK-9211-12	C	199	200	201
217-234	SK-9211-13	C	217	218	219
235-252	SK-9211-14	C	235	236	237
253-270	SK-9211-15	C	253	254	255
271-288	SK-9211-10	C	271	272	273

TABLE IV

ELECTROLYTE VOLUME REQUIRED BY VARIOUS CELL TYPES

<u>Cell Type</u> <u>SK-9211</u>	<u>Volume of Electrolyte</u> <u>(c. c. of 40% KOH $\pm$ 1 c. c.)</u>
-1	40
-2	37
-3	34
-4	36
-5	26
-6	32
-7	32
-8	31
-9	36
-10	38
-11	29
-12	30
-13	36
-14	36
-14	30
-15	30

TABLE V
SEPARATOR CELL TEST PLAN

PERFORM THE FOLLOWING STEPS ON SK-9211 TYPE CELLS TO BE DELIVERED,
IN GROUPS OF 3, FROM THE PILOT PLANT

1. Perform activation, soak, formation charge, let-down discharge and operational charge as directed by Service and Operating Instructions No. 137.
2. Inform Project Engineer so that electrolyte level can be adjusted and electrolyte volume recorded.
3. Discharge cells at 2.4 amperes to 1.30 volts/cell at room temperature.
4. Divide each group of three cells into two sub-groups; A containing 2 cells and B, 1 cell.
5.
 - a. Compute capacity removed from A cells in Step 3 and recharge 120 percent of capacity removed at constant current at 0.5 ampere at room temperature (capacity must be computed for each cell individually).
 - b. Charge the B cell at a constant potential of 1.97 ± 0.02 volt, current limited to 0.5 ampere, for 23 hours. Make certain same cell is treated as B cell in subsequent testing.
6. Repeat Step 3.
7.
 - a. Repeat Step 5a.
 - b. Repeat Step 5b.
8. Repeat Step 3.
9. Contact Project Engineer, immediately after completion of Step 8, for further instructions.

TABLE VI
TEST CELL CAPACITY SUMMARY

Cell Type	S/N	1st Charge	* 1st Discharge	2nd Charge	2nd Discharge	3rd Charge	3rd Discharge
SK-9211-1	44	14.8	14.2	17.0Δ	16.7	20.0Δ	17.5
	47	15.7	15.0	11.5○	11.8	20.0□	19.0
	49	15.0	14.2	17.0Δ	17.3	20.8Δ	17.5
End of Charge Voltage O Type Charge				1.93		1.97	
SK-9211-1 (Repeat)	55	20.6	20.0	24.0Δ	19.7	23.6Δ	See Text
	56	20.7	20.3	11.5○	10.2	11.5○	10.6
	57	20.8	19.9	23.8Δ	19.7	23.6Δ	20.8
End of Charge Voltage O Type Charge				1.91		1.92	
SK-9211-2	1	19.2	17.6	21.0Δ	18.3	22.0Δ	16.6
	6	17.9	16.8	20.3Δ	19.2	23.0Δ	17.5
	13	18.3	17.4	11.5○	12.7	18.9□	16.3
End of Charge Voltage O Type Charge				1.94		1.97	
SK-9211-3	20	18.8	17.9	21.4Δ	19.2	23.0Δ	17.2
	21	19.5	18.6	22.3Δ	19.3	23.2Δ	19.1
	36	18.8	18.0	11.5○	12.1	18.1□	17.5
End of Charge Voltage O Type Charge				1.95		1.97	
SK-9211-4	91	20.7	20.2	11.5○	10.0	11.5○	10.2
	92	20.7	19.7	23.6Δ	22.1	26.4Δ	20.0
	104	20.6	19.3	23.1Δ	21.8	26.1Δ	20.0
End of Charge Voltage O Type Charge				1.94		1.90	
SK-9211-5	73	20.6	19.9	23.8Δ	22.1	26.4Δ	20.6
	74	20.9	20.6	11.5○	10.0	11.5○	10.4
	75	20.6	19.7	23.6Δ	21.7	26.1Δ	20.0
End of Charge Voltage O Type Charge				1.94		1.90	
SK-9211-6	109	20.8	20.2	11.5○	10.0	11.5○	10.0
	110	20.6	19.7	23.6Δ	20.7	24.8Δ	20.6
	111	20.6	19.5	23.4Δ	19.7	23.6Δ	20.6
End of Charge Voltage O Type Charge							
SK-9211-7	127	20.6	19.5	23.4Δ	21.2	25.4Δ	19.8
	128	13.3	13.3	11.5○	11.1	11.5○	9.8
	129	20.6	19.8	23.7Δ	22.0	26.5Δ	20.1
End of Charge Voltage O Type Charge				1.93		1.905	

TABLE VI (contd)

Cell Type	S/N	1st Charge	1st Discharge	2nd Charge	2nd Discharge	3rd Charge	3rd Discharge
SK-9211-8	163	20.8	19.5	23.4Δ	21.0	25.2Δ	20.0
	164	13.7	13.4	11.5O	10.9	11.5O	9.8
	165	21.0	19.7	23.6Δ	21.8	26.3Δ	19.5
End of Charge Voltage O Type Charge				1.92		1.91	
SK-9211-9	181	21.0	20.8	11.5O	10.0	11.5O	10.2
	182	20.9	19.5	23.4Δ	22.1	26.6Δ	20.6
	183	20.7	19.8	23.7Δ	21.4	25.8Δ	20.1
End of Charge Voltage O Type Charge				1.94		1.90	
SK-9211-10	271	19.6	18.0	21.6Δ	21.0	25.2Δ	18.7
	272	19.6	18.6	12.5+	13.2	11.0O	10.2
	273	19.6	18.6	22.2Δ	21.0	25.2Δ	18.8
End of Charge Voltage O Type Charge				1.92		1.91	
SK-9211-11	145	20.9	19.5	23.4Δ	21.0	25.3Δ	19.7
	146	20.8	20.4	11.5O	10.8	11.5O	10.1
	147	20.6	19.3	23.1Δ	20.7	24.8Δ	19.5
End of Charge Voltage O Type Charge				1.93		1.90	
SK-9211-12	199	20.5	19.7	23.6Δ	20.8	25.0Δ	20.2
	200	20.8	19.8	12.5+	12.8	11.0O	10.2
	201	19.6	18.6	22.2Δ	21.2	25.4Δ	20.6
End of Charge Voltage O Type Charge				1.93		1.92	
SK-9211-13	217	20.0	18.4	22.1Δ	20.8	25.0Δ	19.0
	218	20.4	19.1	22.9Δ	21.0	25.2Δ	19.0
	219	16.7	14.9	12.5+	14.3	11.0O	10.1
End of Charge Voltage O Type Charge				1.945		1.93	
SK-9211-14	235	17.5	16.1	12.5+	12.8	11.0O	9.5
	236	17.0	15.7	18.8Δ	18.8	22.6Δ	17.6
	237	17.5	16.4	19.7Δ	20.1	24.1Δ	18.7
End of Charge Voltage O Type Charge				1.96		1.96	
SK-9211-15	253	16.4	13.9	16.6Δ	18.8	22.6Δ	18.7
	254	14.6	13.9	12.5+	11.3	11.0O	9.5
	255	16.8	14.0	16.8Δ	19.1	22.9Δ	17.7
End of Charge Voltage O Type Charge				1.94		1.96	

(*) 1st charge is after formation charge and let-down per Service and Operating Instructions No. 137 (0.8 amp. to 2.05 v/cell).

Δ Charge at 0.5 amp to 120% of capacity removed during previous discharge.

O Charge C.P. 1.97 v/cell current limited to 0.5 amp max. for 23 hours (11.5 amp-hour maximum).

□ Should have been per O - allowed to run beyond 23 hours current decayed to c.a. 0.3 amp.

+ Should have been per O - allowed to run 25 hours.

TABLE VII

TEST CELL DISCHARGE VOLTAGE SUMMARY.

Cell Type SK-9211	S/N	Initial Load Voltage			Plateau Voltage			Cell Type SK-9211	S/N	Initial Load Voltage			Plateau Voltage		
		Cycle			Cycle					Cycle			Cycle		
		1	2	3	1	2	3			1	2	3	1	2	3
-1	44	1.77	1.71	1.72	1.51	1.49	1.49	-8	163	1.73	1.72	1.75	1.47	1.46	1.47
	47	1.81	1.61	1.62	1.50	1.48	1.47		164	1.70	1.69	1.67	1.48	1.49	1.48
	49	1.80	1.74	1.77	1.49	1.48	1.48		165	1.76	1.72	1.74	1.49	1.47	1.48
		X̄ Plat.			1.50	1.48	1.48			X̄ Plat.			1.48	1.47	1.48
-1 Repeat	55	1.78	1.72	1.76	1.52	1.51	--	-9	181	1.76	1.60	1.66	1.50	1.51	1.52
	56	1.76	1.76	1.70	1.52	1.53	1.53		182	1.77	1.73	1.76	1.50	1.48	1.49
	57	1.79	1.78	1.74	1.52	1.50	1.51		183	1.73	1.70	1.75	1.50	1.48	1.48
		X̄ Plat.			1.52	1.52	1.52			X̄ Plat.			1.50	1.49	1.50
-2	1	1.73	1.69	1.68	1.47	1.44	1.44	-10	271	1.69	1.73	1.78	1.49	1.50	1.48
	6	1.74	1.73	1.69	1.48	1.45	1.46		272	1.72	1.57	1.58	1.50	1.50	1.48
	13	1.72	1.53	1.70	1.48	1.46	1.46		273	1.68	1.74	1.78	1.50	1.50	1.48
		X̄ Plat.			1.48	1.45	1.45			X̄ Plat.			1.50	1.50	1.48
-3	20	1.74	1.76	1.73	1.50	1.48	1.48	-11	145	1.76	1.70	1.74	1.49	1.46	1.48
	21	1.75	1.75	1.73	1.51	1.48	1.49		146	1.74	1.61	1.72	1.49	1.50	1.50
	36	1.74	1.52	1.71	1.51	1.48	1.49		147	1.70	1.70	1.76	1.48	1.45	1.46
		X̄ Plat.			1.51	1.48	1.45			X̄ Plat.			1.49	1.47	1.48
-4	91	1.76	1.63	1.67	1.50	1.51	1.51	-12	199	1.60	1.62	1.73	1.46	1.47	1.47
	92	1.76	1.74	1.75	1.50	1.48	1.48		200	1.63	1.63	1.65	1.45	1.48	1.48
	104	1.76	1.72	1.76	1.50	1.48	1.48		201	1.52	1.68	1.72	1.48	1.49	1.48
		X̄ Plat.			1.50	1.49	1.49			X̄ Plat.			1.46	1.48	1.48
-5	73	1.76	1.72	1.75	1.50	1.48	1.50	-13	217	1.53	1.53	1.70	1.46	1.47	1.46
	74	1.75	1.62	1.69	1.50	1.51	1.52		218	1.58	1.56	1.72	1.45	1.47	1.48
	75	1.76	1.69	1.74	1.49	1.48	1.49		219	1.53	1.57	1.62	1.46	1.46	1.45
		X̄ Plat.			1.50	1.49	1.50			X̄ Plat.			1.46	1.47	1.46
-6	109	1.79	1.69	1.70	1.51	1.49	1.50	-14	235	1.51	1.54	1.50	1.41	1.42	1.40
	110	1.78	1.74	1.76	1.51	1.47	1.50		236	1.48	1.52	1.66	1.40	1.40	1.40
	111	1.78	1.76	1.72	1.51	1.48	1.51		237	1.57	1.57	1.70	1.42	1.42	1.42
		X̄ Plat.			1.51	1.48	1.50			X̄ Plat.			1.41	1.41	1.41
-7	127	1.74	1.72	1.76	1.48	1.45	1.46	-15	253	1.50	1.44	1.64	1.38	1.39	1.43
	128	1.72	1.66	1.70	1.45	1.48	1.48		254	1.52	1.50	1.51	1.40	1.41	1.41
	129	1.74	1.69	1.78	1.49	1.46	1.46		255	1.54	1.48	1.70	1.41	1.41	1.45
		X̄ Plat.			1.47	1.46	1.47			X̄ Plat.			1.40	1.40	1.43

NOTE: All discharges are at 2.4 amperes (5-hr. rate) at room temperature.

TABLE VIII

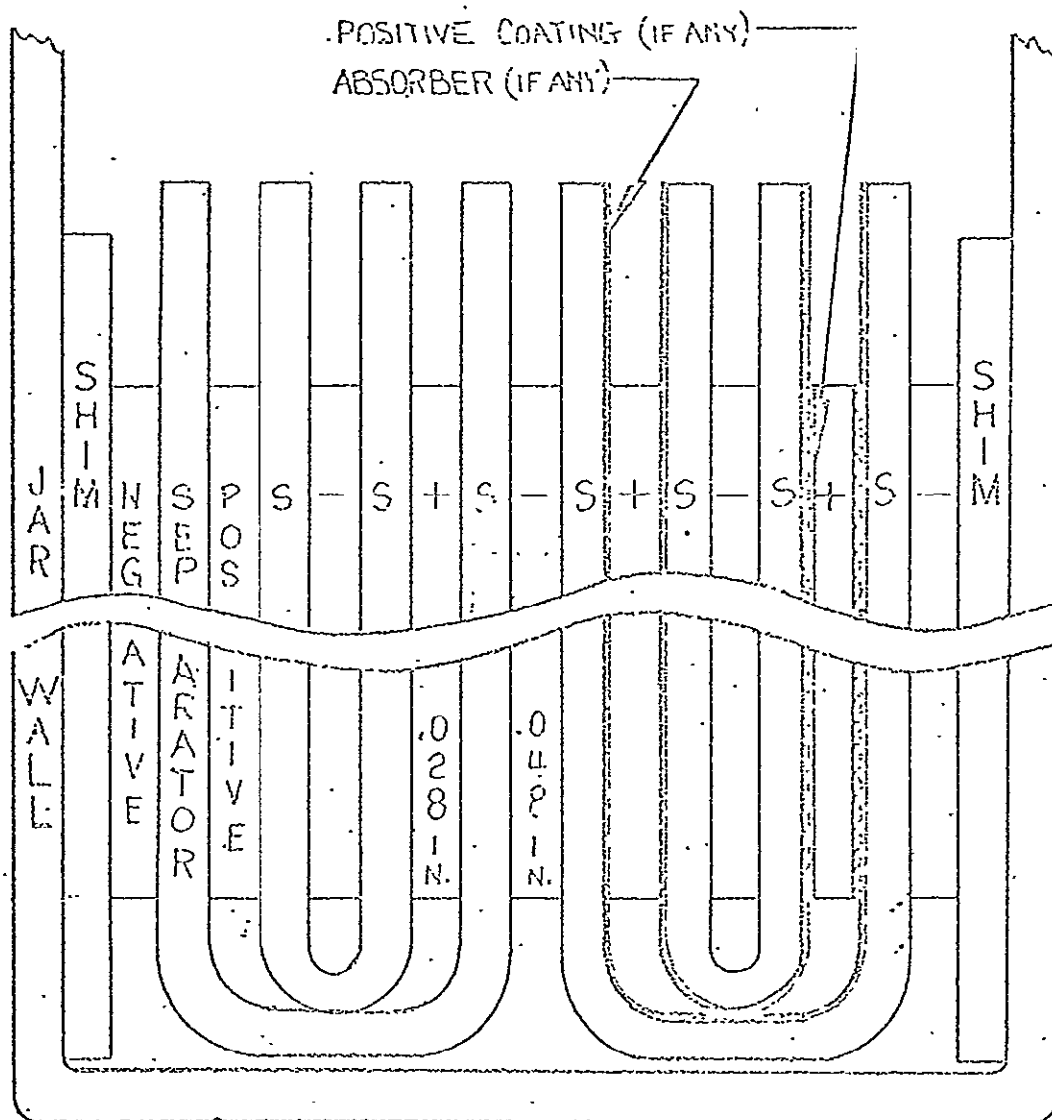
TEST PLAN - FURTHER TESTING OF SEPARATOR CELLS (BEYOND CONTRACT)

AFTER COMPLETION OF THE PREVIOUS CYCLING (ON THE CONTRACT) PER TABLE V.

PERFORM THE FOLLOWING STEPS.

1. Within 24 hours of the completion of Step 8 of Table V, recharge all three cells of each group at 0.5 ampere to 2.05 volts/cell at room temperature.
2. Maintain cells on charged stand at room temperature for 120 ± 5 days, then discharge at room temperature at 2.4 amperes to 1.0 volt/cell (with no top-off charge).
3. Within 24 hours of previous discharge, recharge per Step 1.
4. Maintain on charged stand at room temperature for 30 ± 2 days. Top-off charge at 0.5 ampere to 2.05 volts/cell, then discharge at 2.4 amperes to 1.0 volt/cell.
5. Repeat Step 3.
6. Maintain on charged stand for 30 ± 2 days at room temperature. With no top-off charge, discharge at room temperature 2.4 amperes to 1.0 volt/cell.
7. Continue cycling by repeating sequences of Steps 3, 4, 5 and 6 until each cell shorts or fails to deliver 5 ampere-hours on discharge.
8. During the above testing, acquire accurate capacity data on charge and discharge and enough voltage points to draw a meaningful discharge curve.

BASIC CELL DESIGN



POSITIVE PLATE WEIGHT LOT PLOT

ACCEPTABLE WEIGHT RANGE

2

6

1

6

14

6

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6

130

140

142

144

146

148

150

152

154

POSITIVE PLATE WEIGHT (GRAMS)