FIRST QUARTERLY REPORT

ON

ALKALINE BATTERY SEPARATOR CHARACTERIZATION STUDIES

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ALKALINE BATTERY SEPARATOR CHARACTERIZATION STUDIES

by

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ABSTRACT

This is the first quarterly report on characterization studies designed to evaluate in a comprehensive manner separator materials for alkaline silver batteries. The primary sources of these materials are government funded projects relating to space and defense but it is planned to include all available and practical materials. The characterization tests include measures of the physical and chemical stability of the test speciments, measures of selected transport properties, an assessment of battery performance in a simplified cell design, and the production of 240 cells for evaluation at NAD/Crane. Six materials have been obtained and partially characterized during the first quarter.

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1.0 INTRODUCTION

The objective of this study is to obtain and characterize by bench type screening tests, the most promising materials presently available for use as alkaline silver cell separators. A number of potentially useful materials has been generated recently, both in government sponsored projects relating to space and defense programs and in industrial efforts unrelated to batteries. While each of these has been carefully scrutinized by the developing group, the testing has been, in the main, specific to the requirements of the particular effort. It is the objective of this study to apply the available standardized methods to measure the range of properties considered to be significant in battery separator functioning to those materials which can be obtained from the groups which have developed them. Table 1 lists the organizations which have been contacted and requested to supply materials, and in Table 2 appears a list of the materials received thus far.

The tests are adapted from those appearing in the Aero Propulsion Laboratory Handbook, edited by J. E. Cooper and A. Fleischer, entitled Battery Separator Screening Methods, (AD 447301), and will be described in detail in future reports.

Table 1

Organizations Contacted for Separator Materials

	Organization	Location
1.	Borden Chemical Company	Philadelphia, Pa.
2.	Chemsorb Inc.	Summit, New Jersey
3.	Douglas Astropower Laboratory	Newport Beach, California
4.	E. I. DuPont de Nemours	Wilmington, Delaware
5.	The General Electric Co.	Schenectady, New York
6.	The Kendall Company Fiber Products Division	Walpole, Massachusetts
7.	Pellon Corporation	New York, New York
8.	Monsanto Research Corp.	Everett, Massachusetts
9.	Whittaker Corporation Narmco R&D Division	San Diego, California
10.	RAI Research Corporation	Long Island City, New York
11.	Southwest Research Institute	San Antonio, Texas
12.	Union Carbide Corporation	Tuxedo, New York
13.	Westinghouse Electric Corp.	Pittsburgh, Pennsylvania

Table 2

Separator Materials Received

Number		Material	Supplier
1	PuDo 300	regenerated cellulose	DuPont Wilmington, Delaware
2	SWRI116GX a)	radiation grafted polyethylene	Southwest Research Inst. San Antonio, Texas
3	C-1 b)	9% methyl cellulose 10% polyvinyl methyl ether-maleic anhydride copolymer	Borden Chemcial Co. Philadelphia, Penna.
4	5-9107-21 b)	methyl cellulose film + 9% KOH	" " "
5	5-9107-29 b)	polyvinyl alcohol 42-88	" " "
6	574-151F b)	methyl cellulose film	" " "
7	1021 G	Heterogeneous ion exchange membrane	ESB Incorporated Philadelphia, Penna.

a) Adams, L.M., etal, Development of Battery Separator Material Process, Interim Report, August 25, 1967, Contract J.P.L. No. 951718.

b) Pfluger, H., and Hoyt, H., Improved Separators for Silver Oxide Zinc and Silver Oxide Cadmium Cells, Final Report, (July 1967), Contract NAS 5-9107 Mod. 6.

In addition, all electrical screening tests will be simultaneously performed using the silver-cadmium oxide and nickel-zinc systems. It is expected that correlation will be obtained between the two types of screening tests which will permit the selection of separator materials with maximum usefulness.

On the basis of the property measurements in the two types of screening tests, separators will be selected for fabrication into batteries to be evaluated at the Battery Evaluation Laboratory, the Naval Ammunition Depot, at Crane, Indiana.

2.0 SEPARATOR SCREENING METHODS

The necessity for an evaluative scheme other than battery performance is dictated by the high cost in time, effort and money involved in battery tests. It is also a consideration that the specific constructional features of the battery and the test regime by which the testing is carried out can prejudice the results of the evaluation. The measurement of a range of properties, on the other hand, can serve to indicate not only potentially acceptable materials but also particular properties requiring improvement in unacceptable separators. Favorable combinations of materials will also be apparent from such a study.

It is obvious that exact duplication of the battery environment is an unrealizable goal, without resorting to some type of cell testing. Due to the solubility of the zinc electrode in the electrolyte, under normal conditions, the quantity of electrolyte in a silver-zinc battery is limited to a small excess over and above that contained in the electrodes and separators. In sealed cells, the electrolyte volume is even further reduced to provide electrode surface for recombination. In addition, either one or both of the electrodes is encased in separator material in order to retard electrical shorting due to eroded zinc. During charge and discharge of the battery, hydroxide ion is consumed at one electrode and liberated at the other. The resultant concentration gradient causes diffusive flow to occur through the intervening separator layers. That this transfer can limit the charge efficiency is visually observable in many cells where the difference in electrolyte level is readily apparent during the latter stage of charging. Add to these the differing concentrations of zinc oxide and silver oxides dissolved in the electrolyte with gradients extending from the electrode into the solution and thence into the separator and the problem of simulating the separator environment in a non-battery bench test becomes a virtually insolvable one.

Several separator parameters can, however, be recognized as important for cell performance:

1) the contribution of the separator to the internal resistance of the cell
2) the ability of the separator to absorb electrolyte and, in sealed cells particularly, the retention of absorbed electrolyte under conditions of acceleration
3) chemical stability to both the probable range of concentrations of electrolyte and to the products of the electrode reactions
4) dimensional changes occurring upon absorption of electrolyte

5) the permeability to the various ionic species present, and

6) a measure of the relative resistance to shorting by growth of metallic zinc through the separator.

Screening type methods have been devised by various laboratories to measure each of these characteristics in tests designed to provide comparisons among potential separators. While certain aspects of cell environment are included in each of the tests, the measurements are made under somewhat idealized conditions and the values obtained are best used comparatively.

In Table 2 are listed the materials which have been received thus far for inclusion in this study.

2.1 Dimensional Changes in the Electrolyte

Samples of the separator film were die cut to size 6.50 by 2.50 cm, measured, and placed into stainless steel containers containing approximately 100cc of 40% KOH. Dimensional measurements were made at 24-hour intervals until no further changes occurred. These measurements expressed as percentage change from original dimension are given in Table 3 for the six materials received thus far.

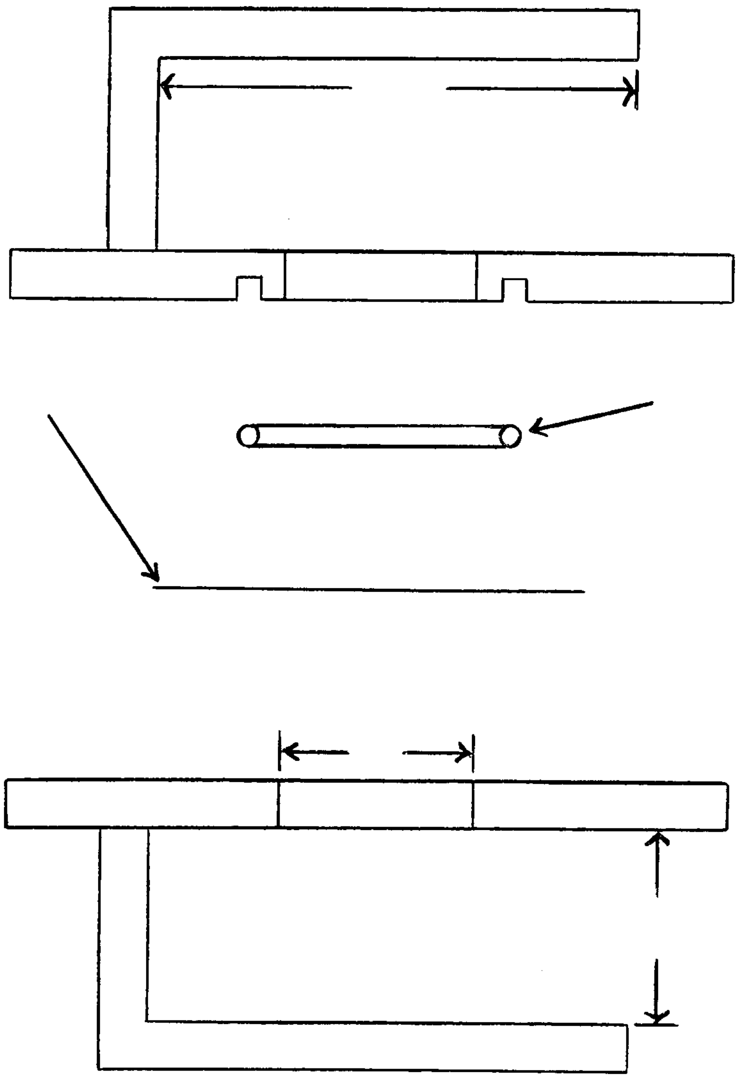
2.2 Electrolyte Absorption and Retention

The samples used for measurement of dimentional changes are pre-weighed before exposure to 40% KOH and again after achieving maximum equilibrated volume, to obtain the weight of electrolyte absorbed. Electrolyte retention is measured by allowing the fully equilibrated sample to drain for 30 minutes on a glass plate positioned at a 45° angle before re-weighing. The results of the absorption measurements are reported in Table 3, Column 7. The data is reported as weight percent increase of the wetted sample compared to original sample weight.

2.3 Electrical Resistance and Wettability

The electrical resistance is measured using an a.c. method and employing a Wayne-Kerr impedance bridge which permits isolation of resistive and capacitive impedances. The conductivity cell has separate voltage and current electrodes with the voltage electrodes positioned close to the separator surfaces.

Measurements are made by placing the fully equilibrated separator sample between the two halves of the cell, filling with 40% KOH and balancing the bridge. A blank is obtained on the cell in the same manner but without the separator and the difference represents the separator resistance.



Cell Case for Silver Diffusion
Figure 1

Measurement of wettability or rate of wetting is made similarly, using an unequilibrated sample and following the resistance until a stable value is achieved.

2.4 Permeability Measurements

In order to function as a separator in the silver zinc system, an ideal material should be permeable to the electrolyte while retarding or preventing migration of the silver or zinc species arising from the electrode reactions. Methods have been devised to measure permeation rates of the oxides of both silver and zinc.

2.4.1 Silver Permeability

The method used for silver is the classical one for measuring the self-diffusion of ions utilizing the radioactive species Ag^{110} and following the migration by changes in the distribution of Ag^{110} in a two-compartment cell. A complicating factor is the reactivity of many of the separator materials with the soluble silver oxide resulting in a concentration of radioactivity in the separator. The method used here is that described by T. Dirkse (Chapter 10, Cooper, Fleischer Handbook of Battery Separator Screening Methods). The apparatus consists of a small polymethylmethacrylate cell case of the type shown in Figure 1.

The dimensions of the compartments are 2-1/2" by 2" by 1" which allows the use of approximately 70 mls. of solution in each compartment. A rubber O-Ring holds the membrane and serves as a seal.

One Compartment A is filled with Ag^{110} saturated 40% KOH which is also saturated with ZnO. An equal amount of 40% KOH saturated with ZnO is placed in the other compartment. One milliliter samples are withdrawn from each compartment after 1,4,8 and 24 hours or until a significant change occurs. The samples are counted using a Baird-Atomics Model 530 Spectrometer and a Baird-Atomics Model 810 NaI (thallium activated) scintillation detector. The loss of activity of Compartment A and the gain in B are measured and finally the Ag^{110} in the separator is obtained by dissolving in HNO_3 acid the silver from a measured area and counting of the dissolved silver. Thus far, six separators have been tested for which the results are given in Table 4. The rate of activity change in Compartments A and B are given in Figures 2 and 3.

2.4.2 Zinc Permeability

Zinc diffusion through separators is measured using the method proposed by Lander (Chapter 11, Cooper, Fleischer Handbook of Battery Separator Screening Methods).

Table 3

Physical Properties of Separators

No.	Sample	Dry Thickness cm	Dimensional Changes % Length	Width	Thickness	Electrolyte Absorption wt%	Electrical Resistance in 40% KOH Ω-cm	Ω-cm^2	Tensile Strength at break -psi roll direction parallel	perpendicular
1	PuDo 300	0.0025	+6.0	-3.0	300	300	9	0.065	22,930	12,210
2	SWRIGX116	0.0030	+5.9	+7.1	+19	78	26	0.095	1,880	1,265
3	Borden C-1	0.0036	+0.6	+0.9	+22	44	1030	4.51	10,340	11,280
4	Borden 5-9107-21	0.0035	+0.8	+0.5	+19	31	310	1.33	6,200	6,110
5	Borden 5-9107-29	0.0040	-6.0	-4.3	+150	134	16.5	0.145	4,315	4,040
6	Borden 574-151F	0.0036	0.0	0.2	+14	30	11,300	47	10,490	10,310

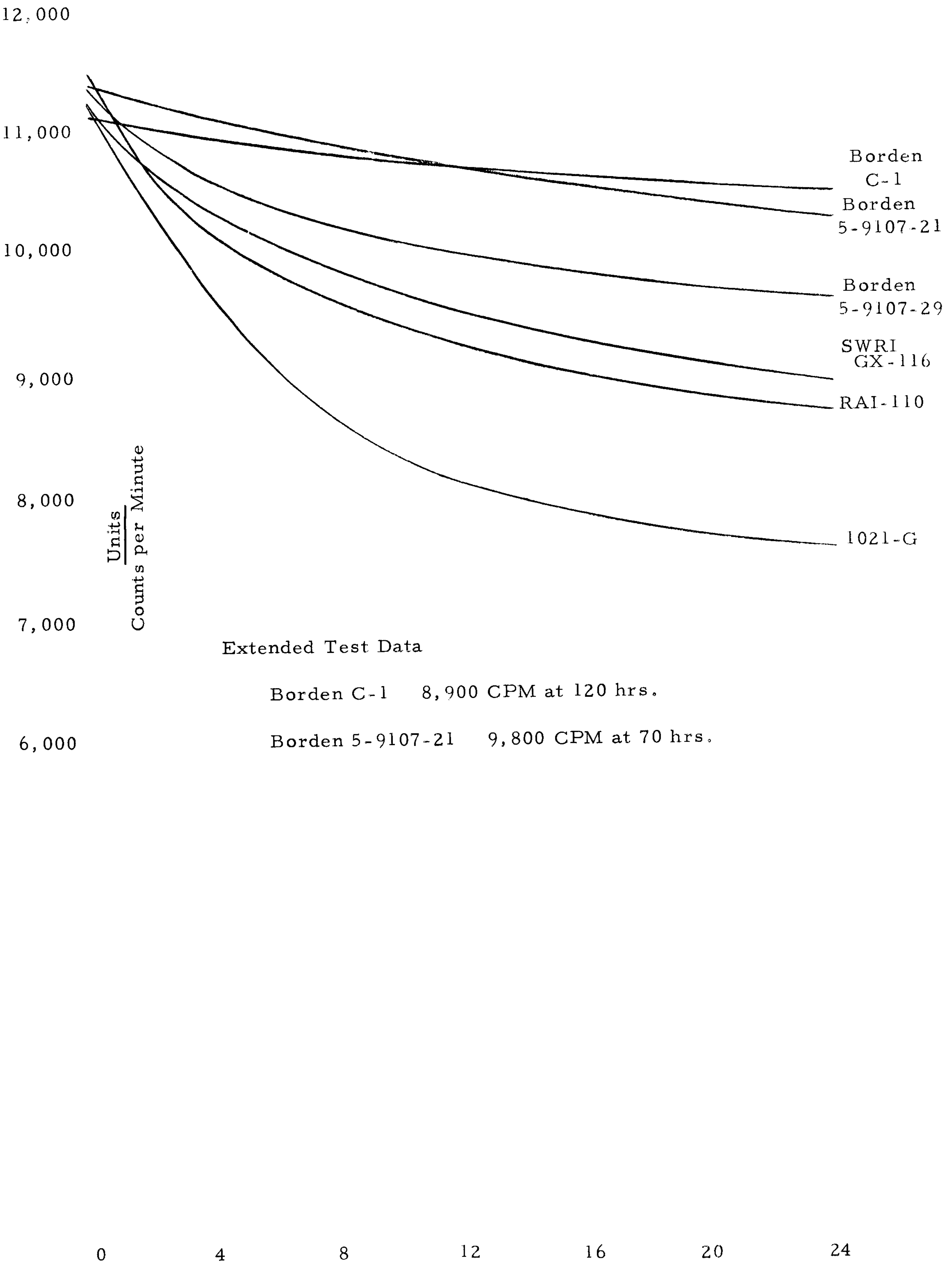
NOTE

(1) Samples equilibrated in 40% KOH - values are for samples cut with the length perpendicular to the machine direction of the film. Samples cut with the long dimension parallel to the machine direction give dimensional changes of - 2.8% in length, + 6.0% in width and + 300% in thickness.

Table 4

Rates of Silver Absorption by Separators

No.	Sample	Rate
1	PuDo 300	-
2	SWRI GX-116	2.42×10^{-6}g Ag_2O/sq. in. /hr.
3	Borden C-1	1.53×10^{-6} " " "
4	Borden 5-9107-21	1.46×10^{-6} " " "
5	Borden 5-9107-29	16.5×10^{-6} " " "
6	Borden 574-151F	0.57×10^{-6} " " "
7	1021-G ESB	25.6×10^{-6} " " "

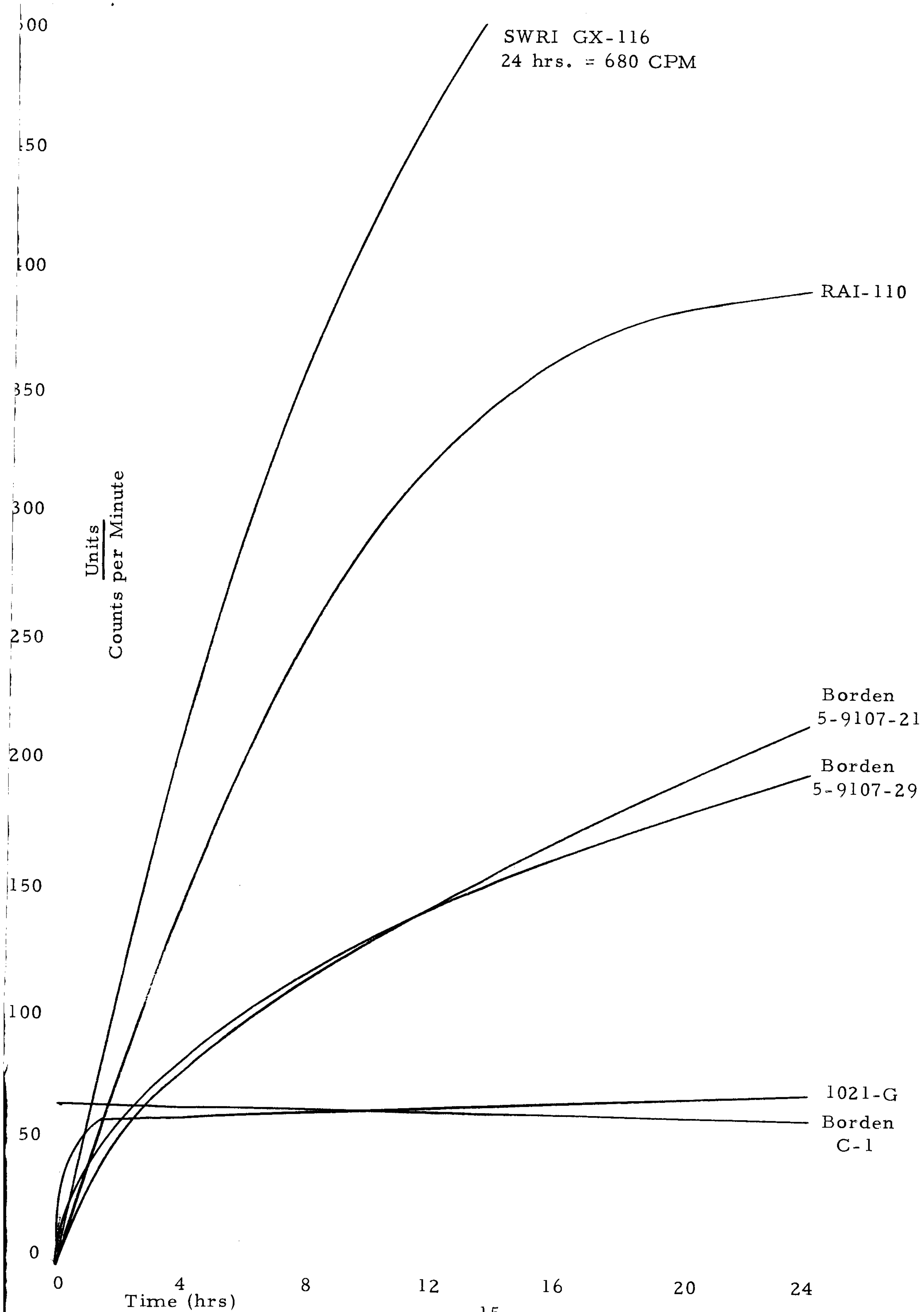


Extended Test Data

Borden C-1 8,900 CPM at 120 hrs.

Borden 5-9107-21 9,800 CPM at 70 hrs.

Loss of Ag^{110} Activity in "Hot" Compartment A



Diffusion of Ag^{110} into Compartment B
Figure 3

A concentration gradient is established across the separator dividing a two-compartment cell. One chamber contains 45% KOH one molar in ZnO while the other contains 45% KOH 10^{-4} molar in ZnO. The rate of permeation is obtained by potentiometrically measuring the voltage change with time of a zinc vs Hg/HgO electrode in the initially zinc oxide free compartment. The potential of the zinc/aincate ion couple varies by 0.0295 volts per ten fold change in zincate ion concentration at constant hydroxide ion concentration. The measurement is made over a period of 115 minutes and the concentration taken from a calibration curve relating zincate concentration and the potential of the zinc-zincate vs Hg/HgO system. Values obtained on samples tested are given in Table 5.

Table 5

Zincate Permeability through Separators

No.	Sample	Permeation Rate moles ZnO^2Cm^2/sec
1	PuDo 300	2.7×10^{-7}
2	SWRI GX 116	2.7×10^{-7}
3	Borden C-1	2.2×10^{-8}
4	Borden 5-9107-21	2.2×10^{-8}
5	Borden 5-9107-29	1.2×10^{-7}
6	Borden 574-151F	6.8×10^{-7}
7	ESB 1021 G	1.8×10^{-7}

2.4.3 Adsorption of Zinc Oxide

Recently, measurements have been made of the distribution of zincate between the pore liquor in separator materials and the equilibrating electrolyte (Stachurski, Z. and McBreen, J., Study To Investigate And Improve The Zinc Electrode For Spacecraft Electrochemical Cells, NASA 5-10231). Differences have been found in zincate concentration between the two phases depending upon the separator tested. A correlation has been suggested between the analytically determined distribution coefficient and the resistance of the separator to zinc shorting. The procedure consists of equilibrating separator samples in excess potassium hydroxide solution containing known amounts of dissolved zinc oxide. When equilibration is complete, the amount of zinc oxide contained in the separator is determined and the distribution coefficient determined.

It is planned to determine the zincate distribution coefficients for a number of the separator materials under evaluation and to examine the correlation of this value with both the zinc penetration test and the results of cycling nickel-zinc oxide cells.

2.5 Pore Size and Tortuosity

2.5.1 Pore Size

Separotor pore size is determined utilizing a modified osmometer and assuming that Poisseuille's law is applicable. This states that the volume of liquid flowing through a tube is proportional to the tube dimensions and the viscosity of the liquid. In applying Poisseuille's Law to membranes, the assumption is made that the pores are constant cross section tubes extending across the separator thickness. The number of pores can be calculated for this model from the measurement of pore volume. The pore diameter is obtained from the measurement of liquid flow through a given separator area under a known pressure.

Methods are given in the Cooper-Fleischer Handbook using both water and potassium hydroxide electrolyte as the permeating liquid. In this work, 40% KOH is used so that errors are not introduced due to the volume changes occurring in swellable membranes in solutions of different concentrations.

2.5.2 Tortuosity

The model chosen for the pore size estimation is unrealistic when applied to swellable membranes. The "pores" are not geometrically ordered but form some complex of varying length and diameter. The result is a longer diffusion path which results in the pore size determined by this method being somewhat too large. A correction can be applied for this more tortuous path by considering the diffusional path to be increased by the steric interference of the membrane structure. The equation used in the calculation of tortuosity T is:

$$T = \frac{\rho \text{ separator}}{\rho \text{ electrolyte}} \times \text{ Separator Porosity}$$

The pore size determination is not completed at this time. The data on pore size and tortuosity of the separator films will be included in the next Quarterly Report.

2.6 Oxidation Resistance

Oxidation resistance is to be gauged using tensile specimens immersed in silver saturated 40% KOH. The changes in tensile strength with immersion time at 50°C will be recorded. This test has not been completed at this time.

2.7 Tensile Strength

Tensile strength is measured using die cut specimens 5" by 1" by film thickness. The film is conditioned for 24 hours at 72 ± 2°F, 50 ± 5% R.H. and the test run at a cross head speed of 2 in/minute. Rubber faced grips insure against slippage in the grips with the specimens so positioned that 3 in. is between the grips. The value reported is tensile strength at break which is given in Table 3 for six separator films for specimens cut parallel and perpendicular to the roll direction of the film. Differences in the two values indicate orientation effects introduced in the film manufacture which could lead to differential swelling in the equilibrated separator. Preferred orientation occurs in PuDo 300 and in the grafted films. The Borden materials are cast from solution and are not drawn to size so that the film is not oriented. The grafted sample SWRI exhibits differential tensile strength being about 50% stronger in the roll direction. This, presumably, is not introduced in the grafting operation but is a carry-over from the original polyethylene film.

3.0 CELL SCREENING TESTS

In addition to the non-battery tests already described, three plate cells are to be constructed using the most satisfactory materials resulting from these characterization tests. Two systems will be used so that a separate measure of the effects of the silver and zinc electrode on the separator can be obtained. The best of the separator systems revealed by the combined screening procedures will finally be evaluated in full cells of 10 ampere hour capacity.

3.1 Silver-Cadmium Oxide Cells

Two layers of primary separator material and a single layer of absorber type material will be used in the construction of three plate cells. A standard pack tightness based on separator expansion in 40% KOH will be used, shimming the cell cases to achieve this spacing. Cells will be vented and flooded.

As planned, the electrical testing will consist of

a) formation

b) constant current discharge at the 5 hour rate to 0.80 volt

c) charge to 120% of previous cycle discharge capacity of previous discharge

d) fifteen cycles as in b and c

e) at fifteen cycles, the cells will be examined to determine the extent of silver penetration.

3.2 Nickel-Zinc Oxide Cells

Three plate cells, as above, will be built using sintered plate nickel electrodes and standard zinc oxide electrodes. Separator systems will duplicate those tested in the silver-cadmium oxide cells except where other screening tests indicate a marked resistance to zinc penetration with only marginal or poor resistance to silver oxide. The electrolyte will again be 40% KOH. The electrical cycling consists of:

a) formation

b) constant current discharge at the 5 hour rate to 1.30 volts

c) constant current charge to 120% of previous cycle discharge capacity

d) cycle as in c and b for a total of 15 cycles or until indications of shorting occur, monitoring current and voltage

e) at 15 cycles, cells will be examined to determine extent of Zn growth.

All cycling will be done under ambient conditions. Where separators are in a form which does not permit evaluation by standard construction, methods will be devised to obtain meaningful results in these systems. Table 6 gives the pertinent details of the electrodes used in this testing.

Table 6

Electrode Data

	Silver	Cadmium	Nickel	Zinc
Dimensions	1.750 by 1.875x.028	1.750 by 1.875x.050	1.750 by 1.875	1.750 by 1.875x.04
Theoretical Capacity ampere-hours	3.12	2.31	-	3.45
Capacity at 5-hour rate ampere hrs.	1.73	1.75	0.75	2.29
Grid Material	2/0 Ag	2/0 Ag	-	2/0 Ag
Electrode Type	sintered	pressed powder	sintered plaque	pressed powder
Manufacturer	ESB Inc.	ESB Inc.	Alkaline Batteries Ltd.	ESB Inc.

3.3 Results of Preliminary Cycling Test

Six cells were constructed using Cellophane PuDo 300 in both silver-cadmium oxide and nickel zinc oxide. Cells were paired, with the variation among pairs being separator expansion factor. By measurement, S.E.F. (wet thickness separator/dry thickness separator) has been found to be 3.0. In these cells, the volume reserved for separator swelling was varied by using S.E.F.'s of 3, 3.5 and 4. In similarly constructed nickel zinc cells, the S.E.F. was varied from 3.5 to 5.0 to examine the effect of this variable on cell performance in the selected electrical cycling regimes. This test has not been completed at this point but no pronounced effect is noted in the incomplete data. The results of these tests will be reported in the next Quarterly Report and will be used to determine the pack thickness to be used in the construction of subsequent test vehicles.

4.0 PROGRAM FOR NEXT QUARTER

Prospective separator suppliers have been canvassed and some materials have been received and others promised. The various test set-ups are completed and the suggested procedures have been examined for reproducibility. During the second quarter, the characterization testing will be completed on the materials on hand and will be applied to other materials as received. The three plate cell testing will be instituted on the most promising of the materials.