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SEPARATOR MATERIALS FOR SILVER OXIDE ZINC AND SILVER OXIDE CADMIUM ELECTROCHEMICAL CELLS

(Interim Report)

BY

THOMAS J. HENNIGAN

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SEPARATOR MATERIALS FOR SILVER OXIDE ZINC AND SILVER OXIDE CADMIUM ELECTROCHEMICAL CELLS

A. INTRODUCTION

The silver oxide zinc cell, and to some extent, the silver oxide cadmium cell, have found wide use in military applications. With the advent of the space age, these electrochemical systems are being used on board satellites where weight saving and non-magnetic properties are required. In these cells, in the charged state, silver oxide (s) is used as the positive electrode and either zinc or cadmium is used as the negative electrode. On discharge, the silver oxide (s) is reduced to metallic silver and the zinc or cadmium is oxidized to form a hydroxide. The electrolyte, which provides the ionic path within the cell, is an aqueous solution of potassium hydroxide. Concentrations of the electrolyte range from 30% to 45% by weight.

These electrochemical cells, as with any conventional cell, require the use of separators. Separators are used in cells to meet the following major functional requirements:

1. Separate the positive and negative electrodes in the cell to prevent contact of the electrodes of opposite polarity which would result in short circuits,

2. Prevent dendritic growths or soluable products from shorting the cell or migrating to the electrode of opposite polarity, and

3. Distribute and retain the electrolyte between the electrodes, especially in cells where the electrolyte level is maintained below the top of the electrode-separator assembly.

In addition to the above requirements, the separator material, especially the type of material used in silver cells, must also possess the following properties or characteristics:

1. Allow free ionic conduction of the potassium hydroxide electrolyte,

2. Be compatible in the cell environment, i.e., be stable in the electrolyte-silver oxide - Zn (Cd) - oxygen media,

3. Be reasonably capable of fabrication into cells and be able to withstand the acceleration and vibration associated with launch vehicles and

4. Withstand temperatures up to 40°C continuous.

Polymer membranes have found wide use as separators in silver cells. The most used separator materials today are cellophanes or various modifications of cellophane. In many applications, cellophane has proven to be quite adequate for silver cell use. However, in space applications, where high reliability is a prime requirement, cellophane has its shortcomings. This will be brought forth later in the report.

Many of the properties of cellophane are characteristic of the requirements imposed on a material that will function as a cell separator. Cellophane is essentially a non porous material but, when wetted with potassium hydroxide, will swell and provide a semi-permeable film that will allow free ionic conduction for the cell operation. Primarily, swelling is in the thickness dimension and the material swells by approximately a factor of three. Cellophane can prevent the migration of silver or its oxides to the negative plate. However, in performing this function, the film is oxidized in the process when silver oxide is reduced on the surface of the cellophane and deposits thereon on as a silver film. This oxidation causes breakage of the molecular chains of the cellophane structure and subsequent degradation of the film. The deposition of silver on the separator materials can cause internal short circuits. Also, as reported in (1), cellophane, and other materials such as polyvinyl alcohol and modifications of polyethylene, in conjunction with the electrolyte can form a transport media for zinc dendritic growths from the negative to the positive electrode. Also, the hydrolysis of the cellophane by the aqueous potassium hydroxide solution (2) will also contribute to the degradation of the film.

Since June, 1962, the NASA/Goddard Space Flight Center has sponsored several contractual programs to attain the following goals:

1. A better understanding of the properties of cellophane and other types of membranes that are advantageous or detrimental to the performance of silver cells,

2. To develop meaningful screening tests to evaluate separator materials prior to cell fabrication and testing and

3. Modify cellophane, investigate available materials and develop new materials for use in silver oxide-zinc and silver oxide-cadium cells.

The work performed in the research and development areas has been reported in the reports of the Electric Storage Battery Company (2), the Borden Chemical Company (3) and the Yardney Electric Company (1) & (4). The screening tests developed by the Electric Storage Battery Company and others are summarized in ref. (5). It is the primary purpose of this interim report to present the data and conclusions to date that have resulted from the cell evaluation tests using separator materials that have resulted from the above programs. The major portion of the evaluation, on silver zinc cells, was performed by the Naval Ammunition Depot at Crane, Indiana under the direction of GSFC. Work pertaining to silver oxide-cadmium/separator performance has been initiated at GSFC. Both evaluation programs are in progress and the work at Borden Chemical and the Yardney Electric Company is continuing.

B. PROGRAM ON MATERIALS DEVELOPED BY THE ELECTRIC STORAGE BATTERY COMPANY ON CONTRACT NAS5-2860

In August 1964, the Electric Storage Battery Company delivered twenty-five secondary silver oxide-zinc cells at the termination of Contract NAS5-2860 (2). Four types of separator systems and one sample of cellophane, as a control, were selected for evaluation in cells. Five cells of each type of separator system and five controls were delivered. The basic structure of the cells and types of separators incorporated in the cell designs are as shown below.

Silver oxide-zinc Secondary 24 Ampere Hour Nominal Cells

Number of plates per cell - 11
Number of positives per cell - 5
Number of negatives per cell - 6
Weight of Ag per cell 90 gms.
Weight of ZnO per cell 99 gms.
Plate size - positive 6.4 × 7.0 × .091 cm.
Plate size - negative 6.4 × 7.0 × .122 cm.
Positive plates wrapped with one layer of Dynel EM309
Negative plates are wrapped with one layer of Viscon
Electrolyte - 40% KOH.

Separator Type	Main Separator System
1-5 (Control)	Eight layers of cellophane
6-10	1. Three layers of cellophane treated with tolylene diisocyanate-nearest to the positive- followed by 2. Five layers of cellophane (untreated).
11-15	1. Two layers of Permion 300-40/30 on positive followed by 2. Two layers of cellophane (untreated) 3. Two layers of fiber-strengthened regenerated cellulose.
16-20	1. One layer PMA 83/17 on the positive followed by 2. One layer of Cellophane (untreated) 3. Two layers of fiber-strengthened regenerated cellulose.
21-25	1. Three layers of cellophane, treated with m-phenylene diamine, on the positive followed by 2. Two layers of fiber strengthened regenerated cellulose.

For a more complete description of the above materials, see ref. (2). The cells were built in lucite cases supplied by GSFC. The cells were of the vented type.

Following two formation cycles, the cycling of the cells during the test program was as follows:

Discharge rate	C/5*
Depth of discharge	100% to 1.3 volts per cell
Recharge	Constant current at the C/20* rate until 120% of the capacity removed on the previous discharge was replaced in each cell.
Ambient temperature	25± 2°C
Electrolyte addition	Initial - 65 cc. of 40% KOH Electrolyte level was adjusted at the end of charge to the top of the plates with 20% KOH

---

*C = nominal capacity or 24 ampere hours

Stand times	Between each charge and discharge 16 hours Between each discharge and charge 1-5 hours

Cells were operated in series but were monitored individually on charge and discharge.

In the above test program, the charged stand times would accelerate the attack of the separator material by the soluble silver oxide (s) while the overcharge would accelerate oxidative attack of the separator materials by evolved oxygen. However, since the cells were vented, oxygen attack on the separators would not be as severe as with sealed cells. Also the overcharge would promote zinc growth. Initially, the apparent, negative electrode, current density during charge and overcharge would be 2.7 ma/cm^2. This low current density would promote mossy types of dendritic growths (6). After many cycles, when the zinc electrode would change physical shape due to solubility of the electrode and fall off of active material, higher current densities would promote pine tree and acicular dendrites (6). All types of dendritic growth, if supported by the separator electrolyte system as reported in (1), would be accelerated by the forced overcharge and zinc shorting would result. In order to replace 120% charge into the cells to replace the capacity withdrawn on the previous discharge, in most cases the cells would exceed 2.0 volts. This overpotential would contribute to dendritic growth. Also, in a random mode, the cells would exceed 2.32 volts, the hydrogen evolution potential. The convection currents set up by the hydrogen evolution would tend to supply zincate rich electrolyte to the dentritic tips and accelerate the growths (6). Based on the above, the test schedule used in the program was a severe test of the separator to withstand oxidation and zinc dentritic growths.

At the same time the test program was an overtest of the zinc electrode. As will be seen later, particularly with other types of separators, test results show that the zinc has deteriorated while the separator does not contribute to cell failure.

During the test program, the ampere hours in and out of the cells were determined on each cycle. In figures 1 thru 5, enough data has been plotted to show the variation of discharge ampere hour capacity with cycling. The graphs show the percent of nominal capacity (24 AH) remaining in the cells as a function of cycle life. Also note on the top of each graph is given the number of cells remaining in the battery. For the sake of comparison, 40% of nominal capacity is taken as the cut off point.

Separator types 1-5 and 6-10 showed very random operation. Cells failed within the first eleven cycles. Separator types 11-15 and 16-20 showed failures at 28 and 19 cycles respectively. Separator type 21-25 showed good life up to

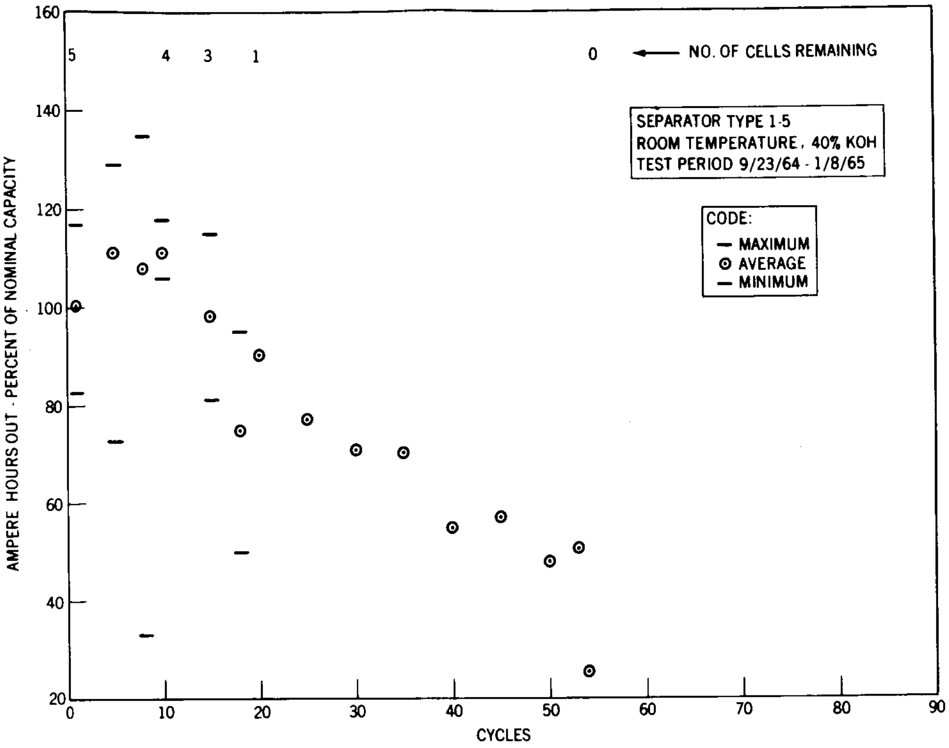

Figure 1

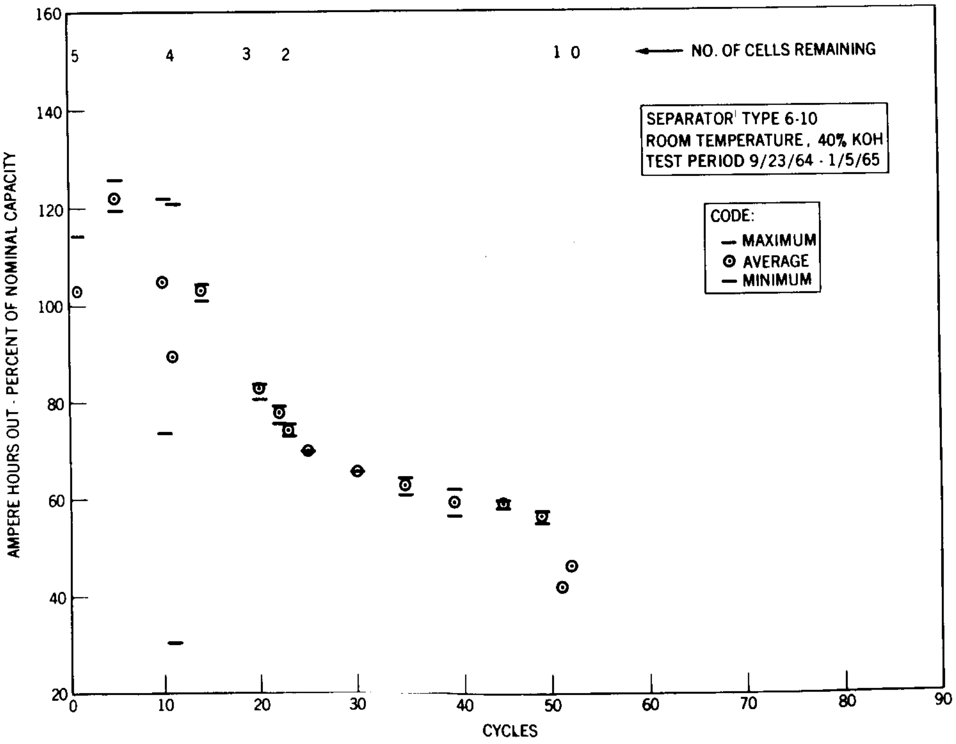

Figure 2

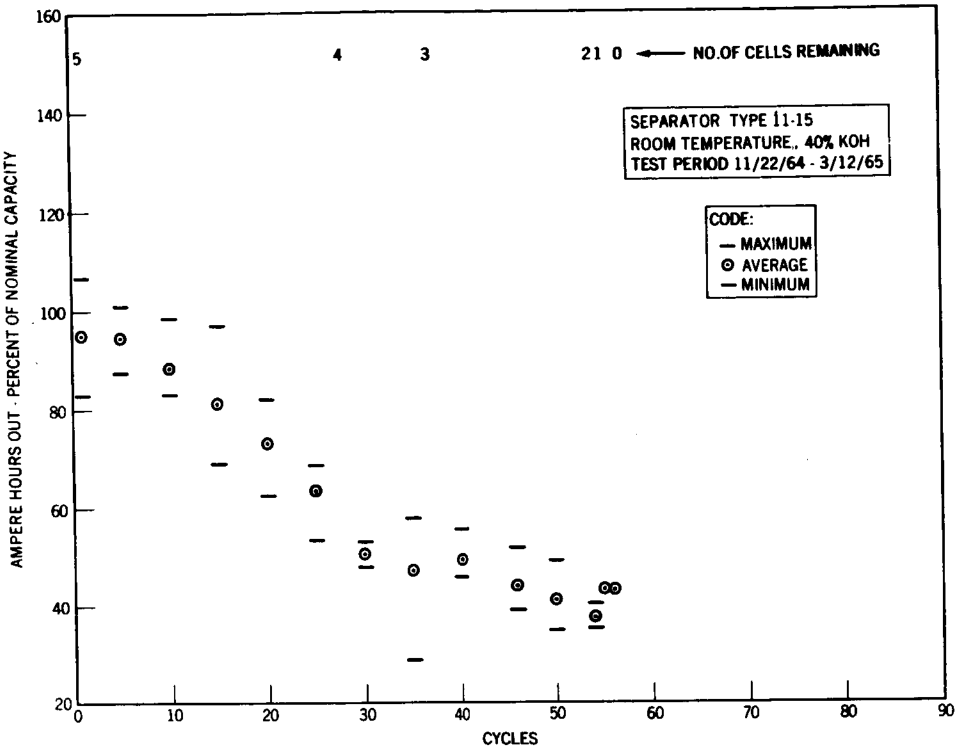

Figure 3

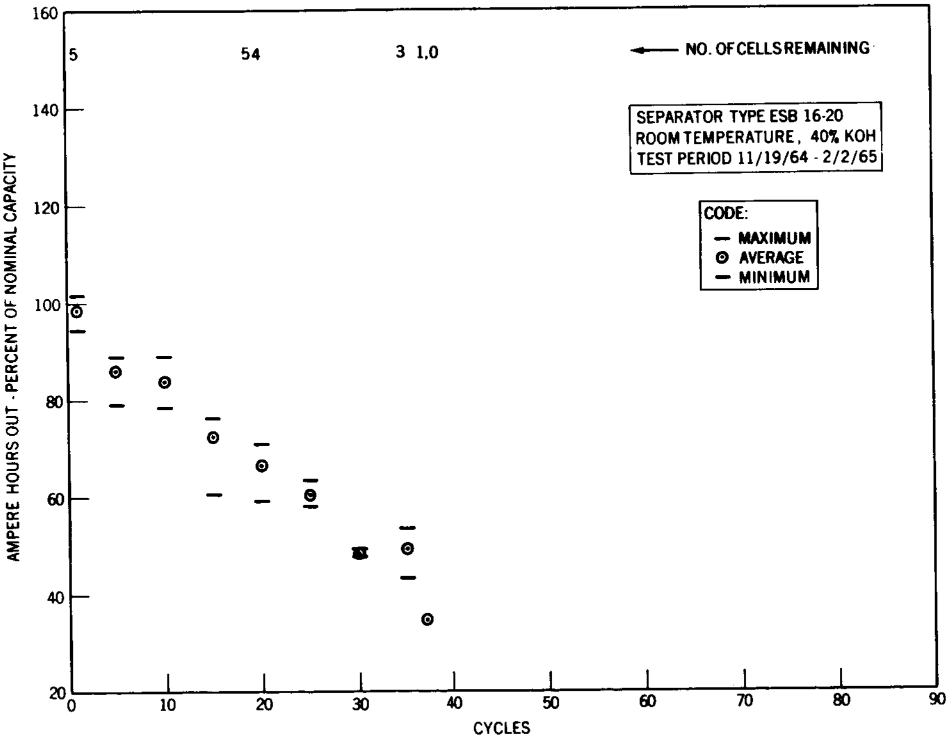

Figure 4

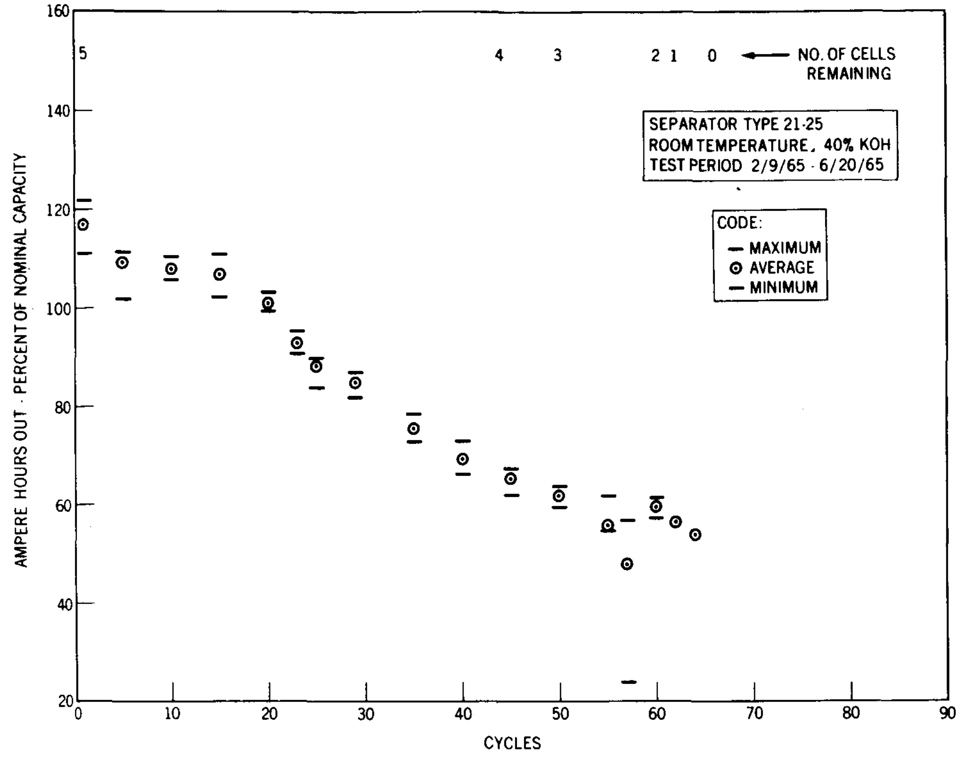

Figure 5

44 cycles but then shorting of the cells commenced. It is noted, in general, that all the cells using the separator types above will fail due to short circuits, can fail early in the cycle regime and failure is catastrophic in that no indication of failure can be detected.

The data from figures 1 through 5 are summarized in the table below. For comparison, two criteria were selected. First, the number of cycles obtained until the first cell fails and secondly, the most number of cycles completed by a separator type to 40% of the nominal cell capacity. As previously mentioned, failure in the first case is catastrophic, i.e., with the possible exception of separator type 21-25, the cells failed above 40% capacity without any positive indication of ensuing failure. In a sealed battery (sealed cells in series) application, where constant potential charging is employed, a one cell failure due to shorting can cause entire battery failure since the voltage across the remaining cells in the battery can increase above the gassing potential. The second criteria indicates the maximum number of cycles obtained with any separator type.

Separator Type	Cycles to First Cell Failure Above 40% Capacity	Most Cycles to 40% Capacity ( ) No. of Cells Remaining
1-5 (Control)	7	53 (1)
6-10	11	52 (1)
11-15	28	56 (1)
16-20	19	36 (1)
21-25	44	66 (1)

Intermediate cell failures may be obtained from figures 1 throughout 5.

From the test data, the following conclusions have been drawn:

1. The use of tolylene diisocyanate (TDI) impregnated cellophane does not improve silver zinc cell performance when used in combination with untreated cellophane.

2. In separator types 11-15 and 16-20, screening tests showed that both Permion 300 and PMA 83/17 were low in reactivity, as compared with cellophane, with silver oxide. Also, the Electric Storage Battery Company found that materials that are resistant to oxidation allow diffusion of the silver species (2). In addition, it was determined that the resistance to zinc penetration of the fiber-strengthened regenerated cellulose is about 1.5 times the resistance of cellophane. It is concluded that the mechanism of failure was as follows: (a) silver oxide readily diffused through the Permion 300 and PMA 83/17 layers, (b) the oxide was reduced on the cellophane to form silver conductive paths and (c) zinc penetration, although somewhat delayed, took place through the cellulose, eventually contacted the deposited silver and shorting commenced. The two layers of cellophane in the separator type 11-15 as opposed to the one layer in the type 16-20 would contribute to the longer life of the former system.

3. As regards separator type 21-25, the treatment of the cellophane with an antioxidant plus the fact that three layers of the treated cellophane were present in the cell would have delayed silver penetration and prolonged the cell life. As aforementioned the fiber-strengthened regenerated cellulose does retard zinc dendritic growths.

4. Most of the base materials evaluated in the above program are manufactured in a continuous process. The processing and available quality control techniques may not be exacting enough to assure materials for high reliability for space use. In addition, the swelling of the materials as a result of wetting with KOH and the folding of the materials during cell fabrication could impart nonuniformities and stresses that in turn could lessen the silver and zinc stopping ability of the materials. The Electric Storage Battery personnel performed a failure analysis of the cells cycled in the program (8). The data is reported in Table 1. Note that in many cases where shorting was determined, it was observed at the edges or bottom of the electrodes. In these areas, the separator materials are bent 180 degrees. It has also been the experience of the author, that silver zinc cells tend to short at the edges of electrodes. It is conjectured that the randomness of operation of the cells in the program is indicative of materials that are not uniform in physical and chemical properties.

During the test program, voltage readings on charge and discharge were recorded on a per cell basis. Examination of the charge data, by no means complete, has not afforded any useful information other than show that end of charge voltages exceeded 2.0 volts. The discharge data has been averaged for every five cycles and is tabulated in Table II. Only the data on the lower or silver monoxide plateau above 1.40 volts was averaged. On initial cycling, the cells in the program discharge at a level 60 to 90 millivolts lower than conventional cells. This is due to the mulitlayered separator systems and/or the higher electrical resistance of Permion 300 and PMA 83/17. The specific resistivities of these materials are 34.8 and 39.6 ohm-cm, respectively. The specific resistances of all the other materials used in the program are the order of 8.0 ohm-cm. (2) On the initial cycles, cells using Permion 300 and PMA 38/17 showed a 10 to 20 millivolt drop as compared to other systems. However, this does not appear to be significant when one considers a resistivity increase of a factor of 4 to 5. Therefore, it is concluded that resistivity of polymers determined in screening tests have to be several orders of magnitude higher than 40 ohm-cm to significantly affect voltage characteristics at the five hour discharge rate at 25°C.

During cycling, the decrease of average silver monoxide (Ag_2O) plateau voltage was about equal for all types except 21-25 which maintained a +10 to +30 millivolt increment of voltage over other test separators and the control, separator type 1-5. In viewing Table II, it must be remembered that the voltage values range from initial average values of the Ag_2O plateau for five cells to average values of the Ag_2O plateau for the one remaining cell.

Table I
Failure Analysis of Electric Storage Battery Cells*

Separator Type	Cell Number	Cause of Failure	Ag Penetration of Separator Layers
1-5	1	Zinc short bottom edge	1-2 deeply stained traces 3rd
	2	Zinc short 2 edge 1 body	1-2 deeply stained 3 moderate traces 4th
	3	Zinc short U fold	1-4 deeply stained 5 moderate traces 6th
	4	Zinc short bottom edge	1-2 deeply stained 3 moderate traces 4th
	5	Zinc short outer plate edge	1-2 deeply stained 3 moderate traces 4th
6-10	6	Zinc short at the U fold	1-3 deeply stained 4 moderate, traces 5th
	7	Zinc short bottom edge	1-2 deeply stained 3 moderate, none on 4th
	8	Zinc short bottom edge	1 deeply stained 2 moderate, trace 3rd layer
	9	Zinc shorts plate corner	1-2 deeply stained 3 moderate, trace 4th layer
	10	Zinc short U fold at plate edge	1-2 deeply stained 3 moderate, trace 4th layer
11-15	11	Undetermined	1-4 deeply stained 5 moderate 6 slight discoloration
	12	Undetermined	1-4 deeply stained 5 moderate 6 slight discoloration
	13	Zinc short bottom edge	All layers deeply stained

*Failure analysis performed by the Electric Storage Battery Company after completion of Contract NAS5-2860.

Table I (Continued)
Failure Analysis of Electric Storage Battery Cells

Separator Type	Cell Number	Cause of Failure	Ag Penetration of Separator Layers
	14	Zinc shorts main plate body	1-3 layers deeply stained 4 moderate 5 slight
	15	Undetermined	1-4 layers deeply stained 5 moderate
16-20	16	Zinc short main plate body	1 deeply stained 2 moderate 3 moderate
	17	Zinc short at U fold	1 deeply stained 2 moderate 3 slight
	18	Zinc short main plate area	1 deeply stained 2 deeply stained 3 and 4 traces
	19	Zinc short main plate area	1 deeply stained 2 medium 3 medium 4 slight
	20	Zinc short main plate area	1 deeply stained 2 medium 3 and 4 slight
21-25	21	Zinc short main plate area	1 & 2 deeply discolored 3 moderate one side 4 traces
	22	Zinc short bottom edge	1 & 2 deeply discolored 3 moderate one side 4 traces
	23	Zinc short main plate area	1 & 2 deeply discolored 3 moderate one side 4 traces
	24	Zinc shorts bottom edge in main plate area	1 & 2 deeply discolored 3 moderate one side 4 traces
	25	Zinc short main plate area	1 & 2 deeply discolored 3 moderate one side 4 traces

Table II

Average Discharge Voltage Readings on the Silver Monoxide (Ag_2O) Plateau

Cycle Number	Separator Type				
	1-5	6-10	11-15	16-20	21-25
1	1.48	1.48	1.47	1.46	1.49
5	1.48	1.47	1.48	1.46	1.49
10	1.47	1.46	1.46	1.45	1.48
15	1.47	1.45	1.46	1.45	1.48
20	1.46	1.44	1.45	1.45	1.47
25	1.45	1.44	1.44	1.44	1.46
30	1.44	1.42	1.43	1.44	1.45
35	1.44	1.43	1.42	1.43	1.44
40	1.42	1.42	1.42	-	1.45
45	1.43	1.43	1.40	-	1.44
50	1.42	1.43	1.41	-	1.44
55	-	-	1.42	-	1.44
60	-	-	-	-	1.44
64	-	-	-	-	1.44

C. PROGRAM ON MATERIALS DEVELOPED BY THE BORDEN CHEMICAL COMPANY ON CONTRACT NAS5-3467

In June 1963, Contract NAS5-3467 was awarded to the Borden Chemical Company to develop new separator materials to improve the life and reliability of the silver oxide cadmium and the silver oxide zinc couples. The Borden approach was as follows:

> "Screening of a wide variety of polymers established that a separator requires a balance of polar and non-polar structural character. Polarity must be sufficient for electrolyte absorption and conductivity. Non-polarity must be sufficient for insolubility in concentrated alkali. One method to achieve the required balance in polarity is to cast films from homogeneous mixtures of more polar with less polar polymers. Systematic studies were made of the effect of composition on the properties of several types of such polymer mixtures. In particular, mixtures of methyl cellulose with several types of alkali-soluble polymers were studied. Ranges of composition were found which gave insoluable but conducting films." (3)

Several types of methyl cellulose formulations with carboxy polymers, a high percent (98%) hydrolyzed polyvinyl alcohol (PVA) and modifications of polyvinyl alcohol were developed during the program. During the course of work performed by Borden, materials that showed promise during the development phase were fabricated into silver zinc cells by the Burgess Battery Company. Single cell tests were run on the cells in a cycle program similar to that described above on the Electric Storage Battery units.

Both from the screening tests and the single cell tests, membranes were selected for a more comprehensive test at the Naval Ammunition Depot. Six types of separator systems and one sample of cellophane, as a control, were selected for evaluation in cells. Seven cells of each type of separator system and seven control cells were delivered. The basic structure of the cells and types of separators incorporated in the cell design are as shown below.

Silver oxide-zinc Secondary 10 Ampere Hour Nominal Cells

Number of plates per cell	13
Number of positives per cell	6
Number of negative per cell	7
Weight of Ag per cell	38 gms.
Weight of ZnO per cell	28 gms.

Plate size - positive	5.4 × 4.4 × 0.071 cm.
Plate size - negative	5.4 × 4.4 × 0.076 cm.

Both positive and negative wrapped with one layer of Webril M1401.

Electrolyte - All cells, unless otherwise mentioned, have 30% KOH.

Separator Type	Main Separator System
Cellophane (Control)	Five layers of cellophane
PVA	Five layers of high percentage (98%) hydrolyzed polyvinyl alcohol
HEPVA	Hydroxyethyl polyvinyl alcohol in which 25% of available hydroxyls are etherified by hydroxyethylation
C1	Six layers of methyl cellulose/Poly (methyl ether/ maleic anhydride) 10%
C3	Six layers of methyl cellulose/Poly(methyl ether/ maleic anhydride) 30%
B3	Five layers of methyl cellulose/polyacrylic acid
E4	Five layers of methyl cellulose hydroxyethyl cellulose

For a more complete description of the above materials, see ref. (3). The cells were built in nylon cases. The cells were of the vented type. Following four formation cycles, the cycling of the cells during the test program at NAD Crane was as follows:

Discharge rate	C/5*
Depth of discharge	100% to 1.3 volts per cell
Recharge	Constant current at the C/20* rate until 120% of the capacity removed on the previous discharge was replaced in each cell.
Ambient temperature	25° ±2°C for most tests, some tests at 40 ±2°C

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*C = nominal capacity or 10 ampere hours

Electrolyte addition	Initial - 30 cc. of KOH Electrolyte level was adjusted at the end of charge to the top of the plates with 30% or 40% KOH, whichever was used on the initial fill.
Stand times	Between each charge and discharge - 16 hours Between each discharge and charge - 1 to 5 hours

Cells were operated in series but were monitored individually on charge and discharge.

In the above test program, the conditions for accelerated attack on the separator system and the over test of the zinc electrode are the same as previously mentioned in the program for the cell/separator units developed by the Electric Storage Battery Company. Note that concentrated electrolyte is added to the cells to replace the amount lost by electrolysis. This was done because the most of the polymer compounds developed by Borden are water soluble and there was some concern that the separators might dissolve in part if dilute electrolyte was added during the cycle program. Work by the Borden personnel has confirmed this fact in that the separator types incorporating modifications of methyl cellulose are questionable as regards to solubility in electrolyte concentrations of less than 20% KOH.

The main test program consisted of five cells of each type of separator system and five control cells at 25°C. During the test program the ampere hours in and out of the cells were determined for each cycle. In figures 6 through 12, enough data has been plotted to show the variation of discharge ampere hour capacity with cycling. The graphs show the percent of nominal capacity (10 AH) on discharge as a function of cycle life. Also note that on the top of each graph is given the number of cells averaged to obtain the mean value. For the sake of comparison, 40% of nominal capacity is taken as the cut off point.

The data from figures 6 through 12 are summarized in the following table. The criteria for comparison were the number of cycles obtained until the first cell delivers less than 40% of nominal capacity (10 AH) and the maximum number of cycles completed by a separator type to 40% of nominal capacity. In the case of these new materials, several types of materials did not tend to short in a catastrophic mode. In fact, the capacities of the cell separator types stayed close together during the test program so that it is possible to express the maximum number of cycles as an average of four or five cells. For instance, all

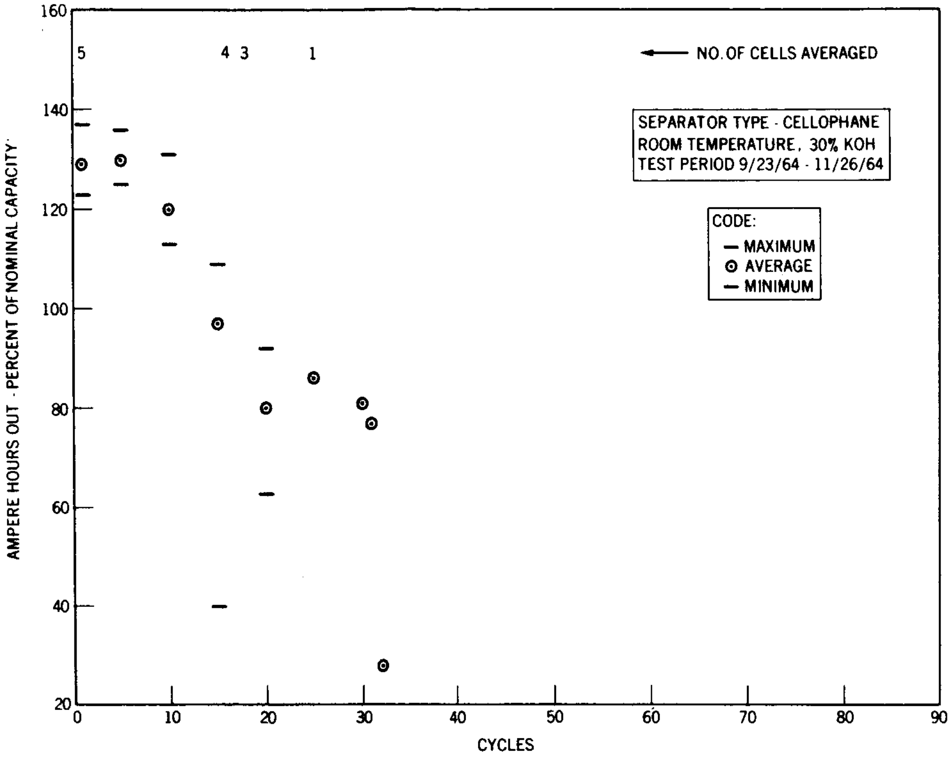

Figure 6

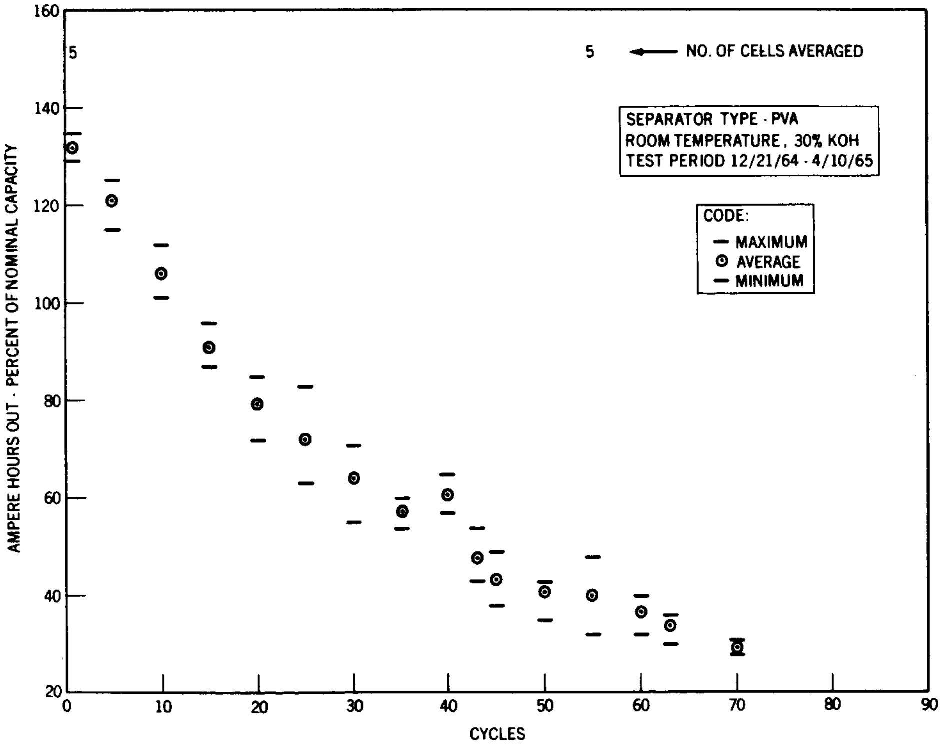

Figure 7

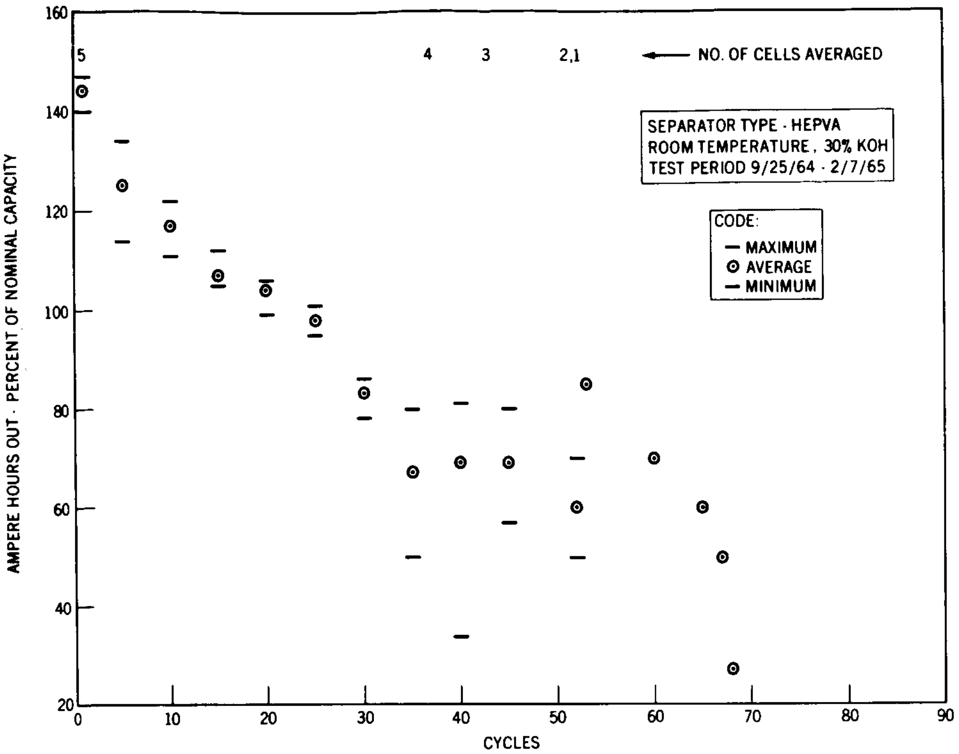

Figure 8

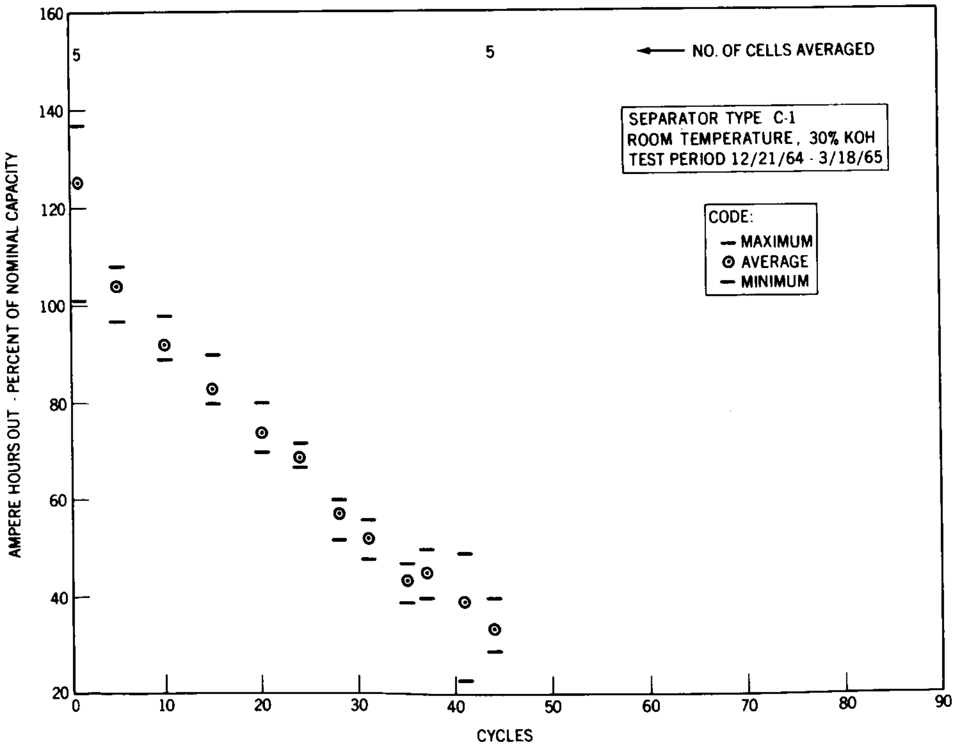

Figure 9

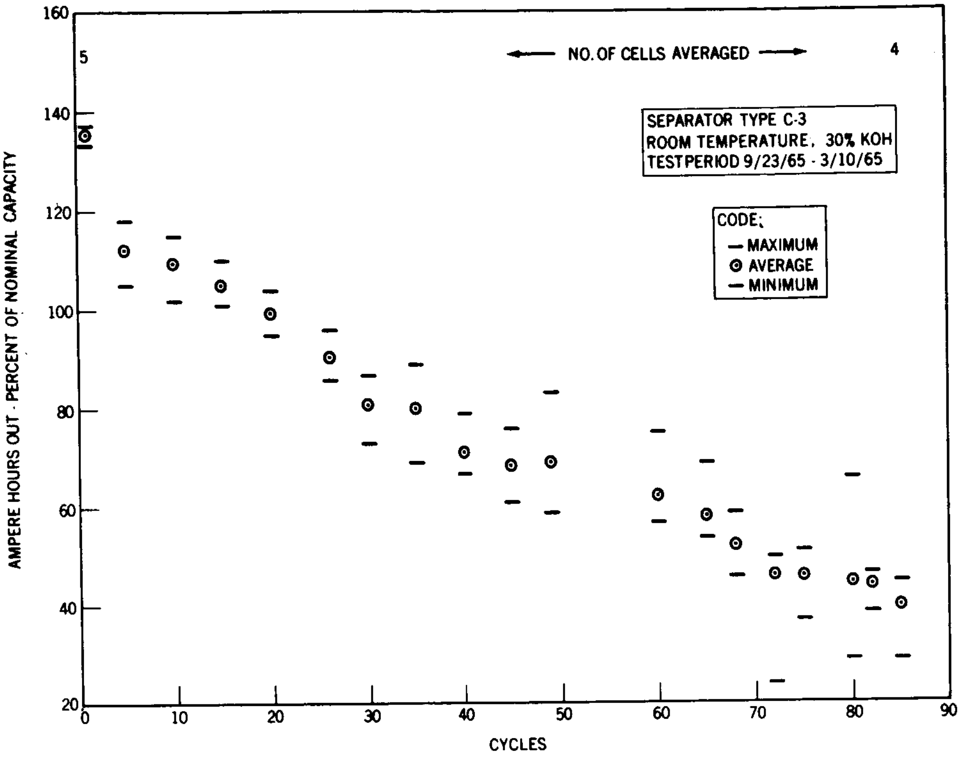

Figure 10

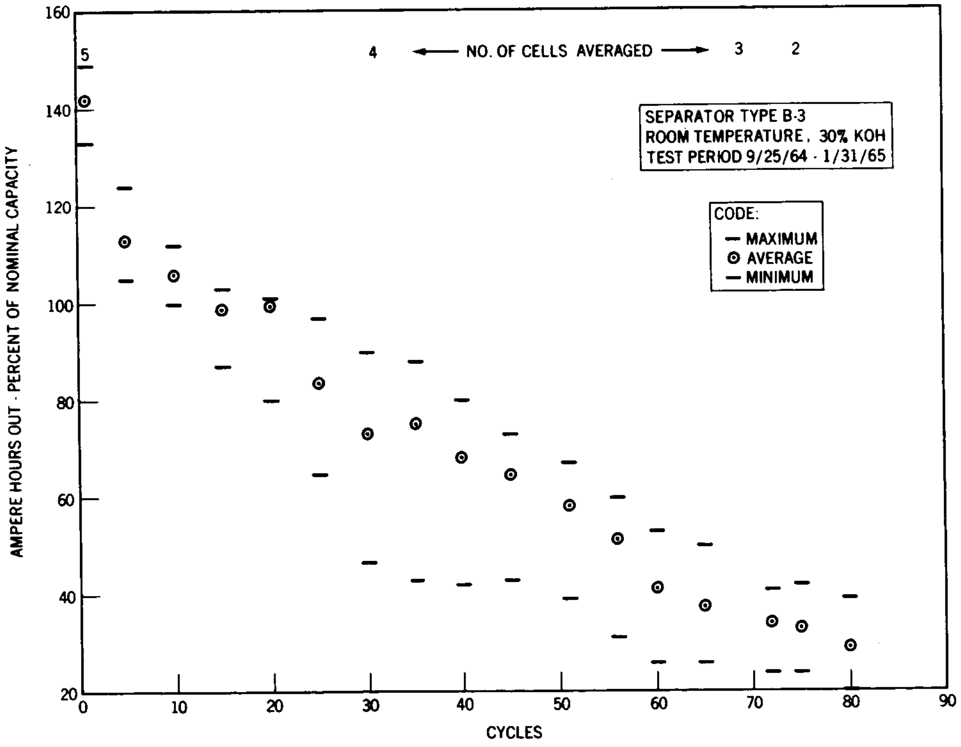

Figure 11

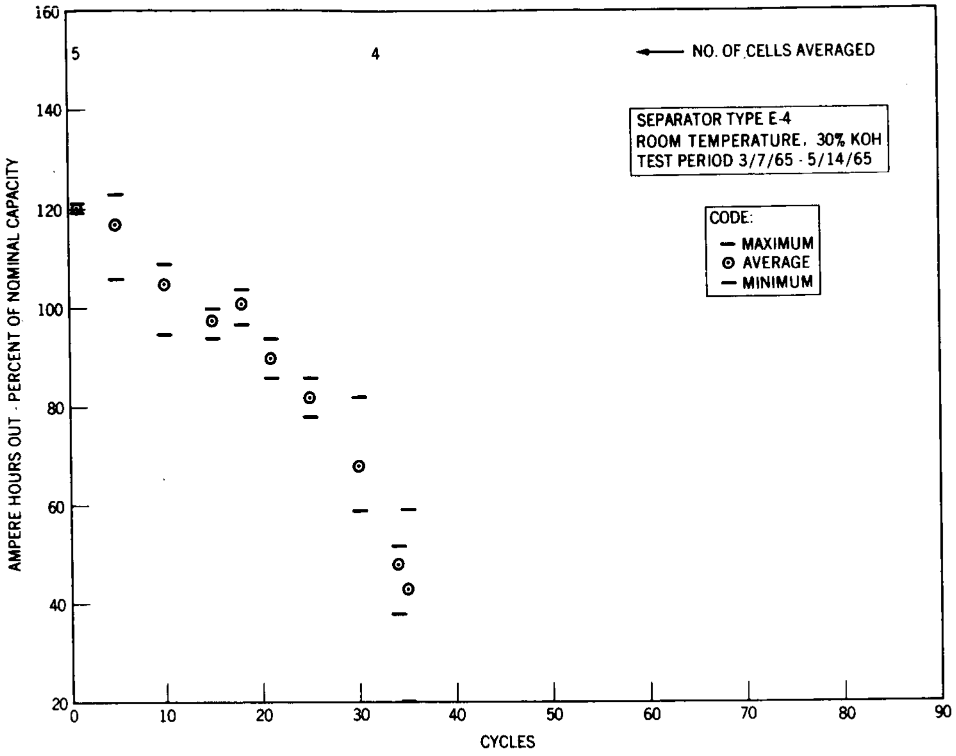

Figure 12

five cells (See figure 7) of the PVA material stay reasonably close together during the entire cycling program so that the five cell average capacity at the 40% cutoff is meaningful. In the case of cellophane and HEPVA, only a single cell value for maximum capacity can be expressed.

Separator Type	Cycles to First Cell to Deliver Below 40% Nominal Capacity	Cycles to 40% Nominal Capacity ( ) No. of Cells Averaged or Remaining
Cellophane	15	31 (1)
PVA	44	55 (5)
HEPVA	37	68 (1)
C1	35	38 (5)
C3	70	85 (5)
B3	31	65 (4)
E4	32	35 (4)

Intermediate cell failures may be obtained from figures 6 through 12.

From the test data, the following observations and conclusions have been drawn:

1. As experienced with the separator type 1-5, the data for cellophane* is random, cells fail above 40% capacity due to short circuits, the cells fail early in the cycle regime and no indication of cell failure can be detected.

2. Cells with separator types PVA, C1, and C3 are quite uniform in operation, no catastrophic failures occurred above the 40% cutoff and it is reasonable to estimate battery life, for the particular cycle regime, from the graphs.

3. The HEPVA material, although better than the control by a factor of two, did commence shorting at cycle 37.

4. The B3 material also was better than the control by a factor of two, but shorting commenced around cycle 30. However, in discussing this data with Borden personnel, they said that they had observed a stratification or separation of the solutions that were used in the fabrication of the B3 film. It is felt that this condition could have resulted in films that were non-homogeneous.

5. The E4 film showed good performance up to about 30 cycles but then the operation of these cells became erratic.

6. The primary reason for the decline of capacity in cells containing the PVA, C1, C3 and B3 materials is the solution and/or fall off of active material from the zinc electrode and zinc deposition in the separators.

Failure analysis was performed by the Burgess Battery Company on two cells of every five cells group of the above program (7). The data is summarized in Table III. Shorting of the cells was determined by charging the cells for fifteen minutes at 0.5 amperes to develop an open circuit voltage of the cell of 1.6 volts. Then the cells were opened, the terminals removed and the individual tabs of each electrode separated. Then the open circuit voltage between adjacent electrodes would be measured immediately, after one hour and after about twenty hours. Decrease of open circuit voltage was an indication of shorting.

Although 40% of nominal capacity was taken as the cutoff, since the materials showed uniformity in capacity at the cutoff cycling of the cells was continued until the capacity delivered by the cells was negligible ($\approx$ 1 AH). The B3 and C3

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*Cellophanes used in both programs are the same material.

materials exceeded 110 cycles. It is noteworthy that the cells did not short and failure appeared to be complete deterioration of the zinc electrode.

During the test program, voltage readings on charge and discharge were recorded on a per cell basis. End of charge voltages, especially as cycling progressed, exceeded 2.0 volts. The discharge data has been averaged, as before, for every five cells and is tabulated in Table IV. Only the data on the silver

Table III
Failure Analysis of Cells with Borden Materials*

Separator Type	Cell Number	Failure Analysis
Cellophane	2 & 3	Open circuit test showed evidence of shorting. Disassembled cells showed zinc shorts at edges of electrodes. Cellophane discolored and weakened. Zinc washed out about 1/4 in. at tops and 1/8 in. on sides.
PVA	1 & 2	No evidence of shorting on open circuit test. No evidence of shorting on disassembly. PVA intact and sturdy. Major portion of zinc washed out.
C1	1 & 2	No evidence of shorting on open circuit test. No evidence of shorting on disassembly. C1 fragile next to silver electrode. Major portion of zinc washed out.
C3	2 & 5	Some evidence of shorting on open circuit test of Cell No. 5. Short appeared to be contact of zinc dendrite and silver deposited on film. Major portion of zinc washed out. Film in good condition.
B3	4 & 5	No evidence of shorting on open circuit test. No evidence of shorting on disassembly. Zinc 75% washed out. Film in good condition. Large amount of zinc between separator layers.
E4	1 & 2	No evidence of shorting on open circuit test. No evidence of shorting on disassembly. Film fragile next to zinc plates. Major portion of zinc washed out.

NOTE: All silver electrodes in good condition. Data on HEPVA not available for this report
*Failure analysis performed by the Burgess Battery Company.

Table IV
Average Discharge Voltage Reading on the Silver Monoxide (Ag_2O) Plateau

Cycle Number	Separator Type						
	Cellophane	PVA	HEPVA	C1	B3	C3	E4
1	1.52	1.51	1.48	1.47	1.51	1.51	1.50
5	1.49	1.50	1.47	1.46	1.50	1.50	1.48
10	1.50	1.48	1.48	1.44	1.49	1.50	1.47
15	1.49	1.47	1.47	1.42	1.49	1.49	1.45
20	1.49	1.45	1.48	1.46	1.48	1.49	1.44
25	1.49	1.46	1.47	1.40	1.48	1.49	1.43
30	1.49	1.44	1.47	1.34	1.48	1.50	1.42
35	---	1.44	1.46	1.34	1.49	1.48	1.42
40		1.43	1.46	---	1.48	1.48	1.43
45		1.42	1.46		1.48	1.47	---
50		1.41	1.46		1.48	1.48	
55		1.42	1.47		1.49	1.48	
60		---	1.47		1.46	1.48	
65			1.46		1.44	1.48	
70			---		---	1.48	
75						1.48	
80						1.48	
85						1.47	

monoxide plateau was averaged. On initial cycling, the cells discharged at a voltage level 40 to 70 millivolts lower than conventional cells. This is due to the multilayered systems and the higher electrical resistance of the materials. In most cases, the addition of concentrated electrolyte during cycling did not have any noticeable effect on discharge voltage. However, the C1 type material was affected in this respect: the resistance of C1 in 30% KOH is 4.1 ohms whereas in the 40% KOH it increases to 34.1 ohms. All the other materials are less than 3.5 ohms in 30% or 40% KOH (3).

Single cells tests were performed on each type of material in cells with 40% KOH at 25°C and in cells with 30% KOH at 40°C. The same cycling regime as used in the main test program was used. Cell life to discharge consistently below 40% cutoff is summarized in the tables below. Complete capacity data is given in Tables V and VI.

Cells with 40% KOH
Temperature 25 ±2°C

Separator Type	Cycles to 40% Nominal Capacity
Cellophane	27
PVA	47
HEPVA	56
C1	42
C3	51
B3	48
E4	44

Cells with 30% KOH
Temperature 40 ±2°C

Separator Type	Cycles to 40% Nominal Capacity
Cellophane	21
PVA	29
HEPVA	23
C1	46
C3	36
B3	55
E4	29

Except for E4, the methyl cellulose modifications give better life than the other materials. Also, as shown in Tables V and VI, the failure of Cellophane is abrupt whereas the other materials tend to decrease in capacity gradually which is an indication of deterioration of the zinc electrode. However, the sudden drop of capacity of the material B3 suggests that a short developed on cycle 54.

In general, the discharge voltages of the cells at 40°C were normal. As one might expect, voltages on the silver monoxide plateau where 10 to 30 millivolts higher than at room temperature. In the 40% KOH test, the discharge voltages of the C1 and E4 materials were depressed. During most of the cycles, the C1 type cells have a plateau voltage of less than 1.40 volts. Initial cycles on the E4

Table V
Separator Test in 10 AH Cells Containing 40% Potassium Hydroxide Electrolyte -25°C

Separator Type	Ampere Hours at Cycle Number									
	1	2	3	4	5	6	7	8	9	10
Cellophane	11.6	14.0	14.0	15.0	13.7	13.0	13.2	13.3	13.0	13.1
B3	11.9	13.0	12.4	11.4	10.5	9.8	10.0	9.5	9.5	9.3
C1	11.1	12.8	12.7	12.5	10.8	12.3	10.5	10.0	10.5	9.8
C3	12.3	13.5	12.8	11.0	10.9	9.9	10.4	9.0	10.1	9.3
E4	9.8	10.0	10.1	9.7	9.3	8.9	8.2	8.7	8.3	8.3
HEPVA	12.2	12.7	12.8	13.2	12.5	12.1	12.0	12.1	12.0	12.2
PVA	12.5	14.0	14.0	13.0	12.9	12.2	10.6	11.7	10.4	10.4

Separator Type	Ampere Hours at Cycle Number									
	11	12	13	14	15	16	17	18	19	20
Cellophane	13.0	13.5			12.0	11.7	11.5	11.4	11.6	11.1
B3	9.2	9.1	8.8	8.6	8.4	8.6	5.9	8.2	8.0	7.0
C1	10.4	9.4	8.8	9.3	7.7	10.7	10.4	10.3	9.5	9.4
C3	9.7	9.4	9.4	9.0	9.0	8.9	9.0	8.2	8.3	7.7
E4	8.0	8.2	8.2	8.2	8.6	8.5	7.5	8.3	8.3	7.9
HEPVA	12.0	12.0	11.9	11.4	11.4	11.0	10.8	10.4	9.8	9.6
PVA	10.1				9.1	9.2	8.8	8.8	8.0	7.9

Separator Type	Ampere Hours at Cycle Number									
	21	22	23	24	25	26	27	28	29	30
Cellophane	10.8	10.2	9.0	9.7	10.2	10.1	0.6	0.0	-	-
B3	6.9	7.1	6.9	6.9	6.4	6.6	6.3	5.9	6.1	5.9
C1	9.7	9.2	9.0	8.6	8.3	7.9	7.0	6.5	7.5	7.9
C3	8.0	7.6	7.5	6.7	7.3	7.5	6.9	6.2	6.4	6.4
E4	8.0	7.7	8.0	6.9	7.2	7.5	7.0	6.6	6.9	6.8
HEPVA	8.5	8.5	9.1	8.2	8.9	8.7	8.4	7.9	7.7	7.9
PVA	8.0	7.1		6.6	7.0	7.3	6.4	6.5	6.5	6.5

Table V (Continued)
Separator Test in 10 AH Cells Containing 40% Potassium Hydroxide Electrolyte -25°C

Separator Type	Ampere Hours at Cycle Number									
	31	32	33	34	35	36	37	38	39	40
B3	5.4	5.3	5.7	5.2	5.0	4.5	5.0	5.0	4.7	3.7
C1	7.0	7.9	6.5	5.7	5.8	4.5	4.6	4.2	4.0	4.4
C3	6.3	5.8	5.9	5.9	5.8	5.4	5.7	5.5	5.4	5.4
E4	6.4	5.8	5.8	5.9	5.8	5.5	5.7	4.7	5.2	4.9
HEPVA	8.4	8.0	7.8	8.2	7.8	6.9	7.5	6.7	6.9	6.7
PVA	6.2	6.1	5.7	5.8	5.6	4.9	5.5	4.6	5.0	5.1

Separator Type	Ampere Hours at Cycle Number									
	41	42	43	44	45	46	47	48	49	50
B3	3.6	4.0	4.1	4.2	3.9	4.0	3.6	3.3	3.3	3.4
C1	6.0	--	--		--	--	--		--	--
C3	5.0	4.7	4.6	4.6	4.2	4.2	4.0	4.2	4.0	4.0
E4	4.5	4.0	0.2	--	--	--	--	--	--	--
HEPVA	6.0	5.2	6.5	6.0	4.7	4.3	4.0	5.4	5.4	4.4
PVA	4.5	4.2	4.3	4.2	4.2	4.2	3.7	3.5	3.2	3.2

Separator Type	Ampere Hours at Cycle Number					
	51	52	53	54	55	56
B3	3.3	3.2	3.2	3.0	3.0	2.8
C3	3.7	3.6	3.8	3.8	3.4	3.3
HEPVA	5.8	6.0	5.2	4.6	5.9	3.2
PVA	3.0	2.8	3.1	3.1	2.8	2.7

Table VI
Separator Test in 10 AH Cells Containing 30% Potassium Hydroxide Electrolyte - Temperature 40°C

Separator Type	Ampere Hours Out at Cycle Number									
	1	2	3	4	5	6	7	8	9	10
Cellophane	12.8	14.0	14.0	14.2	14.5	13.2	12.7	12.7	12.3	12.5
B3	12.6	11.6	11.3	11.0	11.3	10.4	11.1	8.7	7.9	8.0
C1	12.2	12.7	11.6	11.5	11.5	10.9	11.4	10.0	9.2	8.5
C3	13.4	14.0	13.5	12.4	11.9	11.6	11.0	10.8	10.4	10.6
E4	13.1	14.0	14.0	14.5	13.5	13.2	13.1	11.9	12.3	12.1
HEPVA	15.0	13.7	13.4	14.0	14.5	13.8	13.7	13.7	13.0	13.4
PVA	13.6	13.6	13.0	11.9	11.9	11.7	11.1	11.3	10.6	10.2

Separator Type	Ampere Hours Out at Cycle Number									
	11	12	13	14	15	16	17	18	19	20
Cellophane	12.3	12.4	12.1	12.1	11.9	10.9	11.2	10.9	9.9	5.0
B3	8.6	8.7	9.6	9.5	10.0	9.6	9.5	8.9	8.9	8.7
C1	9.2	8.2	8.3	8.0	8.0	7.7	7.7	7.5	7.1	6.8
C3	10.9	10.8	8.6	11.1	11.1	10.6	10.0	10.4	10.3	9.8
E4	12.1	12.1	11.5	11.4	11.0	10.1	9.4	9.7	8.3	8.7
HEPVA	13.1	13.2	13.7	12.1	12.0	11.7	10.8	11.5	10.6	10.2
PVA	10.3	9.1	9.9	9.9	9.9	9.8	9.5	9.6	8.2	7.9

Separator Type	Ampere Hours Out at Cycle Number									
	21	22	23	24	25	26	27	28	29	30
Cellophane	0.0	---	---	---	---	---		---	---	---
B3	8.7	8.6	8.8	8.5	7.6	6.8	6.0	5.0	4.5	4.4
C1	6.8	6.5	6.6	6.5	5.8	6.0	5.8	5.7	5.6	5.4
C3	9.8	9.3	9.2	8.8	9.5	8.6	8.0	7.9	7.6	7.0
E4	8.5	8.1	8.3	7.0	8.2	6.7	5.4	4.0	3.6	2.3
HEPVA	9.7	6.7	1.2	---		---	---	---	---	--
PVA	7.3	6.3	7.5	5.8	3.4	4.4	5.1	5.8	2.2	0.0

Table VI (Continued)
Separator Test in 10 AH Cells Containing 30% Potassium Hydroxide Electrolyte - Temperature 40°C

Separator Type	Ampere Hours Out at Cycle Number									
	31	32	33	34	35	36	37	38	39	40
Cellophane		---	---	---	---	---		---	---	---
B3	4.9	5.2	5.3	6.0	6.9	8.2	9.5	8.9	8.6	
C1	5.6	5.6	5.4	5.3	5.1	5.4	5.0	4.6	4.6	
C3	7.7	8.0	7.0	6.8	5.0	3.0	0.4	0.0	---	---
E4	0.0	---	---	---	---					
HEPVA	---		---	---	---	---				
PVA	2.6	2.9	3.4	3.8	4.4	2.3	0.0+	0.0	---	---

Separator Type	Ampere Hours Out at Cycle Number									
	41	42	43	44	45	46	47	48	49	50
Cellophane	---	---								
B3		8.0	7.9	7.9	7.8	7.6	7.7	7.7	7.7	7.2
C1		4.3	4.2	4.0	4.0	3.7	3.7	3.6	3.6	3.5
C3	---	---								
E4										
HEPVA										
PVA	---	---								

Separator Type	Ampere Hours Out at Cycle Number						
	51	52	53	54	55	56	57
B3	7.3	7.5	7.5	4.9	2.3	0.0	---
C1	3.4	3.5	3.3	3.2	3.1	1.8	1.8

cells were about 1.42 volts but after sixteen cycles this value was less than 1.40 volts. Cycling on the C1 was discontinued when the cells would not deliver greater than 1.0 volts on discharge. PVA discharged at a value about 30 millivolts less than the 30% KOH operation.

Cell tests were continued past the 40% cutoff and material types B3, C3, and PVA had greater than 1.8 ampere hours at 70 cycles in 40% KOH.

D. SUMMARY

Several types of separator materials have been developed that improve the performance of secondary silver zinc cells. One improvement has been the incorporation of antioxidants in cellophane to retard degradation of the cellophane due to oxidative reactions within the cell. New materials, mainly modifications of methyl cellulose, have been shown to improve cell life and particularly to prevent catastrophic shorting due to zinc dendritic growths. Battery life was extended by a factor of five with the use of the new materials. Extension of cell life by a factor of six was accomplished with the use of modified cellophane as compared to untreated cellophane. However, all cells tested using cellophane materials are prone to unpredictable short circuits due to zinc penetration. It is conjectured that shorting and random operation of the cells is indicative of materials that are nonuniform in physical and chemical properties. Careful control of molecular weights, molecular weight distributions, percent impurities and plasticizers, tensile and flexural strength, stress concentrations, electrical resistance and swelling are a few of the properties which, if properly controlled, can result in cells with the degree of reliability required for space missions. Such controls in conjunction with the screening tests developed and limited cell testing could increase the level of confidence of secondary cell operation for space missions. Materials developed on contract to NASA/Goddard Space Flight Center approach these ideal conditions. Several types of separators have resulted from the programs that remain stable in the cell environment and in some cases retard or completely prevent zinc dendritic shorting.

Single cell tests using the new separator materials and operated at 40°C demonstrated that the methyl cellulose modifications are an improvement of a factor between two and three over conventional materials. Operation of the methyl cellulose materials in cells with 40% KOH rather than 30% KOH does not have any particular advantage. High electrical resistance of some of these materials, in 40% KOH, is a disadvantage.

E. FUTURE WORK

The work with the Borden Chemical Company on improved separator materials is continuing. Additional cells of methyl cellulose modifications (types C3 and B3) have been delivered to the Naval Ammunition Depot (NAD) for further testing. Silver cadmium cells, containing C3 type materials, have been formed at GSFC and delivered to NAD for life cycling tests. Initial cycling of these cells was satisfactory.

The deterioration of the zinc electrode continues to be a major problem. Dip coating of the electrodes and using the same material as an electrode binder is under study by Borden and the Burgess Battery Company. Basic problems with the zinc electrode are under study. The Leesona Moos Laboratories are investigating the basic problems of zinc in the electrolyte media while the Yardney Electric Company is investigating the mechanism of zinc dendrite transport through membrane materials.

A contract has been let to the Advanced Technology Laboratory of the General Electric Company to investigate electrodeposited, inorganic separators on the silver electrode. To date, feasibility studies have shown that the deposited coating can prevent silver migration. This would eliminate the problem of oxidation of membrane materials by silver oxide.

A new charge control method has been developed at GSFC that eliminates some of the problems associated with charging of silver zinc cells, especially sealed cells. Overcharge of the cells in series is prevented. This technique lessens the problems of zinc dendritic growths and minimizes oxygen evolution in the cells.

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