ENGINEERING REPORT

From the highway to the stars * * *

Delco-Remy

DIVISION OF GENERAL MOTORS, ANDERSON, INDIANA

HEAT STERILIZABLE SILVER-ZINC BATTERY INVESTIGATION

FINAL REPORT

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Delco-Remy Division
General Motors Corporation
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FOREWORD

This report was prepared by Delco-Remy Division of General Motors Corporation, Anderson, Indiana, on Jet Propulsion Laboratory Study Contract Nr. 950364, subcontracted under NASA Contract Nr. NAS7-100. This work was monitored by Mr. A. A. Uchiyama and Mr. Charles Brooke, Jr. of the Energy Storage Group.

The assistance of Dr. H. C. Prosser of Stanford University, Palo Alto, California, as a consultant on this project was greatly appreciated.

ABSTRACT

Cell component materials were sterilized at 145°C. for 36 hours in sealed containers in 40% potassium hydroxide to determine their ability to withstand sterilization. The effect of a component's degradation products was determined primarily by filling cells of standard construction with the electrolyte obtained from the sterilized cell component and noting cell electrical characteristics. Positive and negative plates were sterilized independently and assembled into cells with unsterilized materials. These tests indicated that the prime cause of failure was due to degradation products from the separator materials.

Teflon and polyethylene base separator materials supplied by Radiation Applications Incorporated survived sterilization. The sterilized materials were built into cells and the polyethylene base material produced the best results; however, when sterilized in situ cell capacity was decreased by 50%. The cell testing phase was modified and expanded in place of battery testing. It was discovered that the positive plates were primarily attacked by the separator degradation products, and cells were redesigned to minimize the effect of attack by degradation products.

Redesigned cells gave fair performance with about a 10-20% loss in capacity even in the presence of the degradation products, but a stand life of nine to twelve months is questionable.

Three types of nylon, Penton and Celcon were investigated as possible case materials. Initial testing indicated that nylon (Zytel 38) was the most suitable case material and that phenol was the best of four methods investigated for sealing nylon.

Molds were made for a redesigned case, which could be used to mold nylon, Celcon and Penton. Pressure tests on cell cases indicated that the nylon case should survive sterilization; however, under actual sterilization conditions, cells with the nylon cases broke at the corners about 50% of the time.

Two problems remain: one, a case is needed which is capable of surviving sterilization; two, a superior separator material is required. The latter problem is considered to be the most difficult at present.

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I. Introduction

This report covers the investigation of secondary silver oxide-zinc cells and cell components to determine their ability to survive heat sterilization at 145°C for 36 hours. In a previous investigation it was found that secondary silver oxide-zinc cells would survive sterilization at 125°C. for 36 hours; however, when the sterilization temperature was raised to 145°C., sterilized cells yielded less than 50% of their rated capacity and voltage characteristics were about 0.3 volts lower than that of control cells[1]. Poor cell performance was suspected to be due to the degradation products of the separator and/or case materials.

This investigation was initiated to determine which cell components were responsible for poor cell performance and those that would survive the sterilization environment. If the plate materials alone failed to withstand the sterilization environment, the program would be dropped. If the case and/or separator material degradation products were responsible for poor cell performance, attempts were to be made to find replacements.

II. Cell Component Evaluation

To determine which cell components were being affected by the sterilization environment, the various components were sterilized individually in electrolyte in stainless steel containers. All components except the plate materials were sterilized in approximately 300 milliliters of 40% potassium hydroxide solution. With the exception of the separator materials supplied by Radiation Applications Incorporated (R.A.I.) the quantity of material sterilized was representative of the quantity needed to construct three cells.

The liquor from the sterilized cell components was used to activate new cells of standard construction which were rated to yield a nominal capacity

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(1) R. S. Bogner, Final Report under J. P. L. Contract Nr. 950177, October 15, 1962

of 25 ampere-hours when discharged at the three-hour rate (nine amperes). The cells were constructed the same as those tested under Jet Propulsion Laboratory Contract Nr. 950177. The cells contained six positive plates and seven negative plates. The cells were designed for cycle life and the positive-to-negative plate active material ratios were 1:2 based on 100% theoretical Faradaic efficiency. The separator system consisted of one layer of dynel next to the positive plates and three layers of Visking's fibrous sausage casing. The effect of the degradation products from the sterilized materials was determined by discharging the cells at the three-hour rate at room temperature and noting the capacity, voltage, and by cycling and determining life of the cells in comparison to control cells on cycle. The cells were recharged at 1.25 amperes to 2.1 volts. These tests were made on three cell groups.

The sterilization containers were formed from 1/16 inch stainless steel sheet and welded across the bottom and up two sides. After welding, the cans were leak tested on a Veco leak detector. The material to be sterilized was placed in the container and the cover welded on. The cans were again leak checked. The covers contained a stainless steel fitting for attachment of a pressure gauge. Marshall Town pressure gauges calibrated from zero to 100 psi were used to measure pressures during sterilization. An assembled sterilization container is shown in Figure 1.

A. Plate Materials

In order to continue this program, it had to be determined whether or not the positive and negative plate materials were capable of surviving the sterilization environment. In these tests actual plates or the plate materials were sterilized at 145°C. for 36 hours submerged in a 40% potassium hydroxide solution.

1. Positive Plate

Twenty positive unformed silver plates were sterilized in stainless steel cans. After sterilization the plates were washed, dried, and assembled into three cells with unsterilized negative

plates and separators. The cells were activated with 85 milliliters of fresh 40% potassium hydroxide solution and cycled. Figure 2 shows the capacity and cycle life of the cells. The voltages on charge and discharge were comparable to the control cells. From the data it is concluded that unformed positive plates are not degraded when sterilized only in the presence of electrolyte.

2. Negative Plate

Negative plates were made by the standard procedure by pressing zinc oxide on a silver grid and sterilized in the stainless steel containers submerged in a 40% potassium hydroxide solution. The plates appeared to survive sterilization; however, the Viscon paper wrap was somewhat degraded. The negative plates could not be washed and dried because the zinc oxide would wash away. The sterilized negative plates were assembled into three cells with unsterilized separators and positive plates. The cells were activated with 85 milliliters of fresh 40% potassium hydroxide and cycled at the three-hour rate.

In Table 1 it will be noted that the pressure developed during sterilization of the negative plates was in excess of 100 psig. Because of this high pressure, it was decided to try two additional experiments to determine what constituents of the negative plates were producing the pressure. In one test, the plates were built by the standard method except the polyvinyl alcohol binder was omitted. In the other test only a mixture of the negative material powder (zinc oxide and mercuric oxide) was sterilized in potassium hydroxide. As noted in Table 1, the negative plates without the polyvinyl alcohol produced a maximum pressure of 62 psig while the active material mix produced a pressure of 32 psig. From these results it is concluded that both the polyvinyl alcohol and the Viscon paper wrap on the negative plates contribute to the pressure build up.

Three sets of three cells each were assembled with unsterilized separators and positive plates with the three variations of sterilized

negative material. Figure 2 shows the cycle and capacity data for the three sets of cells made from the three variations in negative plates. It is understood, of course, that the negative material mix had to be made into plates after sterilization. From the results of the negative plate tests, it is concluded that the negative plates are not appreciably affected by the sterilization procedure. Furthermore it is concluded that the polyvinyl alcohol binder can be removed from the plates without significantly affecting their cycle life as tested. By removing the polyvinyl alcohol, the total pressure developed in a cell during sterilization can be reduced and will enhance the possibility of getting cells through sterilization without bursting the cell case.

B. Separator Materials

It was suspected that separator degradation products were partially responsible for the poor cell performance after sterilization; therefore, it was proposed to sterilize available separator materials and use the liquor to activate standard cells as previously described.

1. Available Separator Materials

The materials tested were as follows:

a. Fibrous sausage casing #7 (FSC) produced by the Food Products Division of Union Carbide Corporation. The material is a regenerated cellulose on a backing of hemp fibers. The casing is desulfured and deglycerinized.

b. Permion 600 (P-600) produced by Radiation Applications Incorporated. The material is cellophane with radiation induced copolymer graft of styrene acrylonitrile.

c. Dynel 470, produced by The Kendall Company, is a non-woven fabric of fibers made from acrylonitrile monomer.

The pressures developed by the separator materials during sterilization are recorded in Table 1. The maximum pressures were: FSC, 54 psig; Dynel, 55 psig; Permion 600, 57 psig. The liquor from

the FSC was colored dark amber and its odor suggested the presence of an ester. The sterilized material was quite fragile and could not be easily handled without tearing. The liquor from dynel was light amber in color and had a strong ammonical odor. The dynel was more fragile than the FSC and very easily torn. The liquor from Permion 600 was dark amber and had a strong ammonical odor which seemed to mask another odor. Permion 600 was not as easily torn as FSC but it was too fragile to handle to build cells.

Nine cells, three each, were filled with 85 milliliters of the liquor from each of the three separator materials sterilized and put on cycle tests. Cells filled with the liquor from Permion 600 had discharge voltages very similar to the control cells and their capacities were about five ampere-hours lower than the control cells as shown in Figure 3. This represents about a 20% loss in capacity. The cells filled with the liquor from the sterilized P-600 were removed from test at 27 cycles because of low capacities (13 ampere-hours).

The chief effect of the liquor from dynel was that the divalent silver voltage was practically absent as shown by the discharge curve in Figure 5. As shown by the capacity/cycle curve in Figure 4, the liquor from dynel did not have an appreciable effect on cycle life.

As shown by the discharge curve in Figure 5, the cells filled with the liquor from fibrous sausage casing yielded about nine ampere-hours when discharged to 1.2 volts. The discharge voltage was very poor in that it was about 0.3 volt lower than the controls. The cells were given a few cycles to determine if their capacities would increase. The capacity did not increase and the cells were removed from test.

Later one of the cells filled with the liquor from sterilized FSC was charged and discharged to attempt to determine if the negative or positive plates were affected by the sterilization liquor. A strip of zinc was used as a reference electrode. The electrolyte level was about midway to the tops of the plates so the zinc strip

could not be immersed in free electrolyte and consistent readings were difficult to obtain. From the discharge potentials, it appeared that the negative plates were limiting cell capacity. However, on charge at two amperes the positive plates were found to be charging at a potential of over 2.2 volts with reference to the zinc strip. An adequate explanation is not readily available for this strange behavior, but it might be related to the placement of the reference electrode in the cell which was at the top of the plates and to the fact that the plates do not charge and discharge evenly. This cell was not torn down at the time, but it has been observed that the lower portion of the plates can be discharged while the upper portion still contains charged material. A similar situation was pointed out by Dr. G. A. Dalin[1]. Relying more on the charge data than the discharge data, it was surmised that low cell capacity was due to the positive plate. As discussed later, it was found that this hypothesis was correct.

Since the odor of ammonia was detected in the liquors from dynel and Permion 600, a test on a single cell was made to determine the effect of ammonia. A cell was filled with a solution of 40 milliliters of concentrated ammonium hydroxide and 45 milliliters of 40% potassium hydroxide solution. During charge the cell voltage never got above 1.5 volts and the cell self-discharged overnight, thus demonstrating the harmful effect of ammonia in large concentrations.

2. New Separator Materials

Before this program was initiated, it was surmised that separators might be the chief reason for cell failure, and Radiation Applications Incorporated was contacted about the possibility of obtaining separator materials or membranes that would survive the sterilization

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(1) Orientation Conference on Heat-Sterilization of Silver-Zinc Batteries, held at Delco-Remy, June 3, 1964

environment. Radiation Applications Inc. indicated that they might be able to make some suitable materials that would be relatively stable in the sterilization environment.

The following separator materials were prepared by Radiation Applications Inc. and supplied to Delco-Remy for evaluation:

R.A.I. Nr.	Separator Material
155-79-3	Teflon (TFE) with acrylic acid graft (AA)
155-85	Teflon (TFE) with methacrylic acid graft (MAA)
155-79-5	Teflon (TFE) with sulfonated styrene graft
157-87	Crosslinked high density polyethylene with acrylic acid graft (XLHDPE-AA)
157-92	Crosslinked high density polyethylene with methacrylic acid graft (XLHDPE-MAA)

Fifteen square feet of each type of material was received. It was decided that the best method to screen test these materials was to use half of the material to build a control cell and sterilize the other half and build a cell from the sterilized material. Half of each sample was sterilized in a stainless steel container filled with about 200 milliliters of 40% potassium hydroxide. The pressures developed during sterilization are recorded in Table 2 and were about equal to the pressures calculated from the partial pressures of air and potassium hydroxide, indicating little or no volatile products were produced.

After sterilization the membranes were washed and dried, and the sulfonated styrene graft on teflon was the only sample which could not be used to build a cell. After drying the sulfonated styrene graft on teflon became quite brittle and could not be handled without splitting. One cell each was assembled from the other four sterilized samples. The cells were built from standard plates (six positives and seven negatives) with four layers of separator between the plates. A .200 inch thick shim was used in the cells because of the difference in thickness between the R.A.I. separators and the fibrous sausage casing separators. The cells

were activated with 70 milliliters of 40% potassium hydroxide solution and cycled by charging at 1.25 amperes to 2.1 volts and discharging at 9 amperes to 1.3 volts. Data on the test and control cells are shown in Figures 6, 7, and 8.

Two cells were activated with the liquor from the sterilized sample of AA on teflon. On cycling the cells delivered around 25 a.h. and gradually dropped below 15 a.h. after 85 cycles as shown in Figure 4.

Based on the initial data it appeared that the teflon base materials were quite good, but on cycling it soon became apparent that the teflon base separators were inferior to the crosslinked high density polyethylene base separators. The methacrylic acid graft on teflon control cell failed on the fifteenth cycle due to a short while the sterilized sample failed on the eighth cycle also due to a short. The cells containing the acrylic acid graft on teflon gave about twice the life of the methacrylic acid graft with the control cell failing at 26 cycles and the sterilized sample failing at fifteen cycles due to shorts.

In the case of the crosslinked high density polyethylene base materials, the sterilized samples were better than the controls in cycle life, capacity and voltage. Although it was apparent from the data that sterilization did something to the materials, it appeared to be beneficial to cell performance. From the cell performance data it appeared that the crosslinked high density polyethylene materials should produce cells that could be sterilized and 120 foot samples of the material with each type of graft were ordered for further evaluation in cells.

Various parameters were measured on sterilized and unsterilized separator samples in an attempt to get additional data that could be used to predict what properties were needed to yield an adequate separator material. The properties measured by R.A.I. are shown in Table 3 and those measured at Delco-Remy are shown in Table 4. Based on the cell results and the data in the tables, it becomes quite apparent that at best the various parameters measured can only be

used to make a broad qualitative judgment and not to accurately predict how the material will behave in cells.

The procedures for determining resistivity, potassium hydroxide diffusion, and zinc dendrite growth through the membrane are discussed in detail in Delco-Remy engineering report Nr. 4480-X, which was forwarded to J.P.L. with the proposal for this program. A brief discussion of the various procedures, however, is presented in Appendix I.

The Final Report of R.A.I's Development Program for the preparation and testing of the experimental separator materials is in Appendix II.

C. Case Materials

In the previous contract (Nr. 950177) the nylon case interior showed very little evidence of alkaline attack after fully assembled cells were sterilized at 125°C. for 36 hours. When fully assembled cells were sterilized at 145°C. for 36 hours the interior of the nylon case exposed to the alkaline electrolyte was severely spalled as shown in Figure 9. It was thought that cell failure might have been due partly to the degradation products from the nylon case; therefore, a program was outlined to evaluate various nylons, coatings for nylon, and other high temperature thermoplastics that might be suitable for case materials.

1. Nylon

A trip was made to E. I. duPont deNemours and Company at Wilmington, Delaware on June 28, 1963 to discuss the problems of nylon degradation in hot caustic. DuPont's representatives could not provide us with any data on the ability of their nylons to withstand attack in potassium hydroxide at 145°C. They suggested that we try Zytel 121, a hydrolysis resistant 6/6 nylon, and Zytel 38, a heat resistant 6/10 nylon. Originally we had been using Zytel 101, a general purpose 6/6 nylon.

In order to determine if nylon degradation products impaired cell performance, samples of Zytel 101, 121, and 38 molding pellets were sterilized at 145°C for 36 hours in stainless steel cans in a 40% solution of potassium hydroxide. An adequate quantity of the molding pellets was cooked to assure that it was representative of the surface area of the interior of the nylon case. The pressures developed in the cans during sterilization are shown in Table 2. The maximum pressures were from 35 to 40 psig which indicates little or no gaseous degradation products were produced. The liquors from all three nylon samples contained some suspended substance, but no distinguishable odor was detected.

Visual examination of the sterilized nylon samples revealed that all three types of nylons were attacked. Zytels 101 and 121 showed the greatest attack in that their surfaces were severely spalled. Zytel 38 showed the least attack as its surface was only slightly crazed. Figure 10 is a photograph of some test bars which were sterilized and used for seal testing and illustrates the difference in the severity of the surface attack on Zytels 101, 121, and 38.

Nine cells of standard construction were assembled, and three cells each were filled with 85 milliliters of the liquor from each sample of sterilized nylon. The cells were formed and cycled as previously described. The capacity and cycle data for each group of cells are shown in Figs. 3 and 4. While there might be some question that the liquor from Zytel 121 had a slight effect on capacity and cycle life, it is quite evident that the cells containing the liquor from Zytel 38 gave excellent results with all three cells surpasing the performance of the control cells. From this test it was concluded that the degradation products from nylon were not the cause for poor cell performance.

Infrared analysis was attempted on the sterilized samples in the Process Department Laboratory, but no useful information as to the possible nature of the degradation products was obtained.

2. Coating Material for Nylon

During the visit to duPont, the possibility of coating nylon with some material to protect it from attack by potassium hydroxide during sterilization was discussed. The duPont representatives said it is very difficult to get any material to adhere to the surface of nylon and that they could not recommend any material that would be satisfactory. In spite of duPont representatives remarks, it was decided to check out the possibility of coating nylon as outlined in the proposal. After some preliminary experimentation, the Process Department was able to produce what appeared to be good coatings of two different materials on some nylon test strips. The coating materials were Logo Clear EJ-2741 supplied by the Bee Chemical Company, Lansing, Illinois, and Emralon 315, a Teflon dispersion produced by the Acheson Colloids Company, Port Huron, Michigan.

The coated nylon bars were sterilized at 145°C for 36 hours in a 40% potassium hydroxide solution. As shown in Figure 10 both coating materials were stripped from the nylon during sterilization and the surface of the nylon was spalled as if it had not been coated. No further attempts were made to coat nylon. Since the coatings did not hold up, it was decided that it would not be worthwhile to activate cells with the sterilization liquor.

3. New Case Materials

Penton, Celcon, fluorocarbons, and epoxy molding compounds were examined as possible candidates for case materials but only the liquors from Penton and Celcon were tested for their effect on cell performance.

a. Penton

Penton is a chlorinated polyether manufactured by the Hercules Powder Co., Inc. An adequate quantity of Penton molding pellets was sterilized in stainless steel cans at

145°C for 36 hours in a 40% potassium hydroxide solution. Examination of the sterilized Penton pellets indicated there was only a very slight surface attack in that the sterilized sample lost its glossy sheen. No distinguishable odor was detected and the liquor did not contain suspended material. The maximum pressure reached during sterilization was 42 psig as shown in Table 1.

Three cells of standard construction were filled with 85 milliliters of the liquor from the sterilized Penton, formed and cycled at the three-hour rate. The initial capacities of the Penton cells averaged 24 to 25 ampere-hours as shown in Fig. 4 and compared favorably to the controls. As shown in Fig. 5 the discharge voltage of the cells was the same as the control. The cells failed near seventy cycles due to loss of capacity. From the results of this test it is concluded that Penton did not affect cell capacity or cycle life.

b. Celcon

Celcon is an acetal polymer manufactured by the Celanese Chemical Company. It is a thermoplastic similar to duPont's Delrin, but according to representatives of the two companies, Celcon has better properties for the sterilization requirements.

An appropriate quantity of Celcon molding pellets was sterilized in stainless steel cans at 145°C for 36 hours in a 40% potassium hydroxide solution. Visual examination of the sterilized Celcon pellets did not reveal that it was attacked, but the pellets had a yellow tinge. No distinguishable odor was detected and there was only a very slight residue in the liquor. The maximum pressure reached during sterilization was 40 psig, and the pressure dropped to zero at room temperature as shown in Table 1.

Three cells of standard construction were filled with 85 milliliters of Celcon liquor, formed and cycled at the three-hour rate. Although they are not plotted, the discharge

voltages of the Celcon cells were the same as shown for Penton and the control in Fig. 5. The initial capacities were near 25 ampere-hours and the cycle life ranged from about 80 to 110 cycles which compares very favorably to the controls as shown in Fig. 3. From the data obtained on this test, it is concluded that the liquor from Celcon had no effect on the cells.

c. Fluorocarbons and Epoxies

The fluorocarbons were not investigated in detail because equipment was not available to attempt to mold cases from them and it appeared that the new nylon, Zytel 38, would make a sufficient case because it was not appreciably attacked and nylon degradation products did not affect cell performance. It was also doubtful that parts as large as the case could be molded from the fluorocarbons. Some attempts were made to make cases from epoxy molding compounds, but in order to do the job right expensive tooling and time were needed. Epoxy case work was also dropped when it appeared that nylon, Celcon or Penton would do the job.

D. Sterilization at 135°C.

At the request of JPL, the separator materials which produced poor cell performance after sterilization at 145°C. were evaluated at 135°C.

1. Fibrous Sausage Casing

A quantity of fibrous sausage casing representative of three cells worth was sterilized at 135°C. for 36 hours in stainless steel cans filled with 300 milliliters of a 40% solution of potassium hydroxide. The samples did not appear to be as severely degraded

as they were at 145°C and could be handled without falling apart. Three cells of standard construction were filled with 85 milliliters of the liquor from the sterilized fibrous sausage casing, formed and cycled at the three-hour rate. The initial capacities on the cells ranged between 10 and 18 ampere-hours. Upon continued cycling the cells gained in capacity up to about 20 ampere-hours and then receded to 10 ampere-hours between 12 and 17 cycles as shown in Figure 11. The average discharge curve of the cells at the nine ampere rate is shown in Figure 12. The improvement in capacity and voltages of these cells in comparison to cells filled with the liquor from fibrous sausage casing sterilized at 145°C is indicative that we are working in a critical temperature range for the degradation of fibrous sausage casing. It is recalled that actual cells sterilized at 125°C gave good performance when discharged at the three-hour rate (nine amperes) at room temperature[1]. The fact that a temperature near 125°C is quite critical in the degradation of fibrous sausage casing was pointed out by Dr. L. M. Cooke[2]. Therefore, if incremental improvements in fibrous sausage casing can be made by various chemical treatments as suggested by Dr. Cooke, it should be worthy of further investigation.

2. Permion 600

A quantity of Permion 600 equal to the amount needed to build three cells was sterilized in stainless steel cans in 300 milliliters of a 40% solution of potassium hydroxide at 135°C for 36 hours. The odor was the same as noted at 145°C, and the liquor was dark amber in color. Pressure gauges were not used in this experiment. The

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(1) Bogner, R. S., Report of an Evaluation of Delco-Remy Design of Sealed, Secondary, Silver-Zinc Electrolytic Cells for Heat Sterilization, J.P.L. Contract Nr. 950177, June 10, 1962

(2) Comments made by Dr. Cooke during the June 3, 1964 Conference held at Delco-Remy Division, Anderson, Indiana

sterilized Permion 600 was in somewhat better condition than that sterilized at 145°C and was not as easily torn.

Three cells of standard construction were filled with 85 milliliters of the sterilization liquor, formed, and cycled at the three-hour rate (nine amperes discharge). The capacities of the cells on the first few discharges ranged between 14 and 18 ampere-hours and built up to a little over 20 ampere-hours at ten cycles as shown in Figure 11. There was practically no difference in capacity and cycle life between the cells filled with liquors from Permion 600 sterilized at 145°C and at 135°C. The cells were removed from test around 30 cycles because of low capacity. It was concluded that the Permion 600 would not be an adequate separator material.

III. Seal Investigation

Two types of seals are necessary to produce a sealed cell. One involves obtaining a seal between the case cover and the positive and negative plate current carrying leads, commonly called the cell terminals. The other seal problem is at the juncture of the cell case and the cover. The terminal-to-cover seal on nylon was proven to be quite successful and was accomplished by molding a metal insert in the cover at the time the cover was molded. The plate leads were threaded through the metal inserts and sealed with pure tin solder. Bonding the cover to the case had been effected by a chemical seal with phenol which up to the time of this investigation was not considered to be adequate. These two sealing problems were to be investigated for nylon and other possible case materials.

A. Terminal-to-Cover Seal

The terminal-to-cover seal was initially evaluated by molding metal pins in test cups of the material to be tested to simulate the terminal insert in the cover and subjecting the cups to pressure and temperature.

A fixture was built to hold the test cup so it could be subjected to a pressure test. A disassembled and assembled view of the holding fixture and test cup are shown in Fig. 13. The test cup was placed in the threaded female ring and the threaded male plug was screwed down onto the test cup. A high temperature rubber "O" ring was used to effect a seal between the male plug and the flange of the test cup. The male plug was fitted with a male Hansen quick disconnect fitting and a female Hansen quick disconnect fitting was attached to a manifold system so failing samples could be quickly removed without disturbing the other samples. Fig. 14 is a photograph of manifold with the assembled test fixtures. The test cups were filled with about five milliliters of a 40% solution of potassium hydroxide before attachment to the manifold.

The assembled test apparatus was attached to an air line and pressure regulator, and the system was gradually subjected to a total pressure of 90 psig at room temperature and left at this pressure for a minimum of 15 hours. Leaks were detected by swabbing the outside area around the pin with phenophthalein which turned red if a leak occurred. If no leaks were detected at room temperature, the pressure in the system was reduced to 60 or 65 psig and the apparatus was placed in an oven at 145°C. for a minimum of 48 hours. Checks were made for leakage at various time intervals.

1. Nylon

Ten Zytel 38 samples were tested as described above and all samples survived the test. Five out of ten glass-filled Zytel 38 samples failed at room temperature at 90 psig, while five samples survived both tests. The fact that the glass filler does not allow the nylon to shrink as much as unfilled nylon was thought to be the chief reason for failure and associated with the shrinkage factor were the insert design and molding conditions. Figure 15 is an illustration of the metal pin in a test cup compared to the actual insert design in the cover. From the illustration, it can be seen that the test cup should be more apt to leak than the actual

terminal; therefore, it was decided to mold actual covers and test them in a similar manner. Disassembled and assembled views of the cover test fixture are shown in Figure 16.

Five covers molded of glass filled Zytel 38 were tested as outlined above. Four of the covers leaked at 90 psig at room temperature and the one which did not leak at room temperature leaked after two hours at 145°C. and 65 psig. No further tests were made on glass filled nylon because of problems also encountered in the case-to-cover seal.

2. Penton

Ten test cups molded of Penton were evaluated as described above. Five of the samples leaked at 90 psig at room temperature and five of the samples survived the test. The five samples that survived at room temperature were placed in the oven at 145°C. under 65 psig pressure and all five of the samples leaked after two to three hours. As described above, actual covers were tested. Ten Penton covers were tested and three covers leaked at 90 psig at room temperature. Six of the seven covers leaked when tested at 145°C. at 65 psig. One cover survived the test for 48 hours. From these tests it was concluded that the present terminal-to-cover seal for Penton was not reliable and no further testing was done.

3. Celcon

Five Celcon test cups were evaluated and none of the samples leaked at 90 psig at room temperature. At 145°C. at 60 psig two samples broke at the flange of the test cup within 24 hours, two samples broke at the flange between 30 and 48 hours, and one sample survived the test for 48 hours. Three Celcon covers were tested. No leaks were detected at 90 psig at room temperature or at 145°C. and 60 psig after 48 hours. Examination of the inside of the covers revealed cracks about half way through the corner of the covers. From these tests it appeared that the terminal-to-cover seal on Celcon was adequate; however, the breakage of the cups and covers indicated that at 145°C. Celcon was not as strong as nylon or Penton.

B. Cover-to-Case Seal

The case-to-cover seal was investigated on nylon, glass-filled nylon, Penton, and Celcon. Four methods of sealing nylon were investigated and the phenol seal proved to be the best. The sealing of Penton and Celcon was accomplished with heat (hot gas welding) since there was no known chemical seal for these materials.

1. Penton

Penton cases and covers of the old case design as shown in Figure 18 were heat sealed in the Process shop by means of a hot gas welding technique. Two of the cases which appeared to have the best seals were supported up to the seal joint in metal cans (the cases could not be placed all the way into the cans because of the welding bead at the case-to-cover joint) and subjected to a pressure test at room temperature. One of the cases broke at 56 psig at the weld joint and the other case also broke at the seal between 20 and 30 psig. From these results it was decided to wait and test cases of the new design. Two heat sealed cases of the new design were supported in metal cans and pressure tested at room temperature. One of the cases leaked at the seal at 25 psig and the other case leaked at the seal at 30 psig. The cases were removed from the supporting metal cans to determine how much pressure the cases would take before bursting. The side of one of the cases broke at 30 psig and the other case leaked too rapidly to build up a pressure over 25 psig. Since the case-to-cover seals and the terminal-to-cover seals on Penton were not as good as the nylon seals, and in view of the fact that nylon degradation products did not impair cell performance, no further experimental work was done on Penton.

2. Celcon

Celcon cases and covers of the old design were molded with the same tools as used for nylon and Penton. The cases and covers

were heat sealed in the Process shop similar to the way Penton was sealed since there is no known solvent seal for Celcon. Two cases were delivered for testing. The cases were supported in metal cans up to the seal joint and gradually subjected to air pressure up to 65 psig at room temperature. One case had a pin hole leak at the weld and the other case did not leak. The case that leaked was removed from the supporting metal can and gradually subjected to air pressure. The side of the case blew out at 89 psig. The other case was placed in the oven at 145° C under 60 psig. The seal cracked between seven and twenty-two hours after being placed in the oven. It had been planned to test celcon cases of the new design, but because of time and manpower and the fact that nylon appeared to be satisfactory, no further tests were made.

3. Nylon

The sealing of nylon was initially investigated by sealing nylon test bars together by different methods. The test bars were cut from molded cases and measured 0.100 inch thick, 0.500 inch wide, and were about three inches long. Twelve test samples of each of the following three types of seals were made:

a. 88% aqueous phenol solution

b. A solution of 10 parts calcium chloride, 22.5 parts nylon, and 67.5 parts ethanol

c. Epoxy (Armstrong A-11)

The strips were overlapped 0.5 inch to make a seal area of 0.25 square inches. A pressure of about 10 psi was applied to the seal area on the strips sealed with phenol and nylon-bodied calcium chloride ethanol and the seals were cured for two hours at 135° F and at room temperature for at least three days before testing. The epoxy seals were cured at 135° F for two hours.

Six samples of each type of seal were sterilized in stainless steel cans in a 40% potassium hydroxide solution for 36 hours at 145° C and six samples of each seal were used as controls. The

seals were evaluated by clamping the ends of the test strips in the jaws of a tensile test machine and subjecting them to a tensile pull along their longitudinal axis.

The results of the tensile tests on the nylon seals are reported in Table 5. The data are somewhat scattered but indicate that phenol produces the best seal before sterilization in that the nylon test strips broke before the seal gave way. After sterilization the epoxy seals were quite weak, whereas the nylon strips broke before the bond gave way on the phenol and the nylon-bodied calcium chloride-ethanol seals. These data indicated that it should be possible to seal cells with phenol if pressure could be applied to the seal area during the sealing operation. In order to evaluate the seal further, covers were machined from one-half inch thick Zytel 38 sheet stock to fit inside the present case design after the top sealing lip was cut off of the case. A disassembled and an assembled case and cover (prototype of the new case design) used to evaluate case-to-cover seals are shown in Fig. 17. The cover was drilled and tapped to accommodate a pressure gauge or a fitting for attachment to a pressure line. The prototype case and cover were used to evaluate all three of the previously described seals and a heat seal.

The phenol seals and the nylon-bodied calcium chloride ethanol seals were made by coating the mating surfaces with their respective sealant and inserting the block into the case. Pressure was applied to the seal area with "C" clamps. The sealed cases were placed in an oven at 135°F. for two hours and then cured at room temperature for a minimum of three days before testing. The epoxy seals were made in a similar manner but pressure was not applied to the seal area. The heat seals were made in the Process shop. A hot inert gas (nitrogen) was used to fuse the two surfaces together. The three kinds of seals were also made on cases molded of glass-filled Zytel 38. The sealed cells were filled with approximately 80 milliliters of a 40% potassium hydroxide solution and a

pressure gauge was screwed into the top. The cases were supported in stainless steel cans and placed in the oven at 145°C. for a minimum of 54 hours. Leaks were detected by observing the pressures developed which were about 30 psig if no leaks were detected. If the seals survived sterilization, the cases were checked at room temperature up to a maximum of 90 psig after dumping the potassium hydroxide. The results of these tests were as follows:

Phenol Seals

1. Seal OK after 96 hrs at 145°C - OK at R.T.** and 60 psi
2. Seal OK after 54 hrs at 145°C - OK at R.T. and 90 psi
3. Seal OK after 54 hrs at 145°C - OK at R.T. and 90 psi
4. Seal OK after 54 hrs at 145°C - OK at R.T. and 90 psi
5. *Seal OK after 54 hrs at 145°C - OK at R.T. and 90 psi
6. *Seal OK after 54 hrs at 145°C - Leak at R.T. and 54 psi
7. *Seal OK after 54 hrs at 145°C - Leak at R.T. and 30 psi

Epoxy Seals

1. Leak after one hour at 145°C
2. *Leak after two hours at 145°C
3. *Leak after one hour at 145°C
4. Leak after one hour at 145°C
5. Leak after one hour at 145°C

Nylon-Bodied $CaCl_2$ - Ethanol Seal

1. Leak after three hours at 145°C
2. Leak after three hours at 145°C
3. OK after 54 hours at 145°C - Leak at R.T. and 35 psi
4. Leak after one hour at 145°C

Heat Seals

1. Seal broke at 54 psi at R.T.
2. Leak between 2 - 5 hrs at 145°C
3. *Leak between 2 - 5 hrs at 145°C

* Cases molded of glass-filled Zytel 38

** Room Temperature

From the results of these initial seal tests it was concluded that phenol produced the best seal and that the glass filled cases did not allow a good seal. It was also observed that the interior of the glass filled cases were attacked by the electrolyte more readily than the unfilled cases. The glass fibers left small bumps on the surface of the cases which was probably the cause of the poor seal in comparison to the unfilled cases. It was also questionable as to how well the glass fibers were covered with nylon or if there was a wicking effect due to fibers at the surface.

One of the phenol sealed cases was plugged and inverted on November 26, 1963 to determine how long the seal would hold up. At present no leakage of electrolyte at the seal has been observed as of March 15, 1965.

Further tests were made on the case-to-cover phenol seal to test the seals unsupported during sterilization. Two glass-filled cases and four unfilled cases were sealed with phenol as described above. One glass-filled case and two unfilled cases were supported in metal cans and the other cases were unsupported during sterilization at 145°C. The unsupported glass-filled case developed a leak within four hours and the supported case failed between six and twenty-one hours. Both of the supported seals on the unfilled cases survived sterilization for 48 hours. One of the unsupported cases cracked along one of the vertical edges of the case between six and twenty-one hours in the oven. The pressure started to drop after two hours on the second unsupported case, but after sterilization it was found that the leak occurred at the pressure gauge instead of between the case and cover.

To determine if a snug fit and pressure were needed to make a good seal, six cases were sealed taking little care to fit the nylon blocks to the case. The cases were sealed as before but no pressure was applied to the seal area. Three of the cases leaked at 30 psig at room temperature and three of the cases held 90 psig supported in metal cans. The three cases that held 90 psig were filled half full with a 40% potassium hydroxide solution and placed in the oven at 145°C. for 48 hours. One of the cases leaked within two hours and the other two

cells survived the test. From this test it was concluded that the case-to-cover fit should be tight and that pressure must be applied in making the seal.

IV. New Case and Cover Design

From the initial testing of the prototype of the proposed new case design, it appeared that the redesigned case molded of nylon, Zytel 38, would survive sterilization. Also Penton and Celcon could be molded with the same tools. The drawings for the new design were shown to J.P.L. representatives at a meeting held at J.P.L. on October 22, 1963. Drawings of the case and cover molds are shown in Figures 24 and 25. New case and cover molds were ordered about the first of November of 1963 and were finally delivered in January of 1964. Photographs of the new case and cover molds are shown in Figures 22 and 23.

The outside cell dimensions of the new case were about the same as the old case. The wall thickness of the new case was increased from 0.10 to 0.125 inches for additional strength. The weight of the new case and cover was 134 grams. The main feature of the new design was the cover-to-case fit or seal area in that it had three advantages over the old design. One, it was considered more applicable for heat sealing the cover to the case if either Celcon or Penton was used as the case material. Two, pressure could be applied to the seal area between the cover and case. Very little pressure could be applied to the seal area on the old case design because the walls of the case bowed in when pressure was applied to the seal area. The third advantage was that there were no weak spots due to shoulders, ledges or sharp corners such as there were in the old design. As shown in Fig. 18, the case wall thickness was only one-half that of the body of the case and at the detent or notch molded in the sides of the case to provide a snap fit of the case and cover the case wall was only about 0.01 inch thick and was a source of failure. During the previous investigation most of the leaks occurred at the seal area due either to poor seals or cracks in the case at the seal area. The new case and cover are shown in Figure 19. The terminal-to-cover seal was not changed since past experience had proven it to be adequate.

A. Testing of New Case and Covers

Cases and covers of the new design became available for testing in January of 1964. The first covers did not fit snug in the case and five cases were sealed for a preliminary check before attempting to build cells.

The cases were sealed similar to the method described for the prototype case and cover tests except instead of using "C" clamps to apply pressure to the seal area, a special clamping fixture made in the Process shop was used. The clamping fixture is shown in Figure 20.

One case was checked at room temperature unsupported. Air pressure was gradually introduced into the case up to 90 psig, and after about 5 minutes at 90 psig the case blew up. The old design cases held about 50 psig. The other four cases were filled with about 80 milliliters of a 40% potassium hydroxide solution and sterilized at 145°C. for 44 hours and only one case survived the test without leaking at the case-to-cover seal. It was decided that the cover mold should be reworked so the cover would fit tighter in the case.

No further seal tests were made on the new nylon case and cover because of the time schedule. Actual cells were built when covers were available from the reworked mold. Six cells were built using R.A.I. separator materials and sterilized to start the cell testing phase of the program. All six cells survived sterilization without leaking and it appeared that the case and seal problem were solved. However, it was soon discovered that the R.A.I. separator materials seriously affected cell performance and cells were built to test other separator materials. At this time it was found that several of the cases cracked and leaked along the edges and some of the cases leaked at the seal area. Further tests on the case and cover-to-case seal were then initiated.

1. Initial Gas Pressure Tests at 145°C.

Six cases and covers of the new design were sealed with phenol in the manner described previously except pressure was applied to the seal area with a fixture made by the Process shop for the cell

testing phase. Copper tubing was soldered to one of the terminals to accommodate attachment to an air pressure line. The other terminal was soldered shut. The cases were supported in metal cans and subjected to 90 psig at room temperature. No leaks were detected when the cases were submerged in water.

Case No. 1 was placed in the oven at 145°C. supported in a metal can at 60 psig but the copper tube broke lose from the terminal. In an attempt to silver solder the copper tube to the terminal, the terminal got too hot and melted the cover which caused a leak at the terminal. The leak was not rapid and the unsupported case held 90 psig after being in the oven over 36 hours.

Case No. 2 was aged 36 hours in the oven at 145°C. The unsupported case was gradually subjected to air pressure and the seal broke at 75 psig.

Case No. 3 was supported in a metal can under 60 psig air pressure and placed in the oven at 145°C. for 40 hours and no leaks or cracks were observed. The pressure was released and the case was removed from the metal can. The unsupported case was subjected to 60 psig pressure and placed back in the oven for 16 hours. No leaks were observed so the pressure was increased to 90 psig. The cover-to-case seal broke between 57 to 72 hours at 90 psig.

Case No. 4 was tested similar to Case No. 3 but was removed from the oven after 48 hours stand at 90 psig.

Case No. 5 was heat aged at 145°C. for 40 hours and then gradually subjected to air pressure. The case-to-cover seal broke at 65 psig. The case was not supported.

Case No. 6 was heat aged for 40 hours at 145°C. and gradually subjected to air pressure unsupported up to 90 psig. This pressure was held for about five hours and the test was stopped.

2. Mechanical Pressures Versus Gas Pressures

When pressure was applied to the unsupported cases at 145°C,

the broad, flat sides bulged out to about double the original thickness of the case as shown in Figure 21. From this test it was assumed that gas pressures developed in the cells during sterilization were not entirely responsible for case breakage. To determine if mechanical pressure produced by the swelling of the cell element during sterilization was causing the cases to crack at the corners, three cells were constructed using only nine plates instead of the thirteen plates which reduced thickness of the element by approximately 0.20 inch. The three cells were supported in a metal can and sterilized at 145°C for 48 hours. The center cell leaked at the seal after about 24 hours but no leaks were observed on the outside cells. Upon removal from the metal can, it was observed that the two outside cells had cracks laterally on the broad sides of the case between the cover and top of the element. Fine cracks were also observed at the edges of one outside case and the center case. The cell that leaked at the seal was bowed in slightly indicating that there was a negative pressure in the cell; however, the other two cells were not bowed in. The cells were weighed before and after sterilization with the following results:

Cell Nr.	Wt Before (grams)	Wt After (grams)	Wt Loss (grams)
9-3-15-1	515.3	514.0	1.3
9-3-15-2	515.5	475.8	36.7
9-3-15-3	508.8	507.7	1.1

This test was considered inconclusive and another experiment was run in an effort to elucidate the cause of cell case cracking.

Nine cases were envolved in the second experiment, three contained electrolyte only, three contained electrolyte and fibrous sausage casing, and three were actual cells. The electrolyte in each instance was a 45% potassium hydroxide solution. One of the cells was of the new 13 plate design (discussed under Section IV, E.) and two of the cells contained undersized elements in that they contained only nine plates of the 13-plate element design.

Pressure gauges of the Bourdon tube type with a scale of zero to 100 psi were mounted on the cells by means of a copper tube which was soldered to one of the cell terminals. The copper tubes were about 30 inches long which allowed the pressure gauges to be mounted outside of the oven. Heretofore cell gas pressures had been measured with pressure gauges mounted directly on the cell, and the gauges were subjected to the sterilization environment which probably affected the accuracy of the pressure reading because of the thermal effect on the Bourdon tubes. The pressures developed by the samples during sterilization at 145°C for 36 hours are presented in Table 6. The maximum pressures developed by the three groups were: 15 psig for potassium hydroxide, 23 psig for potassium hydroxide and sausage casing, 27 psig for complete cells. The cases were supported in metal containers during sterilization, three samples in one can and six samples in another can.

None of the cases broke during sterilization, but one of the cases containing electrolyte only leaked at the connection between the copper tube and the terminal. The gas pressures developed during sterilization certainly did not appear to be high enough to produce case breakage, and since the 13-plate cell case did not crack, it was questionable if mechanical pressures from the elements were causing the cases to break.

The samples were weighed before and after sterilization, and the cases containing electrolyte and sausage casing lost approximately one gram while the actual cells lost about six grams. The difference in the weights is unexplainable unless there was an undetected leak or an error was made in weighing.

Twelve cases were tested to determine if molding conditions and annealing were important factors in case breakage. Six of the test cases were injection molded in the Process Department's four ounce machine, and six of the test cases were molded in a twelve ounce production machine in Plant 11. It was

thought that the larger machine could push the material in the mold faster than the small machine and possibly get better knitting of the nylon as it flowed into the mold. Three cases from each machine were annealed in Glyco wax S932, manufactured by Glyco Chemicals, Williamsport, Pennsylvania, at 350° F for one-half hour and cooled slowly in the annealing wax. To remove the wax the cases were washed in boiling water and then in methylene chloride. All twelve cases were sealed with phenol in the usual manner. The annealed cases shrunk and the covers had to be forced into the case, since the covers were not annealed.

The six annealed cases were placed in an oven and equilibrated at 145° C in about one-half hour and pressure tested unsupported with nitrogen. As recorded in Table 7 the case-to-cover seals let go on all six cases between 95 and 115 psig. The seal failure might have been due to the fact that most of the phenol was wiped off the seal area when the covers were forced into the annealed cases. It was also questionable whether or not all of the annealing wax was removed from the case. Since the seals broke this test did not prove whether annealing was beneficial or not.

The six unannealed cases were pressure tested at room temperature. From the pressure data in Table 7 it can be seen that the cases molded in the twelve ounce machine burst at 155, 202, and 200 psig. The seals let go on two of the four ounce cases at 200 and 130 psig and the case wall broke at 205 psig on the third case. From this test it was concluded that the size of the molding machine did not make any difference in the strength of the case.

It was pointed out that tests simulating the actual conditions during sterilization were needed and further tests were made. Sixteen cases molded in the twelve ounce machine were sealed in the usual manner and a copper tube was silver soldered to one of the terminals and the other terminal was plugged. Nitrogen was gradually injected into five of the sealed cases at room temperature

until they burst. The burst pressures were 250, 100, 80, 120, and 130 psig. The other four cases were heat aged in the oven at 145°C for 36 hours and tested at room temperature. The burst pressures on the heat aged cases were 50, 50, 40, and 50 psig. The effect of heat aging the nylon cases is at least a 50% reduction in the strength of the case at room temperature. All of the cases broke in the same general pattern. One side of the case blew out breaking at the wall corners and below the cover. This, of course, indicates that the corners are the points of stress. However, the burst pressures were still high enough on the heat aged cases to withstand the gas pressures developed in the cells during sterilization. The considerable spread in the burst pressures of the cases tested at room temperature is not explainable.

Seven of the cases were pressure tested unsupported at 145°C after 36 hours at temperature. As shown in Table 7 the seals let go on six of the cases between 50 and 80 psig and the case wall broke at 170 psig on one of the cases.

In a further attempt to elucidate the case breakage problem, tensile tests were made on Zytel 38 bars cut from molded cases and tensile bars of other nylons, Teflon, Penton, Celcon and Polypropylene. The tests were made on a Tinesis-Olsen tensile machine and the strain was measured with an extensometer. Some of the tensile bars were sterilized at 145°C for 36 hours in a 40% potassium hydroxide solution, but all tensile tests were made at room temperature.

The tensile data on the various test strips are recorded in Table 8. The data indicate that there is only about a 16% decrease in the strength of the sterilized samples of Zytel 38, but, perhaps, the most significant difference is in the strain data. The sterilized Zytel 38 samples became quite brittle and stretched only 5-10% in comparison to about a 200% elongation in unsterilized samples. Before any definite conclusions can be made, test data at elevated

temperatures under various loads for various periods with KOH present is needed. The present data indicate that the cases should not be breaking due to gas pressure alone. There is a possibility that mechanical pressures from the element might be bursting the cases; this is doubtful. The effects of KOH and molding parameters on the physical properties of case materials also need further study.

V. Cell Testing

When it became evident from the cell component tests that the cross-linked high density polyethylene with the acrylic and methacrylic acid grafts were the best of the five separator experimental materials, 120 foot samples of each material were ordered from Radiation Applications Inc. (R.A.I.) for evaluation in cells.

Cells of standard plate construction, except for the omission of PVA in the negative plate, using the R.A.I. separator materials were built and sterilized. It soon became evident that the separator materials were emitting a degradation product when sterilized in situ that decreased cell capacity by about 50%. The cell testing program was modified in an attempt to solve the problem. Finally the cell element was redesigned and it was possible to get capacities of about 40 ampere-hours with fibrous sausage casing separators. Testing of new element designs using standard FSC separators was initiated. Modified FSC separators were also tested in situ. A separator material (C19-300) which initially looked promising was purchased from Yardney Electric Company and evaluated in cells. A detailed description of the various test parameters and the findings is presented in this section.

A. Sterilization and Evaluation of Cells Built With R.A.I. Separators

Table 9 lists the capacities, cycle and stand life data on the various cells tested using R.A.I. separator materials, and the pertinent construction details are outlined in Table 11.

Initially thirty cells (fifteen each) were assembled from the two

separator materials supplied by R.A.I. The separators were acrylic acid graft on crosslinked high density polyethylene and methacrylic acid graft on crosslinked high density polyethylene; AA-XLHDPE and MAA-XLHDPE or just AA and MAA are used to designate these materials in cells. Six cells, three each of C1, 2, 3 AA and C1, 2, 3 MAA, were selected at random and used for control cells. The cells were formed at 1.25 amperes to 2.1 volts and discharged at nine amperes to 1.30 volts. Their initial capacities were 23 to 25 ampere-hours as shown in Table 9, and it was decided to sterilize three cells built with each type of separator. The cells were supported three in a group in metal cans and sterilized at 145°C. for 36 hours. After sterilization the cells were examined for leaks and none were detected indicating that the new case design and seal solved the breakage and seal problems. The cells were placed on formation charge at 1.25 amperes overnight with an integrator in the circuit. The following morning it was discovered that five cells had exploded during the night. From the integrator reading, it was calculated that the cells had only received 18 ampere-hours charge. One cell was still sealed and another cell was broken near the top so performance checks were made on these two cells. The cases of the other four cells were split and broken on the sides, and three of the five broken cells had their tops blown off, breaking the lug wires from the plates.

The one remaining sealed cell was placed back on charge and it accepted only about three ampere-hours before the counter EMF reached 2.1 volts and pressure started to build up in the cell as noted by the bulging cell case. On the first discharge the sealed cell (AA 2) containing the acrylic acid graft on crosslinked high density polyethylene separator yielded 17 ampere-hours, whereas the broken cell (MAA 3) containing the methacrylic acid graft on crosslinked high density polyethylene yielded 11.2 ampere-hours. The cells were recharged at 1.25 amperes to 2.1 volts, and cells AA 2 and MAA 3 accepted 18 and 14 ampere-hours respectively. A hole was drilled in the top of the sealed AA cell and the positive and negative plate voltages were read using a strip of zinc metal as a reference electrode. The reference electrode readings

indicated that the positive plates were polarizing in both cells during charge. Twenty milliliters of 45% potassium hydroxide were added to both cells, but this did not have any effect on cell charge acceptance. The cells were given several cycles but no improvement in cell capacity was accomplished as can be noted in Table 9. From the third electrode measurements and the cell behavior on charge, it was believed that the cells exploded because of oxygen gas pressure rather than a chemical explosion.

1. Sterilization at 135°

After the poor performance of cells sterilized at 145°C., it was decided to sterilize cells at 135°C. to get an indication of how critical the sterilization temperature might be. Six cells, three each with each type of separator material (AA 4, 5, 6 and MAA 7, 8, 9), were sterilized at 135°C. for 36 hours in sets of three supported in metal cans. The cells survived sterilization with no apparent leaks. The cells were formed at one ampere to an end of charge voltage of 2.1 volts and discharged at nine amperes to 1.3 volts. The initial capacities of the cells were about 13 ampere-hours as shown in Table 9. The cells were cycled a few times and on the third and fourth cycles, the cells were yielding from 16.5 to 20 ampere-hours. Although there was some improvement in the cells sterilized at 135°C., it was not considered significant enough for further consideration; however, cycle and stand life data were obtained on the cells and are summarized in Table 9. The AA cells yielded very good capacities after 30 days stand, but began to show signs of shorting in 90 days. Cell AA 4 stood about 6.5 months before shorting.

2. Presterilization of R.A.I. Membranes and Special Testing

After the disastrous results obtained on the sterilized cells constructed with the two types of crosslinked high density polyethylene base separators, it was thought that a presterilization

of the separator material might leach the degradeable deleterious material from the separator. In the cell component tests, cells constructed with the sterilized separator gave good capacities. At the same time it was decided to evaluate Permion 300, Permion 600, and the sterilization liquors from the sterilized separator materials. It was also planned to determine if the addition of palladium in the positive plate would increase cell performance. The possibility that the Viscon paper wrap on the negative plates was causing poor cell capacity was also checked.

a. Crosslinked High Density Polyethylene

The remaining cells which were built for cell testing were torn down to remove the separator material since it would take at least another month to reorder additional material. Enough of each type of material to build five cells was sterilized at 145°C. for 36 hours in stainless steel cans in about 200 milliliters of a 40% solution of potassium hydroxide. The sterilization liquor was used to fill two cells of standard construction to determine if the degradation products affected cell performance. The sterilization liquor contained a slight quantity of a white suspension. It was also noted that when the material was washed a white colored material could be rubbed off the membrane with one's fingers and formed a milky suspension in the water. No attempt was made to rub this product off all of the sterilized membranes. After washing the membranes free of the electrolyte, they were hung up to air dry at room temperature. A sample of the precipitate was retained for infrared analysis, but the material could not be identified by the analyst.

Six cells, AA 1, 2, 3 P and MAA 1, 2, 3 P, were built from each of the presterilized membranes with the following modifications:

(1) Negative plates were built with the sterilized membranes in place of the Viscon paper and contained 4% mercuric oxide instead of 1%.

(2) The positive plates were made from a 1% palladium alloy silver powder.

(3) The electrolyte was a 50% solution of potassium hydroxide.

The cells were sterilized at 145°C. for 36 hours and no leaks were detected. The cells were formed at one ampere to 2.1 volts per cell and discharged at nine amperes. The initial capacities were about 12 ampere-hours as shown in Table 9 and increased on the second and third cycles. Cells containing AA-XLHDPE presterilized separators yielded 28-30 ampere-hours on the third cycle whereas the cells with the presterilized MAA-XLHDPE delivered 20 to 23 ampere-hours. The cells survived a ten-day stand test on the fourth cycle and were placed on a 30-day stand on the fifth cycle and four of the cells shorted in from two to 22 days. An attempt was made to charge the shorted cells but they could not be fully charged. Two of the AA cells delivered 27 to 29 ampere-hours after the 30-day stand and were recharged and put back on a second 30-day stand. One of the cells shorted in seven days and the other cell delivered 27 ampere-hours and was put back on stand but shorted within a month.

To determine if the palladium or the removal of the Viscon paper was instrumental in improving cell performance, two additional cells were assembled without Viscon paper on the negative plate and palladium was not used in positive plates. Cell NSNV was built with non-sterilized separator material, and cell PSNV was assembled with presterilized separators. Both cells were sterilized at 145°C. for 36 hours. They were given several cycles and 10 and 30-day stand tests as shown in Table 9. The capacities ranged between 10 and 13 ampere-hours and the cell with the presterilized material had just a slightly better capacity. The PSNV cell was overcharged on the eighth cycle and its top was blown off, presumably due to gas pressure. Cell NSNV showed no capacity loss after two 30-day stands. The cell was placed on

stand on May 28, 1964 and on January 22, 1965 the cell was reading 1.68 volts, indicating it was self-discharging.

Another cell, XLHDPE 040P, was constructed later when it was found that the positive plates were being affected by the degradation products. The cell contained about double the usual amount of positive active material. Four layers of presterilized crosslinked high density polyethylene were used for the separator. The presterilized material was also used for the negative plate retainer in place of Viscon paper as shown in Table 11. After sterilization at 145°C. the cell delivered 22.2, 33.3, 34.5 a.h. on three successive cycles which is about double the capacity on cells PSNV and NSNV. As will be discussed later in section D, the fact that capacity is increased by increasing the quantity of positive material while reducing the quantity of negative material in a cell is proof that the degradation products are attacking the positive plates. The nature of the degradation products and how they attack the positive plate are unknown.

Cell XLHDPE 040P had fair capacities after 10 and 30-day stands on the fourth and fifth cycles, but the cell shorted on the sixth charge cycle.

From the results of the tests on the cells described above, it is concluded that the Viscon paper was not responsible for poor cell capacities and that presterilization did not eliminate the degradation product. Palladium in the positive plates appeared to nullify the effects of the separator degradation products on cell capacity, but the separator problem was not solved as evidenced by the poor stand lives obtained on the cells.

b. Cells Activated with Sterilization Liquor

Four cells of standard construction (AA 1 and 2 and MAA 1 and 2) were filled with 85 milliliters of the liquor from each of the two types of sterilized membranes (AA on XLHDPE and MAA on XLHDPE) formed and cycled in the usual manner. The initial capacities were

low, ranging from six to 20 ampere-hours. The capacities of the low capacity cells gradually increased to about 20 ampere-hours on the sixth cycle as shown in Table 10. The cells were given 33 cycles with no significant change in capacity, and the test was stopped. This test demonstrated that a soluble degradation product is produced which is partially responsible for the reduction in cell capacity.

c. Testing of Permion 300 and Permion 600

Permion 300 is a polyethylene base separator material with an acrylic acid graft manufactured by R.A.I. Since this material was similar to the experimental membranes, it was tested to determine if it behaved in a similar manner. Enough Permion 300 to build three cells was sterilized in 200 milliliters of a 40% potassium hydroxide solution in a stainless steel can. The sterilized P-300 was washed in deionized water. A white suspension like that obtained from the experimental membranes was noted in the wash water but to a greater extent. The material was severely degraded and only enough material to build one cell was salvaged. The cell (PS P-300) was built with 1% palladium in the positive plates and sterilized at 145°C. for 36 hours. As shown in Table 9 the capacity increased from 14.4 to 25.5 ampere-hours in three cycles but the cell shorted on the fourth charge cycle.

Two cells of standard construction were filled with 85 milliliters of the sterilization liquor and cycled. The initial capacities of the cells, P-300 L-1 and L-2, averaged about nine ampere-hours and gradually increased to a maximum of 20 ampere-hours on the sixth cycle as shown in Table 10. It is concluded that Permion 300 is not stable in the sterilization environment and is not a satisfactory separator material.

Two cells, P-600 .040P and PF-P600, were assembled using Permion 600 as a separator. Permion 600 is a cellophane base material with a copolymer graft of styrene and acrylonitrile

produced by R.A.I. Cell P-600 .040P shorted on the first charge after sterilization at 145°C. Cell PF-P600 was formed and discharged to zero volts prior to sterilization. This cell also shorted on the first charge cycle after sterilization.

d. Re-evaluation of Teflon

After the disastrous results with the polyethylene base separator materials, it was decided to evaluate the behavior of the Teflon separator when sterilized in situ. Cell, Teflon AA, was built using a sample Teflon separator with an acrylic acid graft and sterilized at 145°C. for 36 hours. As shown in Table 11, the cell contained 1% palladium positive plates and Viscon was not used on the negative plate. The cell was formed and cycled in the usual manner. The capacity was low, ranging from about 13 to 18 ampere-hours through nine cycles indicating that the Teflon membrane also emitted a degradation product. The cell shorted during the tenth charge cycle substantiating the previous findings that teflon base separators do not exhibit good life characteristics.

e. Effects of Acrylic Acid in the Electrolyte

In an effort to get some idea of the nature of the degradation product from the separators, it was decided to test two cells of standard construction with acrylic acid added to the electrolyte. One cell was filled with 85 milliliters of 45% potassium hydroxide which contained 1% by volume acrylic acid. The second cell was filled with electrolyte which contained 2% by volume acrylic acid. The cells were formed and cycled in the usual manner, and on the first two cycles the cells, 1% AA and 2% AA, yielded 20 to 23 ampere-hours as shown in Table 9. On the fourth and fifth cycles the cells yielded 26 and 28 ampere-hours. From these results, it is concluded that acrylic acid monomer in the range tested does not reduce cell capacity.

B. Sterilization of Yardney Element

A Yardney LR-40 Silvercel was purchased for evaluation. According to the Yardney data sheet, the cell had been previously formed and discharged. The cell case was molded of styrene and would melt at 145°C. so the electrochemical element was removed from the styrene case and inserted into a Delco-Remy nylon case.

The cell was sterilized at 145°C. for 36 hours, supported in a metal can. During sterilization the cell leaked at the case-to-cover seal area. It was surmized that the leak was probably due to an inadequate job of cleaning the seal area after inserting the wet element in the case. Deionized water was added to the cell to bring the electrolyte level back up to the top of the plates. On the first discharge the cell yielded 14.7 ampere-hours; however, the cell had not been fully charged. On the second discharge the cell yielded 35.6 ampere-hours and subsequently on six additional cycles it yielded 33 to 38 ampere-hours. On the eighth cycle after a ten-day stand, the cell yielded 34.6 ampere-hours. The cell shorted during charge on the ninth cycle as shown in Table 10. The initial results on this cell were very encouraging, and it was thought that the Yardney separator material was worthy of further evaluation; therefore, 100 square feet of the Yardney separator material, C19-300, was purchased for further testing in Delco-Remy cells. The construction and testing of the cells built with the C19-300 material are discussed in section V, E.

C. Treated Fibrous Sausage Casing Separators

Two samples of specially treated fibrous sausage casing were used for separators to build two cells of otherwise standard construction. There was only enough material for two layers of separation between the plates. The samples were prepared by the Visking Division of Union Carbide Corp. by soaking their fibrous casing in a silver acetate solution for 24 hours. Sample 13-3 Ag-B was washed free from non-bound silver ions while sample B-3 Ag-F was not washed and contained both bound and free silver ions.

The cells were sterilized at 145°C. for 36 hours supported in metal

cans and charged at 1.25 amperes to 2.1 volts. The cell containing the B-3 Ag-F sample shorted during the formation charge. The cell constructed with the B-3 Ag-B yielded 16.5 ampere-hours on the first two cycles and gradually built up to a little over 20 ampere-hours. The cell was given a 10-day stand on the fourteenth cycle and yielded only 3.4 ampere-hours. Cycling was continued and the cell shorted on the eighteenth cycle. The cycle data up to the 12th cycle are shown in Table 10.

Although the capacity of the cell was low, it demonstrated improvement over past results with untreated fibrous casing where it was only possible to obtain four to nine ampere-hours from cells of the same design; therefore, it seems advisable that this type of separator material be re-evaluated in cells of the new design as discussed in the following sections. Adequate initial capacities could probably be attained, but charged stand life is questionable.

D. Change in Plate Material Ratio

As previously discussed it was noted that the degradation products produced during sterilization were apparently affecting the positive plates and preventing them from accepting full charge and/or preventing them from discharging as indicated by third electrode reading. Therefore, it was surmised that it might be possible to increase the quantity of positive plate material and increase the capacity of the cell even in the presence of the degradation products. To determine if this hypothesis was true, three cells were constructed with three different separator materials.

The weight or quantity of silver in the positive plates was doubled so that the six positive plates contained approximately 163 grams of silver. In order to accommodate the thick positive plates in the case, the seven negative plates were cut down from 20 to 14 grams of zinc oxide per plate. The negative plates then limited cell capacity to 65 ampere-hours on a theoretical basis of 100% Faradaic efficiency. One cell, FSC .040P, was built with two layers of standard fibrous sausage casing.

The second cell, XLHDPE .040P, contained four layers of presterilized crosslinked high density polyethylene, and the third cell, P-600 .040P, contained three layers of Permion 600 separator material.

The cells were sterilized at 145°C. for 36 hours and tested in the usual manner. The cell containing the Permion 600 shorted during the formation charge. The P-600 cell was torn down and it appeared as if the separator might have been torn during assembly, so a second cell was assembled and sterilized. The second P-600 cell also shorted during the formation charge. The cell containing fibrous sausage casing yielded 43.5 and 42.5 amperes on two successive cycles and was placed on stand, but it shorted in four days. The cell containing the XLHDPE separator yielded 22.2, 33.3, 34.5 and 29.7 ampere-hours on successive cycles as shown in Table 10. After a 30-day stand on the fifth cycle, the cell yielded 28.9 ampere-hours; however, the cell shorted on the next charge cycle. The results obtained from this test indicated that it was feasible to increase cell capacity even in the presence of capacity limiting degradation products by increasing the quantity of positive plate material. This test was also further proof that the separator degradation products primarily affect the positive plate.

Preformation Charge and Discharge and Modified Element Design

From the results on the Yardney cell, it was theorized that a formation charge and discharge before sterilization might improve cell capacity. Three cells were built using three types of separator material: fibrous sausage casing, Permion 600, and cellophane. A modification was also made in the element designs. One cell, PF-FSC, contained two layers of FSC and had six 23 gram positive plates and seven 16 gram negative plates. The other two cells contained 15 plates (seven 23 gram positives and eight 16 gram negatives). One cell, PF P-600, contained three layers of Permion 600 and the other cell, PF-Cello, contained three layers of cellophane. The cells were formed at 1.5 amperes and discharged at nine amperes to 1.3 volts and yielded 50, 59, and 61.5 ampere-hours for the PF-FSC, PF-Cello, and

PF-P600, respectively. The cells were discharged to zero volts by shorting the terminals and sterilized at 145°C. for 36 hours. The cell cases cracked at the edges near the top during sterilization so deionized water was added to the cells to bring the electrolyte level to its original position. During charge the two cells built with the P-600 and cellophane separators shorted; however, the PF-FSC cell accepted charge and yielded 44 ampere-hours on the first discharge and 48 ampere-hours on the second discharge (see Fig. 27) after sterilization. It yielded 46.5 ampere-hours on the fourth cycle after a ten-day stand. The cell was given three more cycles and put on a stand test and the cell shorted after 32 days as shown in Table 10. This test indicated that a significant increase in cell capacity can be obtained by a formation charge and discharge before sterilization; however, there is the added problem in this procedure of discharging all of the formed plate materials because they produce excessive pressures during sterilization which burst the case.

E. Redesign of Electrochemical Element

In discussing the sterilization problem with JPL representatives during the program, it was stated that the battery requirement was primarily for stand life rather than cycle life. The load requirements were not known but it was estimated that it would probably be a low rate intermittent discharge, possibly over about a ten-day period. In view of this information and the results of tests discussed in section D, a change was made in the element design. In all of the previous investigations, testing was done with cells designed primarily for cycle life in which the positive-to-negative plate material ratio was 1:2. The nominal capacity rating of the cells was 25 ampere-hours. The 1:2 material ratio was calculated on a 100% Faradaic efficiency of the starting plate materials, silver powder and zinc oxide. The primary reason for doubling the quantity of zinc oxide in relation to silver is because of the "washing" effect of the zinc plate on cycling which is due to the solubility of zinc oxide in the electrolyte. Upon cycling, incremental quantities of zinc lose contact with the bulk of

the plate and also shift position on the plate, consequently the plates gradually decrease in capacity.

Since it was made known that cycle life was not an important factor in the sterilizable battery, the element design was changed so the positive-to-negative plate material ratios were 1:1 calculated on a 100% Faradaic efficiency. In making the change in material ratio, it was conservatively estimated that cell capacity could be increased from 25 to approximately 40 ampere-hours. The gross weight of the cell remained approximately the same near 1.3 pounds. The type of separator system and the number of layers will have some effect on the element design, primarily because of the volume they occupy. The number of plates per unit volume is a factor to consider in element design because as the number of plates decrease, there is a subsequent decrease in the volume occupied by the separator system, consequently the extra volume can be utilized by adding more active material. Since degradation products from all of the separator materials tested thus far limited cell capacity, it was thought that it would be advantageous to increase the plate material to separator material ratios by decreasing the number of plates per cell.

1. Testing of Yardney C19-300 Separator Material

The C19-300 separator material purchased from the Yardney Electric Corporation was used to build twelve cells with three different element designs as shown in Table 11. All of the cells contained seven layers of the separator material between the positive and negative plates. The dry material measured slightly over one mil. in thickness per layer. Two cells, SYS13 and CYS13, were of the standard 13-plate design for a direct comparison with previous cell tests. Cell SYS13 was sterilized at 145°C. for 36 hours, and cell, CYS13, was used for a control. The sterilized cell yielded 11.0 ampere-hours on the first discharge and shorted on the second charge cycle. The control cell yielded 22, 29, 35, and 34.5 ampere-hours on successive cycles. The cell was cycled to failure, and it shorted on the 40th charge.

Ten cells contained revised element designs wherein the plate

materials were in a 1:1 ratio. Four of the cells contained nine plates and had a theoretical capacity of 81 ampere-hours. Six of the cells contained 13 plates and had a theoretical capacity of 68 ampere-hours. Two of the thirteen plate cells, PF-13Y1S and PF-13Y2S, listed in Table 10 were formed and discharged to zero volts before sterilization and yielded 43 ampere-hours. The cells were inadvertently left in the oven at 145°C. for 44 hours instead of 36 hours. The cell cases cracked at the corners during sterilization and electrolyte was added to the cells before they were charged. The cells yielded about 30 ampere-hours on the first two cycles after sterilization; however, they shorted on the third charge cycle after sterilization.

Two of the 9-plate and two of the 13-plate cells (9Y1C, 2C and 13Y1C, 2C) were controls, and the other four cells were sterilized at 145°C. for 36 hours. All of the sterilized cells leaked during sterilization and 15 to 30 milliliters of electrolyte were added to them to bring the electrolyte level to its original position. The cells were charged at 1.5 to 2.0 amperes to 2.1 volts and discharged at 9 amperes to 1.3 volts at room temperature. The 13-plate and 9-plate control cells had about equal capacities being in the range of 50 to 55 ampere-hours as shown in Table 10. The 9-plate sterilized cells had somewhat better capacities than the 13-plate cells indicating that capacity can be increased by increasing the plate-to-separator material ratio. Typical discharge curves for the cells are shown in Figures 26 and 27. On the fourth cycle the cells were given a 10-day stand. The four control cells yielded about 48 ampere-hours, whereas the 9-plate sterilized cells yielded 42 ampere-hours, and the 13-plate sterilized cells had quite a spread, yielding 39 and 25 ampere-hours. The cells were recharged and put on stand on May 20, 1964. None of the cells had shorted up to January 22, 1965 when they were transferred to Crane Naval Depot. Data are insufficient at this time to conclude whether or not the C19-300 separator is better than FSC. The results indicate that a degradation product is formed which reduces cell capacity.

Stand life is questionable, but thus far C19-300 has shown stand life superior to RAI materials.

2. Thirteen Plate Cells Containing Fibrous Sausage Casing Separators

After the encouraging results obtained on FSC, 040P and Pf-FSC cells with fibrous sausage casing separators, three additional cells were built to re-evaluate FSC separators in the new element design. The cells contained 13 plates with a 1:1 negative-to-positive plate material ratio with three layers of Food Product's standard FSC for separators. The cells were formed in the usual manner and discharged as a battery at 15 amperes to 3.9 volts and yielded 49 ampere-hours. The cells were discharged to zero volts by shorting the terminals and sealed.

The three cells (FSC PF 1, 2, 3) were supported in a metal can and sterilized at 145°C., but they were inadvertently left in the oven for 44 hours. During sterilization the cases cracked at the corners and some electrolyte was lost. From 15 to 25 milliliters of electrolyte were added to the cells to bring them to the original level. The cells were given several cycles, discharging at 10 amperes to 1.3 volts and charging at 2.0 amperes to 2.1 volts, and placed on a 10 day stand on the seventh cycle. As shown in Table 10, the capacities of the cells were around 44 ampere-hours which compares favorably with the results obtained on the previous cell and the cells constructed with C19-300. The discharge curve for the 13 plate cells is shown in Fig. 28 in comparison with the discharge curves for the 9 plate cells which are discussed on page 46. The cells gave good capacities after a 10 day stand on the seventh cycle. They were placed on stand on June 6, 1964, and one cell shorted on the seventeenth day. The second cell shorted after 5.5 months. The third cell was transferred to Crane Naval Depot on January 22, 1965 with a voltage reading of 1.56 volts, indicating that it was self-discharging. An attempt was made to recharge the shorted cells, but they would not hold the charge.

3. Addition of Aluminum Oxide to the Electrolyte

Three 13 plate cells with a 1:1 positive-to-negative plate material ratio and three layers of standard fibrous sausage casing as separators were filled with 75 milliliters of 45% potassium hydroxide solution which contained approximately 6% aluminum oxide by weight. The cells (6% AL 1, 2, 3) were supported in a metal can and sterilized at 145°C. for 36 hours. No leaks at the seals or in the cases were observed. The cells were charged and discharged in the usual manner and the capacities of the cells over seven cycles ranged from 22 to 30 ampere-hours as shown in Table 10. The cells were put on a 10-day stand on the sixth cycle and showed no appreciable loss in capacity. The cells were placed on a 30-day stand on the eighth cycle and lost only about three ampere-hours capacity. The capacities of these cells might be compared to the preformed cells which indicates that a formation charge and discharge before sterilization is beneficial to cell capacity. The cells were put back on stand on June 23, 1964. One cell shorted after five months, and the other two cells shorted after about seven months as indicated in Table 10. All three of the cells exploded soon after shorting.

From this test it is concluded that the addition of aluminum is not beneficial to cell performance.

4. High Molecular Weight Fibrous Sausage Casing

Six cells (HMW-1PF, 2PF, 3PF, 4, 5, 6) were constructed with three layers of a specially prepared high molecular weight fibrous sausage casing by Food Products Division. The cells were of the new design with 13 plates and a 1:1 positive-to-negative plate material ratio as outlined in Table 11. The cells were filled with 75 milliliters of 45% potassium hydroxide and their average weight was 591.2 grams. Three of the cells, HMW-1PF, 2PF, 3PF, were formed and discharged before sterilization. The preformed cells were discharged at 15 amperes as a battery to 3.9 volts and yielded 48.8 ampere-hours. The three preformed cells were then discharged to zero volts by shorting the cell terminals and sealed.

All six cells were supported in a metal case and sterilized at 145°C. for 36 hours. All six cells developed leaks during sterilization. Three of the cells leaked at the seals and the cases cracked at a corner on four of the cells. The electrolyte level was adjusted to its original position and the cells were cycled three times charging to 2.0 amperes to 2.1 volts and discharging at nine amperes to 1.3 volts. As shown in Table 10 the preformed cells yielded better capacities. There was no appreciable loss in capacity after 10 and 30 day stands and the cells were put on extended stand on August 5, 1964. Two cells, HMW-1PF and HMW-6, shorted on charge and cell HMW-3PF shorted overnight. The three remaining cells (HMW-2PF, HMW-4, HMW-5) still had an open circuit reading of 1.84 volts when they were transferred to Crane Naval Depot on January 22, 1965 after 5.5 months stand.

From this test it is concluded that the high molecular weight fibrous sausage casing is not superior to the standard fibrous sausage casing.

5. Nine Plate Cells with FSC Separators

Three nine plate cells, 9PF 1, 2, 3, were constructed with three layers of Food Products' standard fibrous sausage casing for comparison with the 13 plate cells. The positive-to-negative plate material ratio was 1:1 and the cells had a theoretical capacity of 80 ampere-hours. The cells were formed at 1.50 amperes and discharged as a battery at 15 amperes to 3.9 volts giving 48.8 ampere-hours. The cells were discharged to zero volts by shorting the cell terminals, sealed, placed in a metal can, and sterilized at 145°C. for 36 hours. One of the cells was observed to leak at the case-to-cover seal; however, they could not be removed from the metal can and it was not possible to determine if the cases cracked or how much electrolyte might have been lost. No electrolyte was added to any of the cells and they were charged at 1.5 to 2.0 amperes to 2.10 volts and discharged at 9 amperes to 1.3 volts. As shown in Table 10, the cells gave excellent capacities on the second and third cycles indicating that not much electrolyte could have been lost.

On the fourth cycle after sterilization, the cells yielded 51.5 ampere-hours after a 10-day stand. The cells were charged and put on stand on July 30, 1964. When the cells were transferred to Crane Naval Depot on January 22, 1963, their o.c. voltages were still at the divalent silver oxide level.

This test tends to prove that cell performance can be improved by decreasing the separator-to-plate material ratio by decreasing the number of plates in the cell. A typical discharge curve of the 9-plate cells is compared to a discharge curve of the 13-plate cells in Fig. 28.

F. Sterilization of Primary Dry Charged Cells

At the request of JPL some preliminary experiments were made on "dry charged" primary cells. Eighteen primary cells similar to those used in the primary battery for the Minuteman Missile manufactured by Delco-Remy were assembled. Six cells were used for controls. Six unsealed cells were sterilized dry at 135°C. for 36 hours and six unsealed cells were sterilized dry at 145°C. for 36 hours. After sterilization the cells were filled with 40% potassium hydroxide and immediately discharged at 10 amperes to an out-point of 1.30 volts. The average capacities of the three groups of cells were: controls, 11.1 ampere-hours; 135°C., 7.1 ampere-hours; 145°C., 6.2 ampere-hours. This represents from 36 to 44% loss in capacity of the cells. The capacities of the cells are recorded in Table 12.

The open circuit voltages of the sterilized cells were 1.61 to 1.62 volts whereas the voltages of the controls were 1.85 to 1.86 volts. The difference in the open circuit voltage indicates that the reason for loss in capacity of the sterilized cells was due to the decomposition of the divalent silver oxide to monovalent silver oxide during sterilization according to the equation:

$$2\,AgO \xrightarrow{\Delta} Ag_2O + \tfrac{1}{2}\,O_2\uparrow$$

G. Plate Thickness Evaluation

Twelve cells were constructed to determine cell performance as a

function of plate thickness. Four groups of three cells each were built to evaluate four plate thicknesses keeping the positive-to-negative plate material ratios approximately 1:1. The negative plates contained 1% mercuric oxide and were wrapped with one layer of Viscon paper. The cells contained three layers of standard fibrous sausage casing separators with a "u" wrap around the positive plates, leaving the negative plates open. Other construction features are listed in Table 13. The theoretical capacities of the cells are based on the weights of silver in the positive plates and as stated in the 3 September 1964 Status Report, they were recalculated from weights obtained after tearing the cells down after they failed because it was suspected that an error had been made in the weights during manufacture.

Table 14 lists the charge and discharge variables by cycle for the cells. The cells were charged and discharged in series, and as noted in the table when a cell reached 2.1 volts, it was removed from the charge circuit. Short leads with alligator clips were used to connect the cells together so the circuit was momentarily broken when a cell was removed. A Model 1473 Weston integrator was placed in the circuit so an accurate measure of the capacity input and output of the cells could be made.

The charge procedure was varied somewhat through the first five charge cycles to determine its effect on cell capacity. Table 15 lists the average capacity input and output of each three cell group over the first seventeen cycles. The twelfth cycle was omitted because the out point was missed on several of the cells. On the fifth cycle the cells were charged at an ambient temperature of 100°F., and although the cells accepted an average of about 10% more charge, the discharge capacity remained about the same.

Figure 29 shows the charge and material efficiencies averaged over the first five cycles as a function of positive plate thickness. The percent material efficiency is defined by $\frac{\text{actual capacity}}{\text{theoretical capacity}} \times 100$, and the charge efficiency is defined as $\frac{\text{Discharge capacity}}{\text{Charge capacity}} \times 100$. From Fig. 29

it can be determined that the material efficiency decreases at a rate of .33% per mil of plate thickness increase while the charge efficiency decreases only .066% per mil. This indicates that the decrease in material efficiency is due primarily to the fact that the plates accept proportionally less charge as their thicknesses increase.

Five different discharge rates ranging from 2 to 50 amperes were made at room temperature and three rates each were made at 100° and 30°F. Table 14 lists the charge and discharge parameters by cycle. Figs. 30 through 40 show the discharge curves for each set of cells at each discharge rate. Table 16 is a compilation of the energy delivered per unit weight and volume at the various power levels or discharge rates for the three temperatures. The watt-hours per pound is based on the element weight reported in Table 13 which is the cell weight minus the weight of the cell case, which is 134 grams. The element weight includes the weight of the electrolyte. Similarly the watt-hours per cubic inch does not include the volume of the cell case, but only the volume necessary to encase the cell element. The cell case was eliminated from the energy calculations so a more direct comparison could be made among the four plate thicknesses since the five plate cell contained a .180 inch shim inside the case.

The energy yields per pound of element weight and element volume versus the rate of power withdrawal at 75°F. are shown in Figs. 42 and 43. It can be seen that as the rates decrease the cells with the fewer numbers of plates give the greatest energy yields and that the curves intersect between 10 and 20 watts or near a nine ampere discharge rate. The fact that the break even point is near a nine ampere discharge rate is also shown in Figure 44 where the energy yield per pound versus the number of plates per cell is plotted for five discharge rates. It is also interesting to note that the curves intersect at about 15 plates per cell. This indicates that a 15 plate cell is the optimum design to deliver maximum energy at discharge rates between two and fifty amperes.

Figs. 45 and 46 show the effects of temperature on cell voltage and energy yields per pound at the two and fifty ampere discharge rates. These figures show that temperature is an important parameter to take into

consideration in battery specifications and design.

If Delco-Remy had continued work on this project, a similar study would have been made on sterilized cells because of the effects of separator degradation products on cell performance. By increasing the thickness of the plates, the number of plates per cell is decreased subsequently reducing the separator to active plate material ratio. The present study has shown that decreasing the number of plates per cell by making them thicker increases the specific energy yields at moderate discharge rates. The increase in specific energy should be even greater in sterilized cells, because of the reduction of separator degradation products.

From this work it should be evident that it is necessary to set some specifications on the cells or battery such as capacity, discharge rate, voltage and temperature requirements.

VI. Conclusions and Recommendations

Cell component evaluation revealed that poor cell performance after sterilization at 145°C. for 36 hours was due to degradation products from the separators. The nature of the degradation products were not identified. Uncharged positive and negative plates survived sterilization. Initially the negative plates contained a binder of polyvinyl alcohol which produced high pressures during sterilization. It was found that the PVA binder could be removed without adversely affecting the negative plates. The sterilization liquors from nylon, Celcon, and Penton case materials did not have adverse effects on cell performance.

Possible new teflon and crosslinked high density polyethylene base separator materials prepared by Radiation Applications Inc. were sterilized at 145°C. for 36 hours in potassium hydroxide, washed, dried, and assembled into cells. The cells containing the polyethylene base separators gave good capacities and approximately 30 cycles. When cells were built with the polyethylene base separators and sterilized, the cell capacity was reduced by about 50%. A cell constructed with a teflon base separator also lost

50% in capacity. Addition of palladium nullified the effects of the separator degradation products, but the cells exhibited poor stand life. Presterilization of the separator material did not eliminate the degradation products or improve cell capacity.

Third electrode voltage readings on the cells during charge and discharge indicated that the degradation products primarily attacked the positive plates limiting their capacity. Positive plate material was increased while decreasing the negative material. The capacity of these cells was greatly improved, proving that the positive plates were attacked by the degradation products.

It was decided that the battery requirement was one of stand life rather than cycle life, and the element was redesigned so the positive-to-negative plate material was in a 1:1 ratio instead of 1:2. This increased the energy output of sterilized cells from about 12 to 40 watt-hours per pound using fibrous sausage casing separators. Permion 600 and 300 and cellophane did not withstand sterilization in cells. The data indicate there is little difference in the behavior of C19-300 or fibrous sausage casing separators in sterilized cells. Results also indicate that a formation charge followed by a discharge to zero volts before sterilization improves cell performance; however, sterilization produces a capacity loss of at least 10 to 20%.

Several cells with C19-300 and FSC separators were put on charged stand life tests for nine to twelve months and the tests are not complete yet. Some of the cells have shorted after about six months stand while some of the cells have passed eight months stand. It is doubtful that cells with present separator materials will give a satisfactory charged stand life; therefore, superior separator materials must be developed.

With present separator materials such as C19-300 or FSC it might be possible to charge sterilized cells after a six or seven month uncharged stand and obtain 30 to 60 day stands with an energy yield in the range of 30 to 40 watt-hours per pound.

Sterilization of primary dry charged cells resulted in about a 40% loss of cell capacity due to decomposition of divalent silver oxide.

Sterilization of dry uncharged secondary cells was not investigated, but would offer an approach to the problem if wet cells cannot be made to withstand sterilization. The chief problem associated with this mode of operation is the activation of the cells with electrolyte under sterile conditions without intercell leakage.

Operational temperature and load requirements need to be determined for optimum cell design and testing. Future testing should include temperature and stand time tests rather than cycling. The possibility of charging a battery over a six month period could be investigated, or of charging after a six or more month stand after sterilization.

The plate thickness study on unsterilized cells shows that a greater energy yield per unit weight and volume can be obtained at low discharge rates by using thicker plates and fewer plates per cell. A similar study should be made on sterilized cells. Specifications on cell or battery performance and temperature of operation are needed for optimum design.

Preliminary tests indicated that nylon was superior to Celcon or Penton for a case material and that nylon should suffice as a case material. Under actual conditions nylon cases did not survive 100% of the time. Although there was some leakage at the case-to-cover seals, the major problem of concern was the fact that the cases were cracking at the corners. Testing of sterilized tensile bars indicated that the nylon became quite brittle after sterilization, and it is thought that nylon embrittlement is the chief cause of case breakage.

Engineering data on materials for cell cases in the sterilization environment are lacking. Future work should be directed toward obtaining engineering data on materials in the sterilization environment. Probably the best case could be obtained from glass-epoxy filament winding. General Electric Company has recently announced development of a new family of plastics produced by oxidative coupling and given the trade name "PPO". It is claimed to exhibit good physical properties at temperatures above 370°F. and can be injection molded in conventional equipment.

TABLE 1

Pressures Developed by Components During Sterilization at 145°C.

Hours	FSC	Zytel 101	Zytel 121	Zytel 38	Dynel	Permion 600	Celcon	Penton	Pos. Plates	Neg. Plates	Neg. Plates without PVA	Neg. Plate Material ZnO - 2% HgO Only
1	21	26	24	32	26	30	28	32	16	24	28	22
2	36	34	30	34	40	42	33	32	29	50	-	-
3	40	34	33	36	49	44	36	34	32	66	45	30
4	-	34	33	36	-	-	36	34	32	72	47	32
5	42	34	36	36	51	46	40	40	34	80	-	-
6	42	34	36	36	52	47	40	40	34	86	45	31
7	42	34	36	36	54	48	40	40	34	89	50	32
8	44	34	36	36	54	48	40	40	34	89	-	-
9	-	34	36	36	-	-	40	-	-	90	53	32
24	52	34	36	38	55	56	40	40	34	100+	60	30
30	54	35	-	-	55	-	-	-	-	-	-	-
36	54	35	38	40	55	57	40	42	36	100+	62	30
Room Temp.	7	0	0	0	3	6	0	0	0	40	13	0

TABLE 2

Pressures Developed by R.A.I. Separators During Sterilization at 145°C

Time (hours)	XLHDPE Acrylic Acid Graft	XLHDPE Methacrylic Acid Graft	Teflon Methacrylic Acid Graft	Teflon Sulfonated Styrene Graft	Teflon Acrylic Acid Graft
1	22	24	28	25	25
2	26	29	34	28	32
3	26	30	35	31	33
4	26	30	35	30	34
5	26	30	35	29	31
8	26	30	35	29	33
9	26	30	35	29	32
24	25	29	36	28	32
28	22	29	38	28	32
30	21	29	38	28	—
36	20	29	38	28	31
Room Temp.	0	0	0	0	0

TABLE 3

Effects of the 48 Hour Soak at 145°C. 45% KOH on Membrane Properties

Sample Composition	Resistance in 40% KOH milliohms-in^2		Exchange Capacity meg/gm		Tensile Data (Wet with 40% KOH) psi		Elongations		Dimensional Changes		Visual Changes	Changes in I.R. Curves
	Before	After	Before	After	Before	After	Before	After	Before	After		
Methacrylic Acid on TFE	40	35	2.7	2.5	2800	1100	75%	50%	3.0 x 3.0 (cm)	3.2 x 2.5 (cm)	None	No qualitative changes
Methacrylic Acid on Crosslinked High Density Polyethylene	30	40	5.8	3.5	2600	2900	40%	50%	3.0 x 4.5 (cm)	3.2 x 3.9 (cm)	Became opaque white	No qualitative change
Acrylic Acid on TFE	40	30	2.7	2.3	1250	900	50%	25%	13.0 x 3.9 (cm)	12.5 x 3.9	None	No qualitative change
Acrylic Acid on Crosslinked High Density Polyethylene	70	60	4.1	3.7	5600	5000	50%	50%	3.0 x 3.0 (cm)	3.0 x 3.0 (cm)	Became opaque white	No qualitative change
Sulfonated Styrene on TFE	60	40	1.3	0.9	2400	2000	100%	0%	3.0 x 4.0 (cm)	3.0 x 4.0 (cm)	Became very brittle	No qualitative change

TABLE 4

Results of Screening Tests on R.A.I. Membranes Before and After Sterilization
(36 Hours at 145°C. in 40% KOH)

Sample Membrane	Resistance in 40% KOH milliohms in^2 Before	After	KOH Diffusion X 10^3 moles/min.in^2 Before	After	$ZnO_2^=$ fusion X 10^6 moles/min.in^2 Before	After	Plateau Cell Voltage 9 Amp Discharge Before	After	Dendrite Growth Time to Penetrate C.D. ma/in^2 Before	After	Cycle Life Before	After
Teflon	44.1	17.6							120 min	Not enough sample	25	14
Acrylic Acid Graft	38.9	13.6	3.05	4.56	2.4	5.8	1.51	1.51	78-280 ma.			
Teflon	61	94							20 min	Not enough sample	14	7
Methacrylic Acid Graft	59	33	1.18	1.20	2.6	10.0	1.51	1.51	175-280 ma.			
Teflon Sulfonated Styrene Graft	888	828										
	7032	1441	0.33	-	1.6	110	1.45	-	-	-	-	-
Crosslinked High Density Polyethylene	85	45							none	105 min	27	45
Acrylic Acid Graft	154	407	1.13	3.96	0.78	2.2	1.41	1.45		105-280 ma.		
Crosslinked High Density Polyethylene	164	160							150 min	Not enough sample	42	46
Methacrylic Acid Graft	219	110	1.10	0.87	0.75	1.75	1.47	1.51	175-280 ma.			
Food Products F.S.C.	30.5	-	0.75	-	4.4	-	1.51	-	none	-	100	-

TABLE 5

Tensile Test Data Nylon Seals

Controls - Unsterilized Samples

$CaCl_2$-Ethanol	Phenol	Epoxy
120	226 *	104.5
144	55	80
121	405 *	77
165	279 *	248
163	353 *	139
150	250 *	95
Samples Sterilized at 145°C. for 36 Hours in 40% KOH		
167 *	180 *	0
211 *	187 *	56
174 *	270 *	74
128 *	244 *	59
129 *	136 *	52
70	140 *	70

* Material broke before seals

Data in Pounds (gage)

The nylon test strips were cut from molded cases.

The strips were 3-1/8 inches long, 1/2 inch wide, and 1/10 thick.

The seals were made by overlapping the strips 1/2 inch.

TABLE 6

Pressures Developed During Sterilization at 145°C.

Sample	PSIG Hours at 145°C. 2	4	8	24	32	36	After Return to Room Temp.
KOH + FSC	15	18	19	21	21	23	4
KOH + FSC	13	16	18	21	21	23	2
KOH + FSC	13	16	18	21	21	22	2
KOH	10	14	15	15	15	15	0
KOH	10	13	13	12	12	11	0
KOH *	10	11	11	5	4	3	0
13 Plate Cell	15	20	22	25	26	26	5
9 Plate Cell	12	17	20	24	26	27	8
9 Plate Cell	12	17	20	23	25	26	7

The electrolyte used in all samples was a 45% potassium hydroxide solution.

* This cell developed a leak in pressure fitting.

Cell Weights Before and After Sterilization

Sample	Weight Before (grams)	Weight After (grams)	Difference (grams)
KOH + FSC	292.7	291.7	-1.0
KOH + FSC	291.6	290.4	-1.2
KOH + FSC	292.4	291.3	-1.1
KOH	282.0	281.6	-0.4
KOH	284.3	283.8	-0.5
KOH	284.9	284.5	-0.4
13 Plate	572.9	566.0	-6.9
9 Plate	494.5	488.1	-6.4
9 Plate	488.5	482.3	-4.2

TABLE 7

Pressure Tests on Cell Cases - Zytel 38

Treatment Before Test; Molding Machine Size	Test Temp. °C	Burst Pressure psig	Mode of Failure
4 oz. machine	25	200	case-cover seal
	25	130	case-cover seal
	25	205	wall at corners
4 oz. machine	145	95	case-cover seal
at temp. ½ hr.	145	105	case-cover seal
annealed	145	110	case-cover seal
12 oz. machine	25	155	wall at corners
	25	202	wall at corners
	25	200	wall at corners
12 oz. machine	145	95	case-cover seal
at temp. ½ hr.	145	105	case-cover seal
annealed	145	115	case-cover seal
12 oz. machine	25	250	Did not fail
	25	100	wall at corners
	25	80	wall at corners
	25	120	wall at corners
	25	130	wall at corners
12 oz. machine	25	50	wall at corners
heat aged 36 hrs.	25	50	wall at corners
at 145°C.	25	40	wall at corners
	25	50	wall at corners
12 oz. machine	145	50	case-cover seal
heat aged 36 hrs.	145	70	case-cover seal
at 145°C.	145	170	wall at corners
	145	50	case-cover seal
	145	60	case-cover seal
	145	80	case-cover seal
	145	80	case-cover seal

TABLE 8

Tensile-Strain Data Sterilized and Unsterilized Plastics

Type of Plastic	Sterilized in 145°C 40% KOH 36 Hrs. Tensile Strength P.S.I.	Strain % Elongation	Unsterilized Tensile Strength P.S.I.	Strain % Elongation
Zytel 38	5840	5 - 10	7500	180-210
	5500	"	7450	"
	5540	"	7050	"
	5250	"	7050	"
	7000	"	7700	"
	5300	"	7260	"
	5540	"	7580	"
	6860	"	7800	"
	6900	"		
	6600	"		
	7350	"		
	6000	"		
	6160	"		
	5760	"		
	7210	"		
	6940	"		
	4960	"		
	6320	"		
	5950	"		
Zytel 121	7160	5	9650	290
	6340	10	9550	150
	6180	5		
	5800	15		
Zytel 101	7450	10	9300	210
	7450	25	9260	275
	7400	20		
Teflon	2080	375	2080	350
Penton	5740	65	5710	25
	5730	60	5720	30
	5750	40		
	5720	60		
Celcon	9000	100	9460	60
	9100	110	9370	25
	9100	75		
	9110	100		
Polypropylene	6130	100	6000	7
	5610	80	6000	10
	5780	150	6050	10
	5350	62		

All samples were tested at room temperature.

TABLE 9

CAPACITY/CYCLE AND STAND DATA FOR CELLS BUILT WITH R.A.I. SEPARATORS

Cell Nr.	Cycle/Capacity 1	2	3	4	5	6	7	8	9	10
Control Cells							10-5-64	10-20-64	1-22-65	
C1-AA	24.0	24.8	26.2x	31.0x	28.5*	on	1.83	1.58	1.57	
C2-AA	25.5	24.8	25.5x	29.6x	28.5*	stand	1.86	1.86	1.83	
C3-AA	23.7	23.7	24.5x	29.6x	27.0*	4-20-64	1.86	1.86	1.84	
Cells Sterilized at 145°C.										
AA-2	17.0	16.5	15.0							
MAA-3	11.2	13.5	13.5	12.9	16.8	13.5	13.5	14.2	14.8	16.0
Cells Sterilized at 135°C.										8-28-64
AA-4	12.6	18.0	20.9	21.0	17.5	16.8x	19.8	20.5	23.8*	1.85 short 11-16-64
-5	12.6	18.0	21.3	21.8	19.2	18.3x	22.2	25.0	28.6*	1.58 short 11-6-64
-6	12.6	16.7	19.5	16.5	15.3	16.0x	23.0	26.3	28.9*	1.58 short 10-26-64
MAA-7	12.4	15.7	20.9	16.5	15.8	16.9x	17.7	16.7 (14)	short	on stand 5-28-64
8	14.2	15.7	19.5	16.5	16.1	17.3x	21.8	21.6 (3)	short	
9	13.6	18.0	19.5	18.0	16.1	16.9x	17.5	17.7	16.6*	1.56 short 9-14-64
Presterilized Separators - 1% Palladium Alloy Positives										
AA-1P	13.5	25.4	30.8	30.0x	short(22 da)					
2P	12.0	23.2	29.1	29.7x	29.4*	27.0*	on stand short no date			
3P	12.0	23.2	28.4	29.7x	27.2*	short (7 da)				
MAA-1P	12.0	20.2	23.4	21.2x	short(10 da)					
2P	13.5	21.5	23.4	21.2x	short (2 da)					
3P	9.0	16.5	20.1	19.5x	short(12 da)					
No Viscon on the Negative Plates								overcharged &		
PSNV	13.3	13.5	12.9	13.5	11.9x	11.7*	9.1	exploded		
NSNV	9.7	10.5	10.5	10.5	9.9x	9.9*	12.5	12.4*	on stand 5-28-64	1-16-65 1.85 1-22-65 1.68
Teflon-AA	13.0	13.6	12.7	21.9	16.4	16.5	16.0	18.0	13.5	short on chg 3-23-64
XLHPDE 040P	22.2	33.3	34.5	29.7x	28.9*	short on charge				
PS P-300	14.4	21.0	25.5	short on charge						
P600 .040P	short formation charge									
PF P-600	61.5	short on charge								

x after 10 to 13-day stand * after 30-day stand

Cells were considered to be shorted when the O.C. voltage dropped to 1.50 volts.

TABLE 10

CAPACITY/CYCLE AND STAND DATA ON VARIOUS CELLS TESTED

Cycle/Capacity

Cell Nr.	1	2	3	4	5	6	7	8	9	10	11
Cells of Standard Construction Filled with Liquor from Sterilized R.A.I. Materials											
P-300L1	10.8	15.8	17.1	19.9	18.8	20.9	20.2	19.9	19.9	20.7	cells were given
P-300L2	8.2	12.9	12.7	15.7	16.8	19.2	19.0	19.9	19.9	20.4	33 cycles. No
AA-1	19.8	21.9	20.9	21.9	21.0	22.6	21.0	22.8	22.5	22.5	significant change
AA-2	7.6	13.5	15.0	17.7	18.1	19.9	18.0	19.9	20.3	20.3	in capacity and
MAA-1	5.9	11.7	14.2	16.5	17.3	19.9	17.9	18.1	18.5	20.5	removed from test
MAA-2	8.8	14.5	15.7	17.7	18.1	19.9	21.0	20.4	19.9	20.7	
Cells of Standard Construction with 1% and 2% Acrylic Acid Added to Electrolyte											
1% AA	20.8	23.0	24.7	26.0	28.6[X]	25.6*	on stand		12-3-64	1-22-64	
									1.84	1.84	
2% AA	19.2	20.2	24.2	26.0	28.4[X]	23.3*	6-22-64		1.83	short 12-16-64	
Cells With Silver Treated FSC Separators											
B3 AgB	16.5	16.5	18.9	19.5	19.5	20.5	21.8	21.9	21.9	22.8	short on 18th cycle
B3 AgF	Short on formation charge										
Yardney Cell	14.7	35.6	35.2	38.0	33.0	38.0	38.3	37.8[X]	short on overnight stand		
Cell With Positive Plate Material Doubled											
FSC .040P	43.5	42.5	short 3 days stand								
Redesigned Elements 1:1 Plate Material Ratio - 13 Plates											
PF-FSC	50.0[X]	44	48	46.5[X]	47.0	46.5	46.0	43.5	on stand 5-8-64 - short 6-7-64		
PF-Cello	59.0[X]	short on charge							9-16-64	10-20-64	12-21-64 1-22-65
FSC-PF1	49.0[X]	45.4	46.5	46.9	46.0	44.5	42.5[X]	on	1.85	1.85	1.75 1.56
FSC-PF2	49.0[X]	42.0	44.5	44.4	44.0	42.5	41.4[X]	stand	1.84	1.58 short 11-20-64	
FSC-PF3	49.0[X]	44.0	45.5	45.5	45.0	45.0	41.8[X]	6-5-64	short 6-23-64		
6% AL-1	30.3	22.2	26.6	27.2	27.0	25.6[X]	25.6*	on	1.58	1.58	1.58 short 1-12-65
6% AL-2	28.9	22.2	25.0	24.4	23.6	23.0[X]	20.8*	stand	1.85	1.85	1.84 short 1-19-65
6% AL-3	29.7	28.1	28.4	29.2	28.4	27.3[X]	25.6*	6-23-64	1.82	1.71	short 11-24-64
9 Plate Cells	1:1 Material Ratio						12-21-64	1-8-65	1-22-65		
9PF-1	48.8[X]	41.0	49.6	51.5	52.5[X]	on	1.86	1.85	1.85		
9PF-2	48.8[X]	41.0	46.5	51.0	52.5[X]	stand	1.86	1.85	1.85		
9PF-3	48.8[X]	46.6	51.5	52.0	52.5[X]	7-30-64	1.86	1.85	1.84		

TABLE 10 (CONTINUED)

CAPACITY/CYCLE AND STAND DATA ON VARIOUS CELLS TESTED

Cycle/Capacity

Cell Nr.	1	2	3	4	5	6					
13 Plates 1:1 Material Ratio High Molecular Weight FSC Separators										12-7-64	1-22-65
HMW-1PF	48.8⊗	32.8	36.0	37.6	35.6x	30.9*	short on charge				
HMW-2PF	48.8⊗	38.0	44.5	43.5	42.0x	40.6*	on stand 8-5-64			1.86	1.84
HMW-3PF	48.8⊗	40.5	44.7	44.5	42.0x	40.4*	short overnight				
HMW-4	36.8	32.0	32.2	31.0x	33.0*		on stand 8-5-64			1.85	1.84
HMW-5	37.0	34.5	36.8	34.2x	33.8*		on stand 8-5-64			1.85	1.84
HMW-6	29.0	29.4	33.0	32.2x	31.2*		short on charge				
Cells with C19-300 Separators								7-13-64	11-2-64	12-18-64	1-22-65
9Y1C	52.0	54.0	58.0	48.4x				1.86	1.86	1.86	1.85
9Y2C	50.0	54.0	57.5	48.5x	on stand			1.86	1.86	1.86	1.85
9Y3S	43.5	20.8	47.8	42.4x				1.60	1.60	1.59	1.58
9Y4S	43.5	43.5	48.7	42.0x	5-20-64			1.86	1.85	1.84	1.82
13Y1C	55.0	51.0	53.5	48.0x				1.86	1.86	1.85	1.84
13Y2C	54.0	51.0	51.7	47.0x				1.86	1.86	1.85	1.85
13Y3S	12.0	19.5	41.6	39.2x				1.86	1.86	1.85	1.84
13Y4S	24.8	27.3	31.5	25.6x				1.86	1.85	1.84	1.84
PF-13Y1S	43.0⊗	30.4	28.6	short on charge							
PF-13Y2S	43.0⊗	31.6	33.3	" " "							
SYS13	11.0	short on charge									
CYS13	22.0	29.0	35.0	34.5	36.4	35.0	- 39th cycle 26.8 short on 40th charge				

x after 10 to 30-day stand * after 30-day stand ⊗ capacities before sterilization

Cells were considered to be shorted when the O.C. voltage dropped to 1.50 volts.

TABLE 11

CONSTRUCTION DATA FOR CELLS LISTED IN TABLES 9 AND 10

Cell Group Nr.	Mat'l Ratio Neg/Pos	Nr. Plates	Separators Type	Nr. Layers	+ Plate add.	-Plate add.	- Plate Retainer	Electrolyte % KOH	Electrolyte add.	Pre-formed	Pre-sterile Comp.	Steri. Temp. °C.	Leak During Steril.
C1, 2, 3 AA	2:1	13	AA	4	None	1% Hg	Viscon	40	No	No	No	No	No
C1, 2, 3 MAA	2:1	13	MAA	4	N	1% Hg	Viscon	40	No	No	No	No	No
AA-2	2:1	13	AA	4	N	1% Hg	Viscon	40	No	No	No	145	No
MAA-3	2:1	13	MAA	4	N	1% Hg	Viscon	40	No	No	No	145	No
AA 4, 5, 6	2:1	13	AA	4	N	1% Hg	Viscon	40	No	No	No	135	No
MAA 7, 8, 9	2:1	13	MAA	4	N	1% Hg	Viscon	40	No	No	No	135	No
AA-1P, 2P, 3P	2:1	13	AA	4	1% Pd	4% Hg	AA	50	No	No	Sep	145	No
MAA-1P,2P,3P	2:1	13	MAA	4	1% Pd	4% Hg	MAA	50	No	No	Sep	145	No
PSNV	2:1	13	AA & MAA	4	N	1% Hg	AA or MAA	50	No	No	Sep	145	No
NSNV	2:1	13	AA & MAA	4	N	1% Hg	AA or MAA	50	No	No	No	145	No
Teflon AA	2:1	13	Teflon AA	4	1% Pd	4% Hg	Teflon AA	50	No	No	No	145	No
*PS P-300	2:1	13	P-300	4	1% Pd	4% Hg	P-300	50	No	No	Sep	145	No
B 3 AgB	2:1	13	B3 AgB	2	N	1% Hg	Vis	45	No	No	No	145	Yes
B 3 AgF	2:1	13	B3 AgF	2	N	1% Hg	Vis	45	No	No	No	145	Yes
*XLHDPE .040P	1:1.6	13	AA & MAA	4	N	4% Hg	AA	50	No	No	Sep	145	?
FSC .040P	1:1.6	13	FSC	2	N	1% Hg	Vis	45	No	No	No	145	?
P600 .040P	1:1.6	13	P-600	3	N	1% Hg	Vis	45	No	No	No	145	?
PF FSC	1:1	13	FSC	2	N	1% Hg	Vis	45	No	Yes	No	145	Yes
PF Cello	1:1	15	Cellophane	3	N	1% Hg	Vis	45	No	Yes	No	145	Yes
PF P-600	1:1	15	P-600	3	N	1% Hg	Vis	45	No	Yes	No	145	Yes
FSC-PF 1,2,3	1:1	13	FSC	3	N	1% Hg	Vis	45	No	Yes	No	145 (44 hr)	Yes
6% AL 1,2,3	1:1	13	FSC	3	N	1% Hg	Vis	45	Al	No	No	145	No

TABLE 11 (CONTINUED)

CONSTRUCTION DATA FOR CELLS LISTED IN TABLES 9 AND 10

Cell Group Nr.	Mat'l Ratio Neg/Pos	Nr. Plates	Separators Type	Nr.Layers	+Plate add.	-Plate add.	- Plate Retainer	Electrolyte % KOH	add.	Pre-formed	Pre-sterile Comp.	Steril. Temp. °C.	Leak During Steril.
9PF 1,2,3	1:1	9	FSC	3	N	1% Hg	Vis	45	No	Yes	No	145	?
HMW 1,2,3 PF	1:1	13	HMW FSC	3	N	1% Hg	Vis	45	No	Yes	No	145	Yes
HMW 4,5,6	1:1	13	HMW FSC	3	N	1% Hg	Vis	45	No	No	No	145	Yes
PF 13Y-1, 2	2:1	13	C19-300	7	N	1% Hg	Vis	45	No	Yes	No	145 (44 hrs)	Yes
SYS13	2:1	13	C19-300	7	N	1% Hg	Vis	45	No	No	No	145	Yes
CYS13	2:1	13	C19-300	7	N	1% Hg	Vis	45	No	No	No	No	No
9Y 1C, 2C	1:1	9	C19-300	7	N	1% Hg	Vis	45	No	No	No	No	-
9Y 3S, 4S	1:1	9	C19-300	7	N	1% Hg	Vis	45	No	No	No	145	Yes
13Y 1C, 2C	1:1	13	C19-300	7	N	1% Hg	Vis	45	No	No	No	No	-
13Y 3S, 4S	1:1	13	C19-300	7	N	1% Hg	Vis	45	No	No	No	145	Yes
The following cells had electrolyte containing degradation products from sterilization													
P-300 L1 & 2	2:1	13	FSC & Dynel	3 & 1	N	2% PVA 1% Hg	Vis	45	P-300	No	Electro	No	-
AA 1 & 2	2:1	13	FSC & Dynel	3 & 1	N	"	Vis	45	AA	No	"	No	-
MAA 1 & 2	2:1	13	FSC & Dynel	3 & 1	N	"	Vis	45	MAA	No	"	No	-
1% AA	2:1	13	FSC & Dynel	3 & 1	N	"	Vis	45	1% AA	No	No	No	-
2% AA	2:1	13	FSC & Dynel	3 & 1	N	"	Vis	45	2% AA	No	No	No	-

TABLE 12

Capacities of Primary Cells

Controls		Sterilized at 145°C. for 36 Hours		Sterilized at 135°C. for 36 Hours	
Cell Nr.	Cap. a.h.	Cell Nr.	Cap. a.h.	Cell Nr.	Cap. a.h.
C-1	10.8	145-1	6.8	135-1	7.1
C-2	11.2	145-2	6.3	135-2	7.3
C-3	11.2	145-3	5.8	135-3	7.2
C-4	11.1	145-4	6.1	135-4	shorted
C-5	11.1	145-5	6.5	135-5	7.1
C-6	11.1	145-6	6.3	135-6	7.1
Avg. Cap.	11.1		6.2		7.1
% Loss of Capacity			44		36

The cells were discharged at ten amperes to 1.30 volts at room temperature.

Cells filled with 40% KOH after being sterilized dry, unsealed.

TABLE 13

CELL CONSTRUCTION DATA FOR PLATE THICKNESS STUDY

Cell Nr.	Negative Plates Nr/Cell	Negative Plates Thick. inch	Positive Plates Nr/Cell	Positive Plates Thick. inch	Theoretical Capacity a.h.	Electrolyte mm of 45% KOH	Cell Weight lbs	Element[2] Thick. inch	Element[3] Volume inch^3	Element[4] Weight lbs.
13 FSC-1	7	.048	6	.030	70	75	1.26	.700	9.64	.97
2	7	.048	6	.030	70	75	1.26	.700		
3	7	.048	6	.030	70	75	1.28	.700		
9 FSC-1	5	.068	4	.050	81	70	1.31	.650	8.95	1.02
2	5	.068	4	.050	81	70	1.31	.650		
3	5	.068	4	.050	81	70	1.31	.650		
7 FSC-1	4	.100	3	.073	110	60	1.50	.735	10.1	1.20
2	4	.100	3	.073	110	60	1.50	.735		
3	4	.100	3	.073	82	60	1.38	.735		
5 FSC-1[1]	3	.095	2	.087	80	50	1.27	.530	7.27	0.86
2	3	.095	2	.087	80	50	1.24	.530		
3	3	.095	2	.087	80	50	1.25	.530		

1. The five plate cells contained a .180" shim in the case. Its weight and volume were 41 gm + 2.5 in^3.

2. Element thickness measured dry under a compression of 12.8 lbs.

3. The volume necessary to encase the element allowing 1 inch separator overhang at tops and 0.25 inch clearance on sides.

4. Element weight obtained by subtracting case weight (134 gm) from cell weight.

TABLE 14

PLATE THICKNESS STUDY

Description of Charge and Discharge Variables by Cycle and Cell Failure

Cycle	Days	Charge (at 75°F unless noted)	Discharge Rate and Temp.	
1	1	1.5 Amp to 2.1 v.	9 Amp to 1.3 v.	75°F
2	6	2 Amp to 2.1 v.	9 Amp to 1.3 v.	75°F
3	13	2 Amp to 2.1 v; 1 Amp to 2.1 v.	9 Amp to 1.3 v.	75°F
4	16	1.5 Amp to 2.1 v; 1 Amp to 2.1 v; 0.5 Amp to 2.1 v.	9 Amp to 1.3 v.	75°F
5	26	100°F.; 1 Amp to 2.1 v; 0.5 Amp to 2.1 v.	9 Amp to 1.3 v.	75°F
6	34	1 Amp to 2.1 v; 0.5 Amp to 2.1 v.	50 Amp to 0.9 v.	75°F
7	43	1 Amp to 2.1 v; 0.5 Amp to 2.1 v.	25 Amp to 1.1 v.	75°F
8	48	1 Amp to 2.1 v; 0.5 Amp to 2.1 v.	5 Amp to 1.3 v.	75°F
9	55	1 Amp to 2.1 v; 0.5 Amp to 2.1 v.	50 Amp to 0.9 v.	75°F
10	63	1 Amp to 2.1 v; 0.5 Amp to 2.1 v.	50 Amp to 0.9 v.	100°F
11	69	1 Amp to 2.1 v; 0.5 Amp to 2.1 v.	9 Amp to 0.9 v.	30°F
12	77	1 Amp to 2.1 v; 0.5 Amp to 2.1 v.	2 Amp to 1.3 v.	75°F
13	83	1 Amp to 2.1 v; 0.5 Amp to 2.1 v.	2 Amp to 1.3 v.	75°F
14	91	1 Amp to 2.1 v; 0.5 Amp to 2.1 v.	50 Amp to 0.9 v.	30°F
15	106	1 Amp to 2.1 v; 0.5 Amp to 2.1 v.	2 Amp to 1.3 v.	30°F
16	114	1 Amp to 2.1 v; 0.5 Amp to 2.1 v.	5 Amp to 1.3 v.	100°F
17	125	1 Amp to 2.1 v; 0.5 Amp to 2.1 v.	2 Amp to 1.3 v.	100°F
18	140	1 Amp to 2.1 v; 0.5 Amp to 2.1 v.	15 Amp to 1.3 v.	75°F
19	147	1 Amp to 2.1 v.	10 Amp to 1.3 v.	75°F
20	152	1 Amp to 2.2-2.3 v; overcharged	15 Amp to 1.3 v.	75°F
21	156	1 Amp to 2.1 v.	15 Amp to 1.3 v.	75°F
22	163	1 Amp to 2.1 v.	15 Amp to 1.3 v.	75°F
23	236	Cycle 34 (same charge and discharge as Cycle 22)		

Cell Failures

5 Plate Cells #3 shorted 12th chg. #1 shorted 21st chg. #2 shorted 22 chg.
7 Plate Cells #1, 2 shorted 16th chg. #3 shorted 26th chg.
9 Plate Cells #2 shorted 14th chg. #3 shorted 18th chg. #1 shorted 26th chg.
13 Plate Cells #2 shorted 29th chg. #1 shorted 30th chg. #3 shorted after 34th chg.

TABLE 15

PLATE THICKNESS STUDY

Charge and Discharge Capacities by Cycle

Cycle	13 Plate Cells			9 Plate Cells			7 Plate Cells			5 Plate Cells		
	Charge a.h. in	Dischg. a.h. out	Matl Util.	Charge a.h.in	Dischg. a.h.out	Matl Util.	Charge a.h.in	Dischg. a.h.out	Matl Util.	Charge a.h.in	Dischg. a.h.out	Matl Util.
1	51	46	67%	53.0	46	57%	59	53	48%	42.0	37	46%
2	49	46	67	44	43	53	50	49	46	44	41	51
3	53	50	71	53	50	62	60	58	53	46	43	54
4	54	50	71	54	46	57	69	59	54	49	43	54
5	56	50	71	59	51	63	74	54	49	56	45	56
6	52	42	60	50	46	57	50	41	37	47	34	42
7	43	42	61	46	42	52	43	43	39	34	35	44
8	46	45	64	52	54	67	47	60	55	50	48	60
9	49	42	60	62	47	58	65	39	35	52	32	40
10	42	39	56	46	44	54	36	38	35	30	28	35
11	41	41	59	47	50	62	41	42	38	31	34	42
*												
13	48	45	64	59	58	72	64	62	56	52	48	60
14	47	27	39	60	41	51	68	34	31	53	29	36
15	33	40	57	44	50	62	40	53	48	33	37	46
16	42	42	60	52	55	68	55	55	50	39	43	54
17	43	44	63	57	53	65	56	58	53	44	49	61

* Twelfth cycle omitted because end of discharge was missed.

TABLE 16

CELL DATA PLATE THICKNESS STUDY

		75°F.					100°F.			30°F		
	Rate Amps	2	5	9	25	50	2	5	50	2	9	50
13 Plates	Cap. a.h.	45.	44.5	48	42.4	42.5	44	42	39.2	40	41	27
	Plateau v.	1.55	1.54	1.53	1.48	1.43	1.55	1.54	1.44	1.53	1.43	1.34
	Watts	3.12	7.7	13.8	37.0	71.5	3.10	7.70	72.0	3.06	12.78	67.0
	Wt. hrs.	69.8	68.5	73.5	62.7	60.8	68.2	64.7	56.5	61.2	58.6	36.2
	Wt hrs/lb *	72.0	70.6	75.8	64.6	62.7	70.3	66.7	58.2	63.1	60.4	37.3
	Wt hrs/in^3***	7.24	7.11	7.63	6.52	6.31	7.7	6.71	5.86	6.35	6.08	3.76
9 Plates	Cap. a.h.	57.1	54	47	42.4	46.4	53	55	44.1	50	50	41
	Plat. volt.	1.54	1.52	1.51	1.42	1.36	1.53	1.51	1.33	1.49	1.33	1.23
	Watts	3.08	7.6	13.2	35.3	68.0	3.06	7.55	66.5	2.98	10.98	61.5
	Wt. hrs.	88.0	82.0	71.0	60.2	63.1	81.1	83	58.6	74.5	66.5	50.5
	Wt hrs/lb *	86.3	80.4	69.6	59.0	61.9	79.5	81.4	57.5	73.0	65.2	49.5
	Wt hrs/in^3***	9.83	9.16	7.93	6.73	7.05	9.06	9.09	6.55	8.32	7.43	5.64
7 Plates	Cap. a.h.	61.0	59.5	55	43	41	58 **	55* *	37.5	53	42	34
	Plat. volt.	1.53	1.51	1.48	1.40	1.28	1.52	1.50	1.29	1.51	1.29	1.16
	Watts	3.06	7.55	13.3	35.0	64.7	3.04	7.50	64.50	3.02	11.61	58.0
	Wt.hrs.	93.4	89.9	81.5	60.9	52.5	88.1	82.5	48.4	80.0	54.2	39.4
	Wt hrs/lb *	77.8	74.9	67.9	50.7	43.7	80.9	75.6	40.3	66.6	45.1	32.8
	Wt hrs/in^3***	9.25	8.90	8.07	6.03	5.20	8.72	8.17	4.79	7.92	5.37	3.90
5 Plates	Cap. a.h.	49	47.5	43	35.1	34.2	49	43	28.3	37	34	29
	Plat. volt.	1.52	1.48	1.44	1.32	1.20	1.50	1.48	1.19	1.42	1.19	.89
	Watts	3.04	7.37	12.9	33	60.0	3.00	7.40	59.5	2.84	10.71	44.5
	Wt. hrs.	74.5	70.4	61.9	46.4	41.0	73.5	63.6	33.7	52.5	40.5	25.8
	Wt hrs/lb *	86.9	81.9	72.0	53.9	47.7	85.5	79.0	39.2	61.0	47.1	30.0
	Wt hrs/in^3***	10.2	9.66	8.49	6.36	5.62	10.08	8.72	4.62	7.20	5.56	3.54

* Elem. weight + electrolyte weight - does not include case weight.

** These two rates based on only Cell 7FSC-3 since the other two cells failed. All of the other data are based on averages of Cells 7FSC-1 and 2.

*** Volume necessary to enclose the element

FIGURE 1

Stainless Steel Sterilization Container

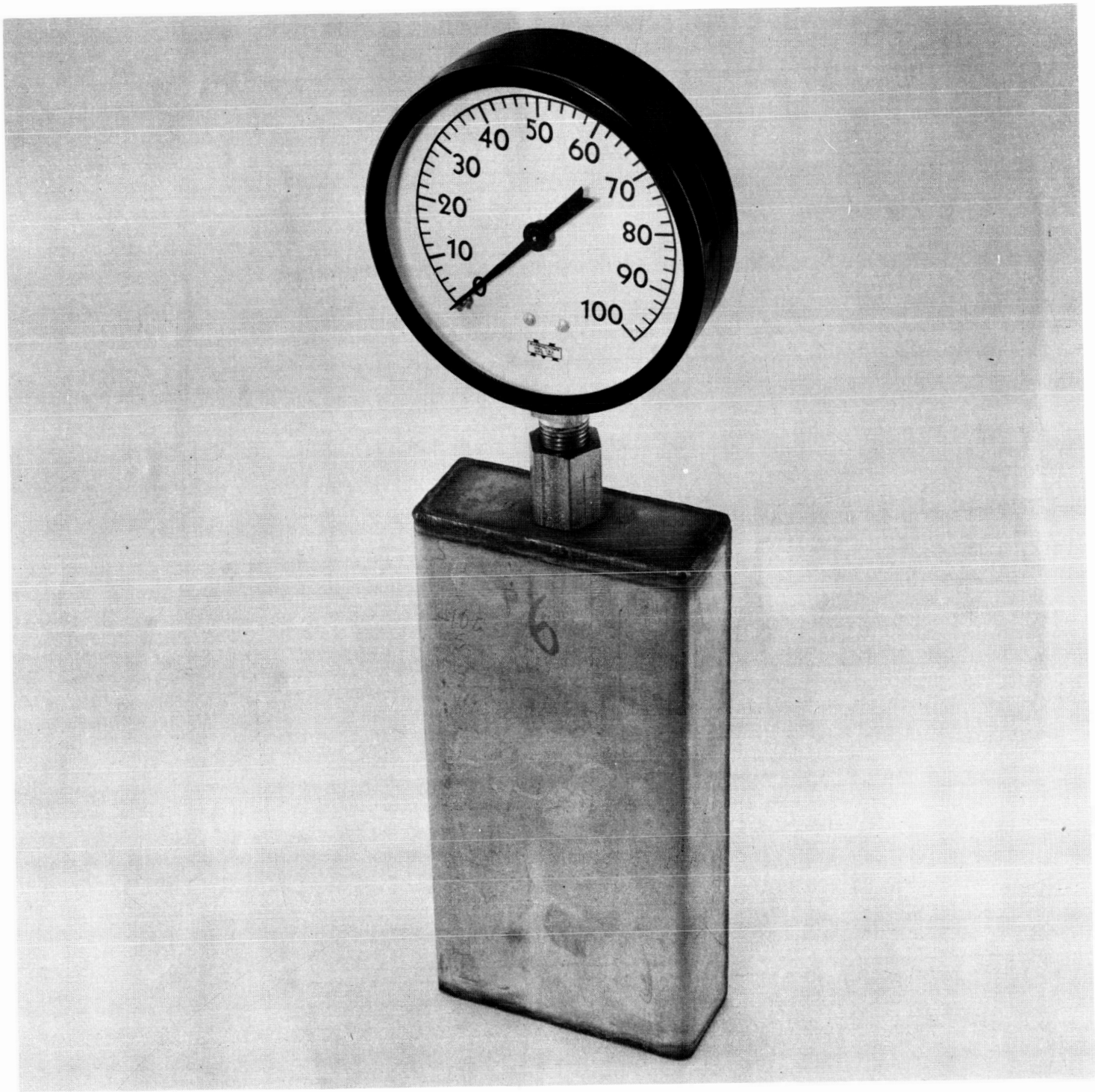


FIGURE 2

Capacity vs. Cycle - Cell Component Evaluation

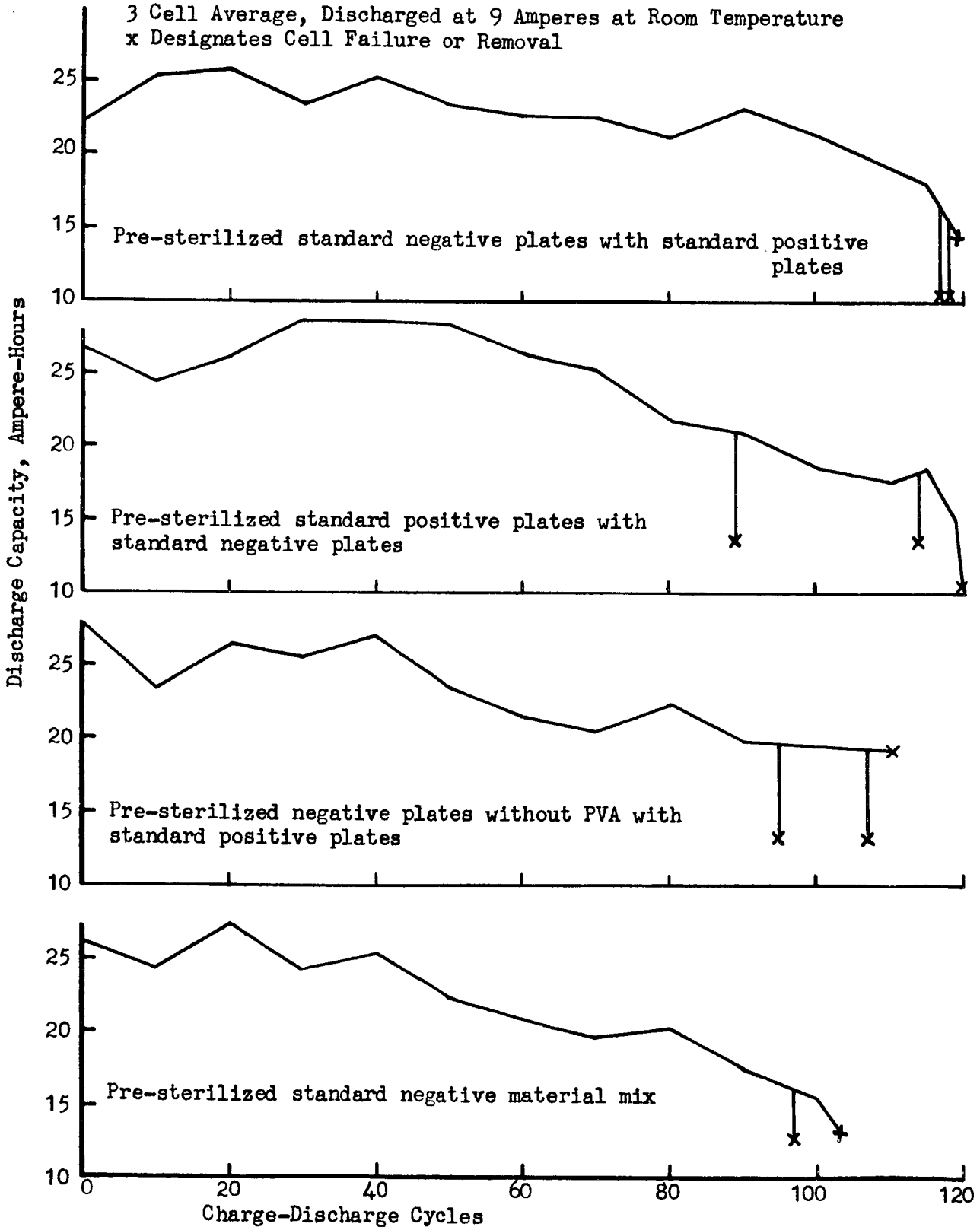


FIGURE 3

Capacity vs. Cycle - Cell Component Evaluation

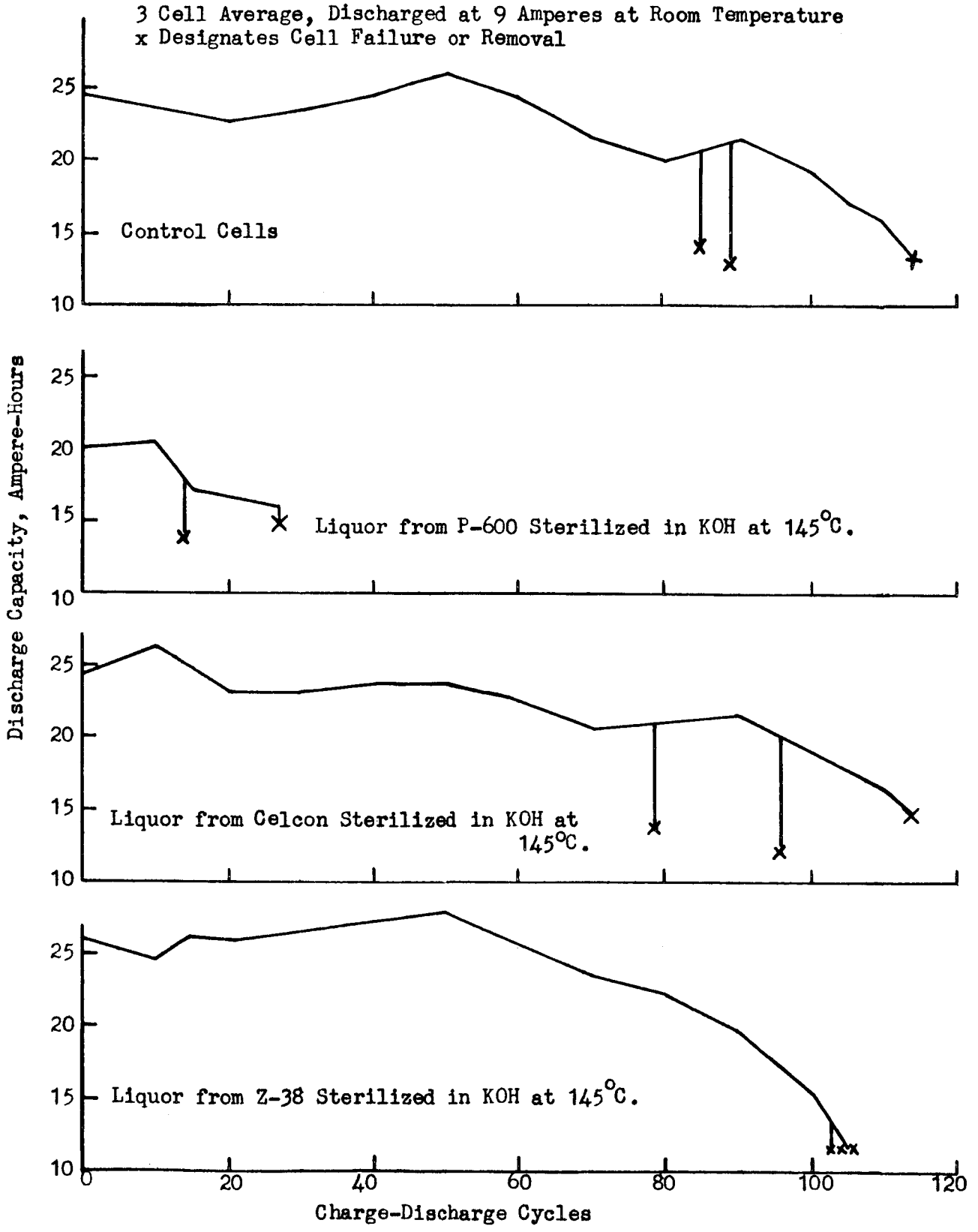


FIGURE 4

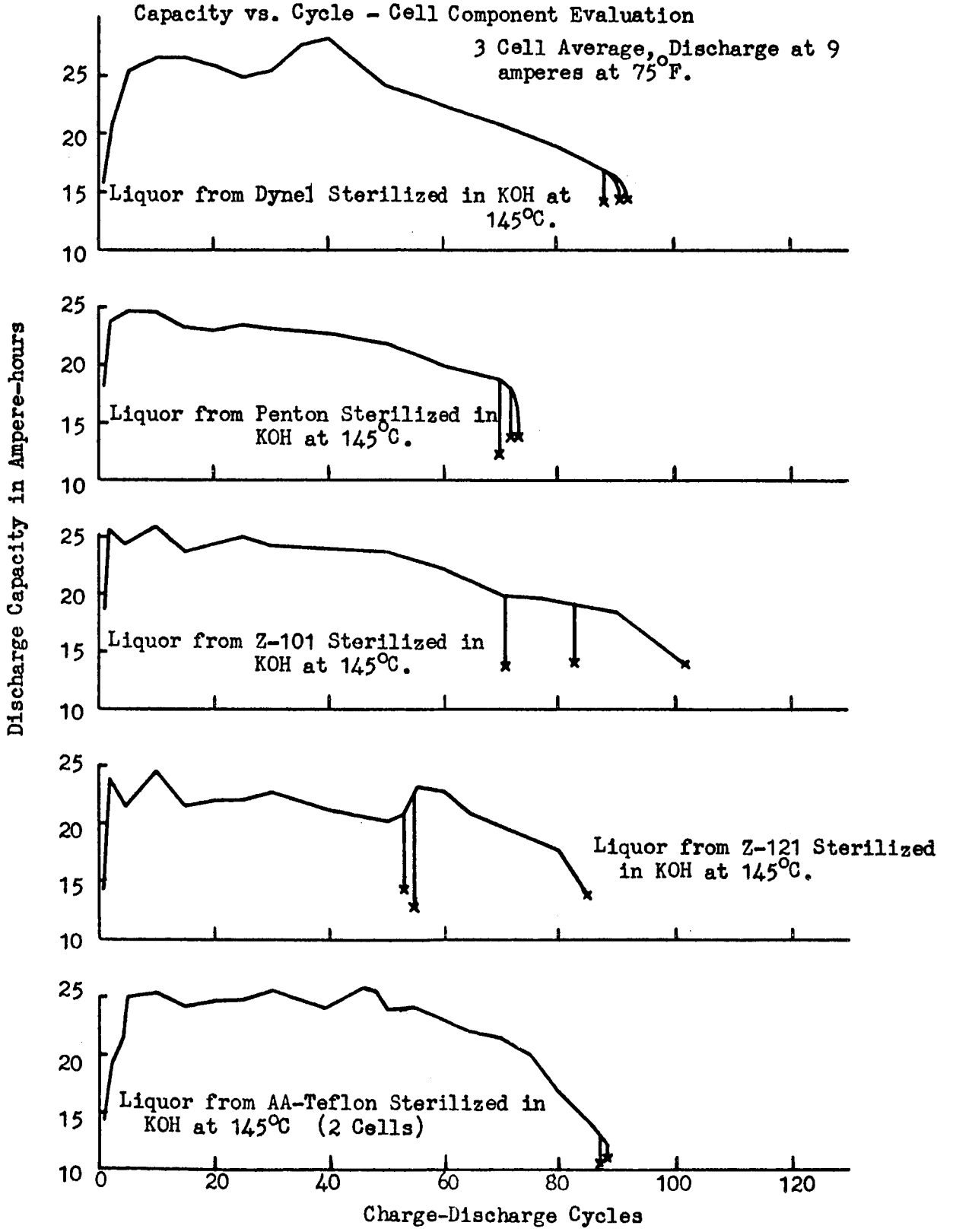

Capacity vs. Cycle - Cell Component Evaluation
3 Cell Average, Discharge at 9 amperes at 75°F.
Liquor from Dynel Sterilized in KOH at 145°C.
Liquor from Penton Sterilized in KOH at 145°C.
Liquor from Z-101 Sterilized in KOH at 145°C.
Liquor from Z-121 Sterilized in KOH at 145°C.
Liquor from AA-Teflon Sterilized in KOH at 145°C (2 Cells)
Discharge Capacity in Ampere-hours
Charge-Discharge Cycles
25
20
15
10
0
20
40
60
80
100
120

FIGURE 5

Typical Discharge Curves at 9 Amperes at Room Temperature

Each Curve is Average of 3 Cells

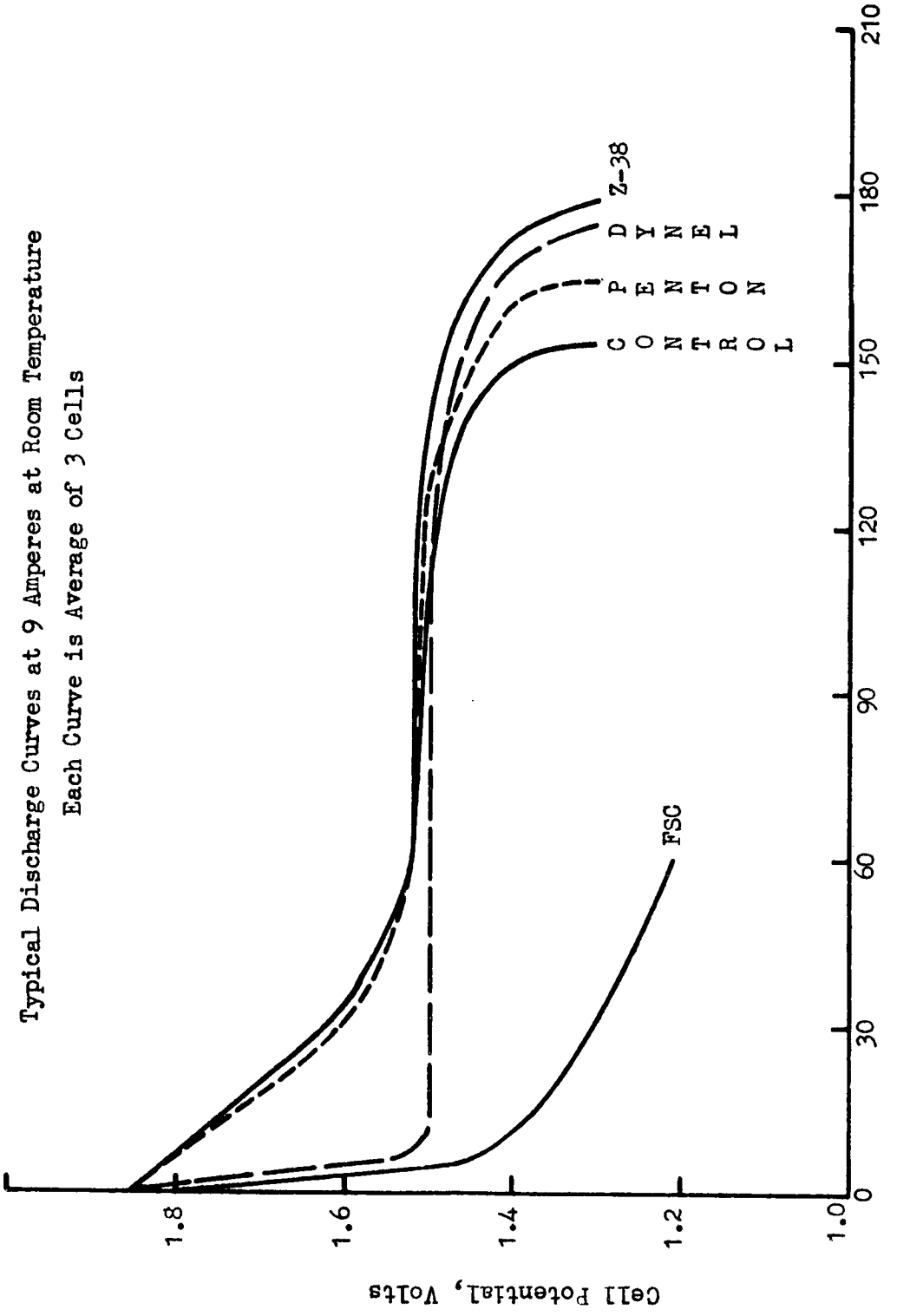


FIGURE 6

Discharge Curves of Cells Built with R.A.I. Separators Discharged at 9 Amperes at Room Temperature

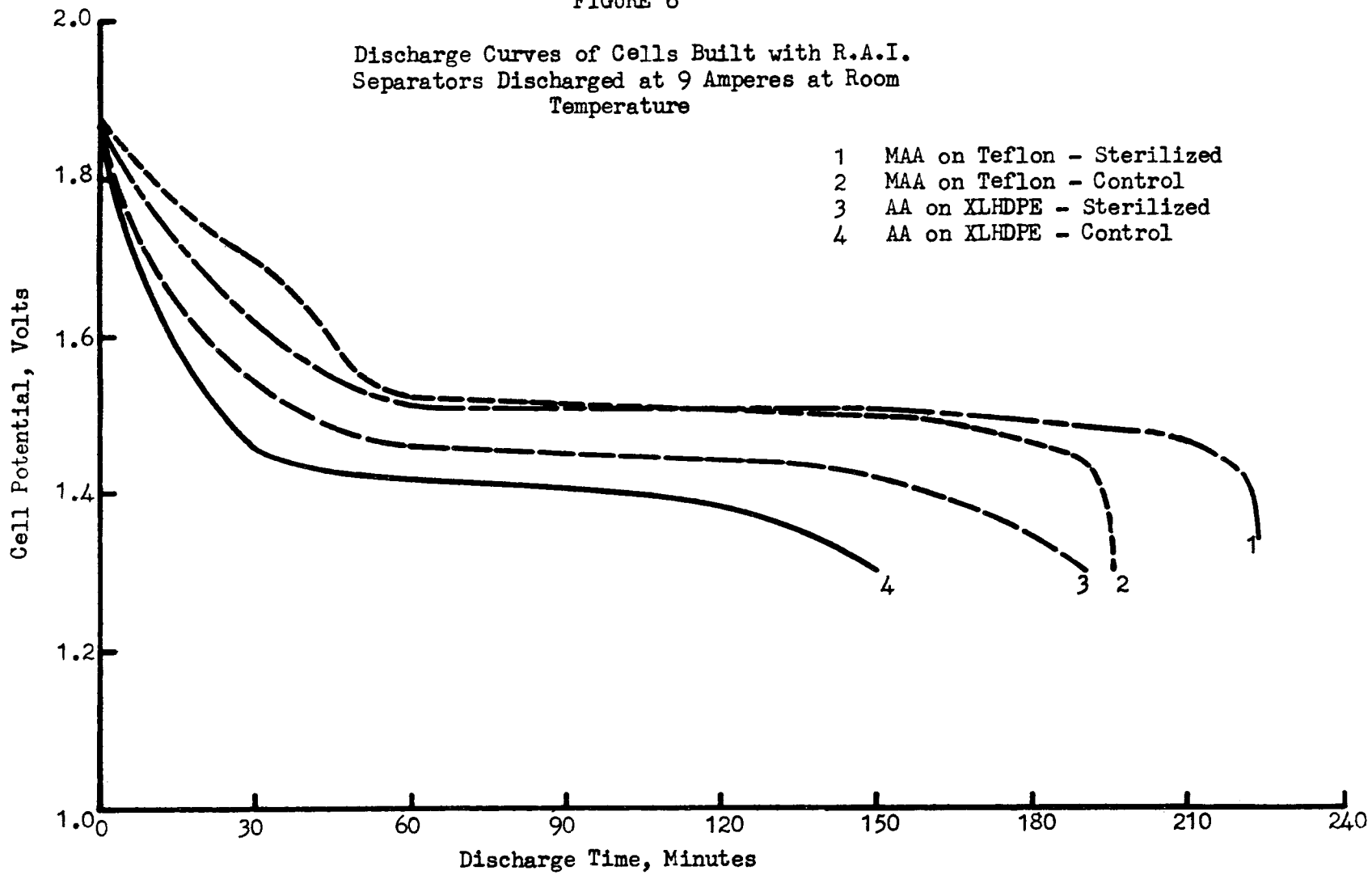


FIGURE 7

Discharge Curves of Cells Built with R.A.I. Separators
Discharged at 9 Amperes at Room Temperature

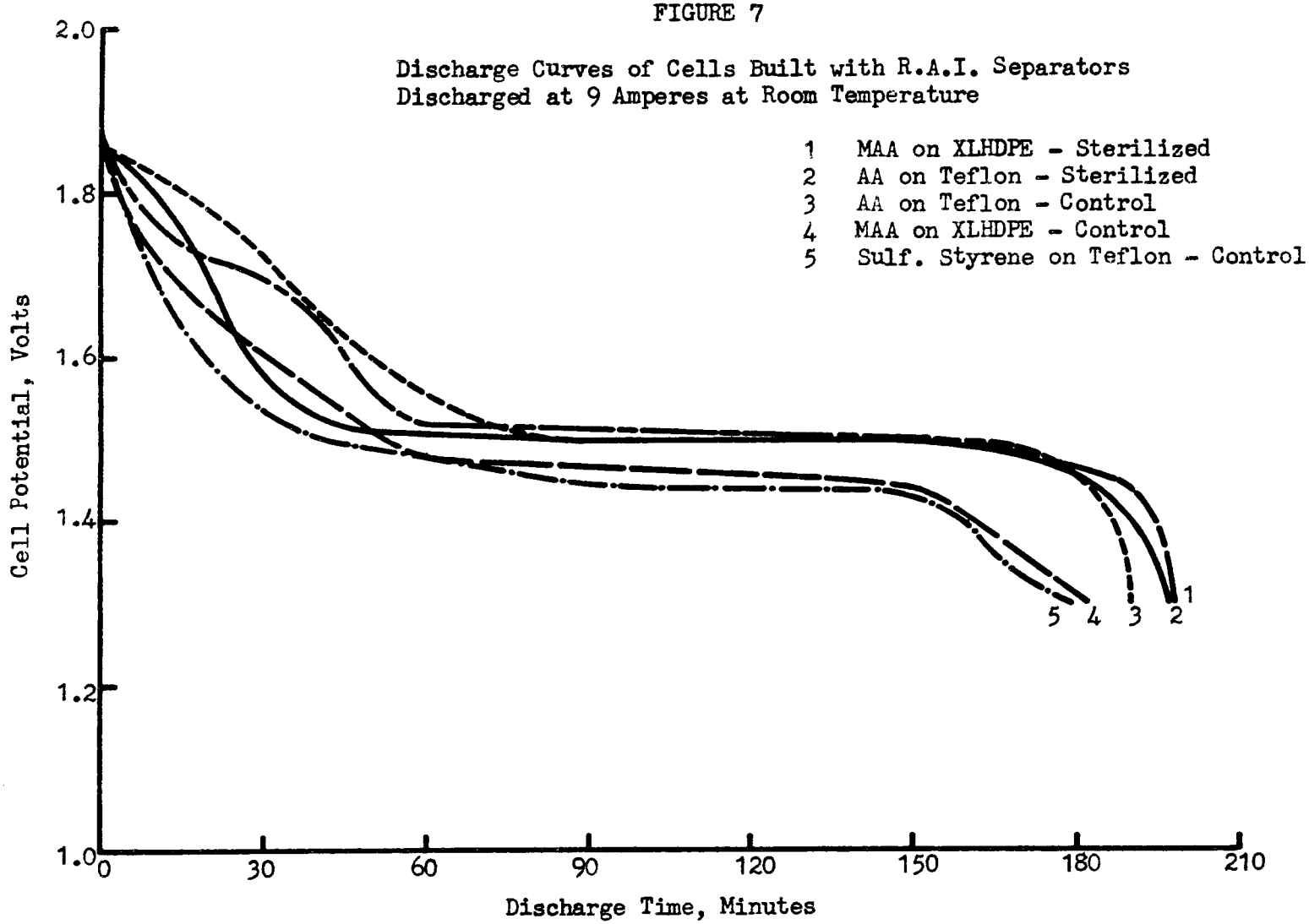


FIGURE 8

Capacity vs. Cycle - R.A.I. Separator
Material Discharged at 9 Amperes

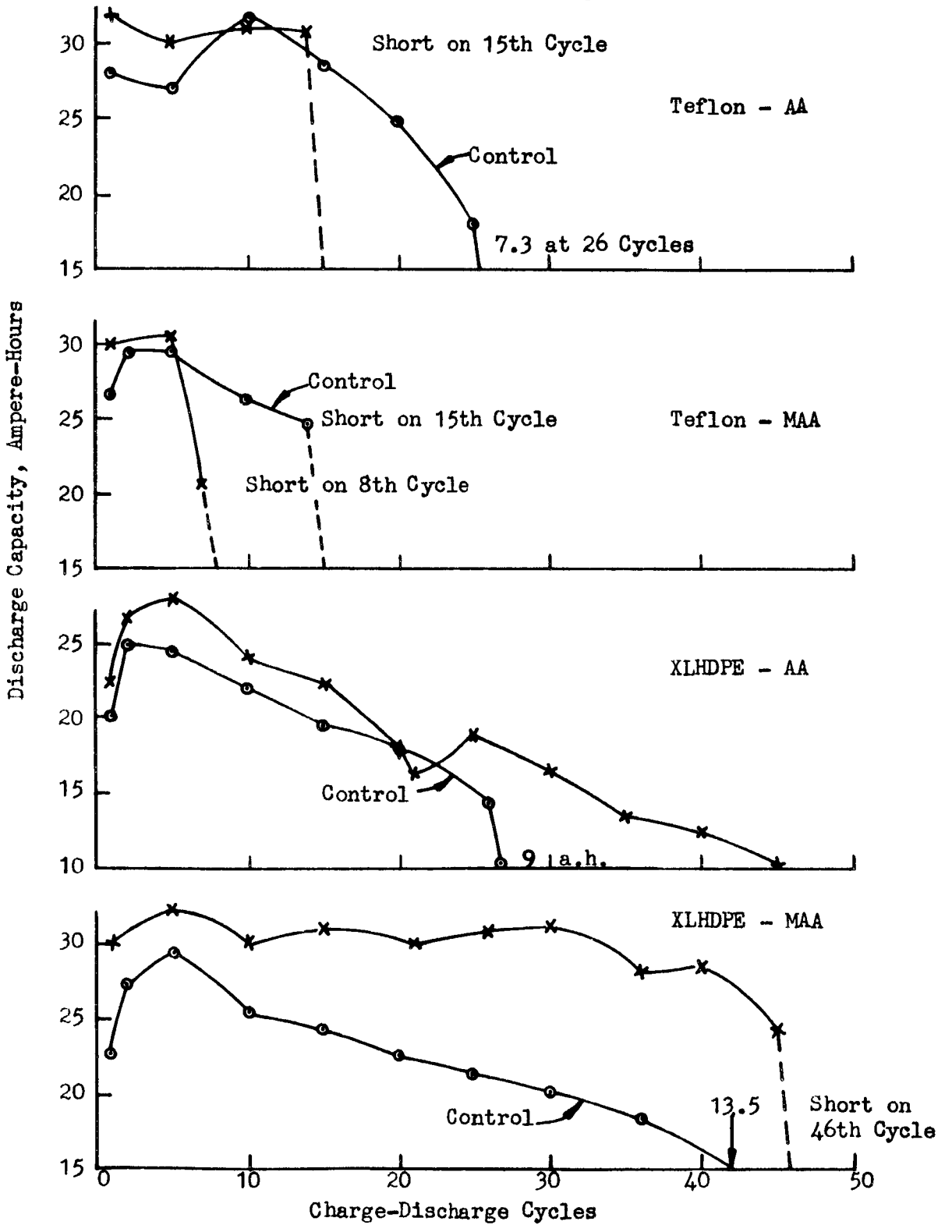


FIGURE 9

Picture Interior of Zytel 101 Case After Sterilization

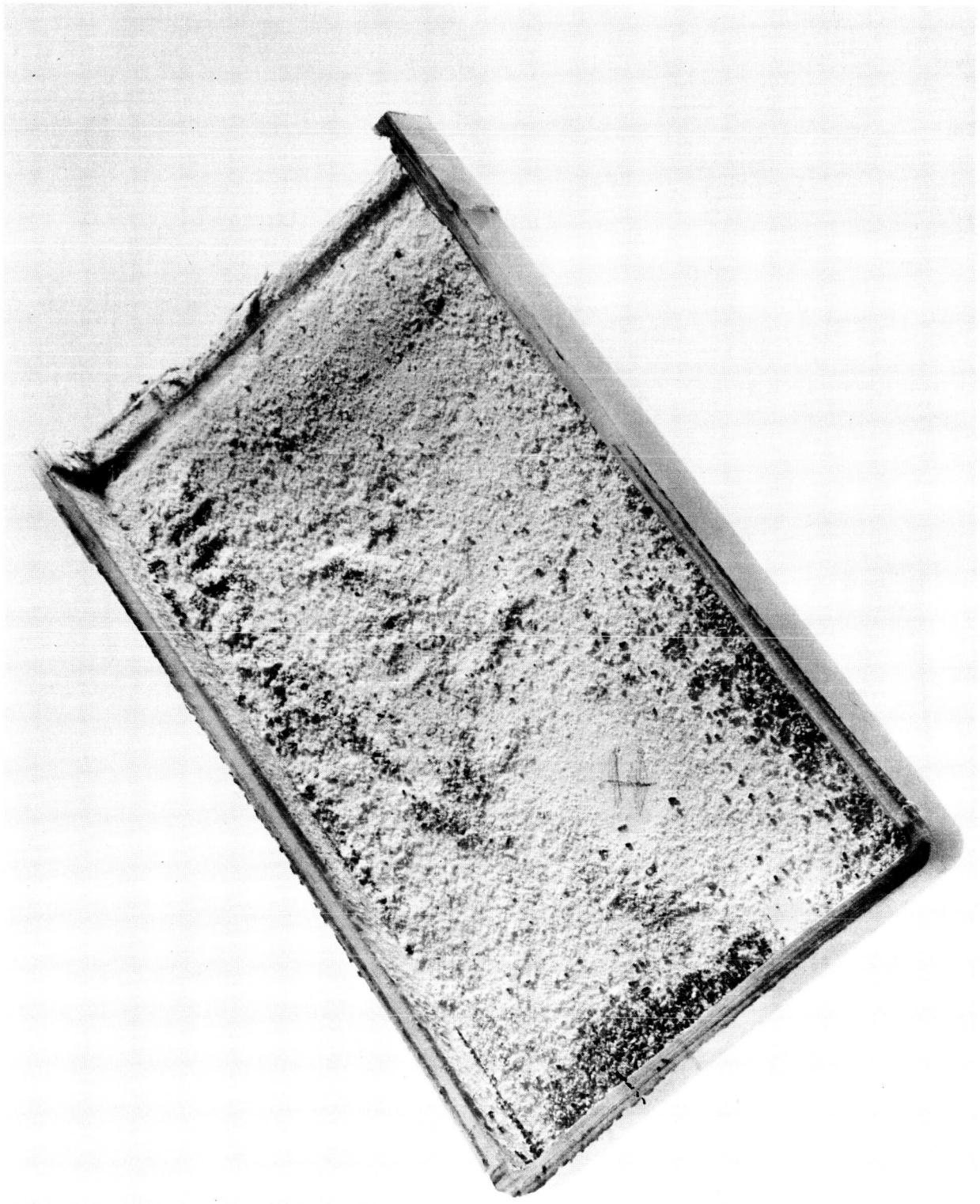


FIGURE 10

Nylon Test Bars Showing Attack of 40% KOH at 145°C for 36 Hours

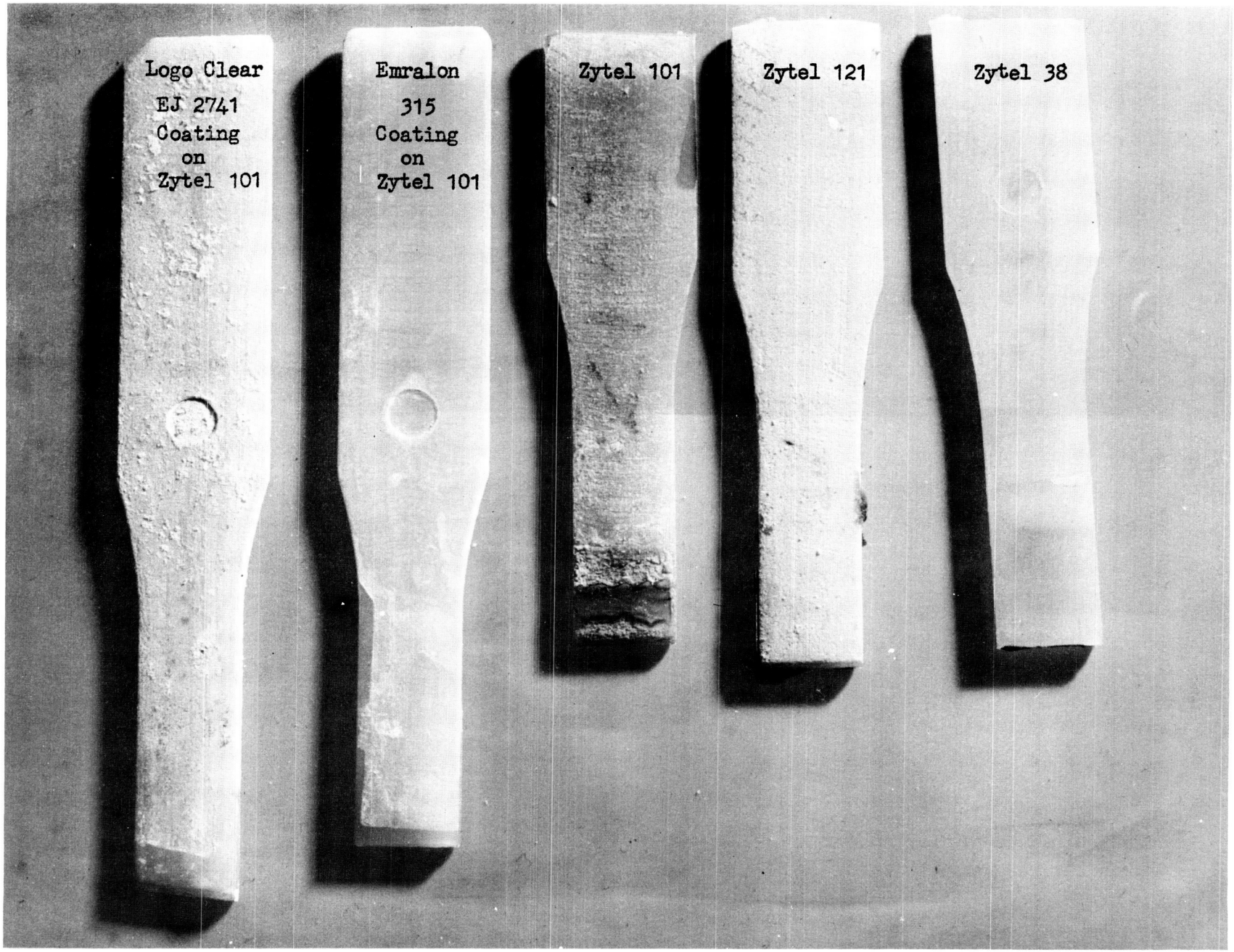


FIGURE 11

Performance of Standard Cells Activated with Liquor from Separators Sterilized at 135°C. Discharge Rate 9 Amperes

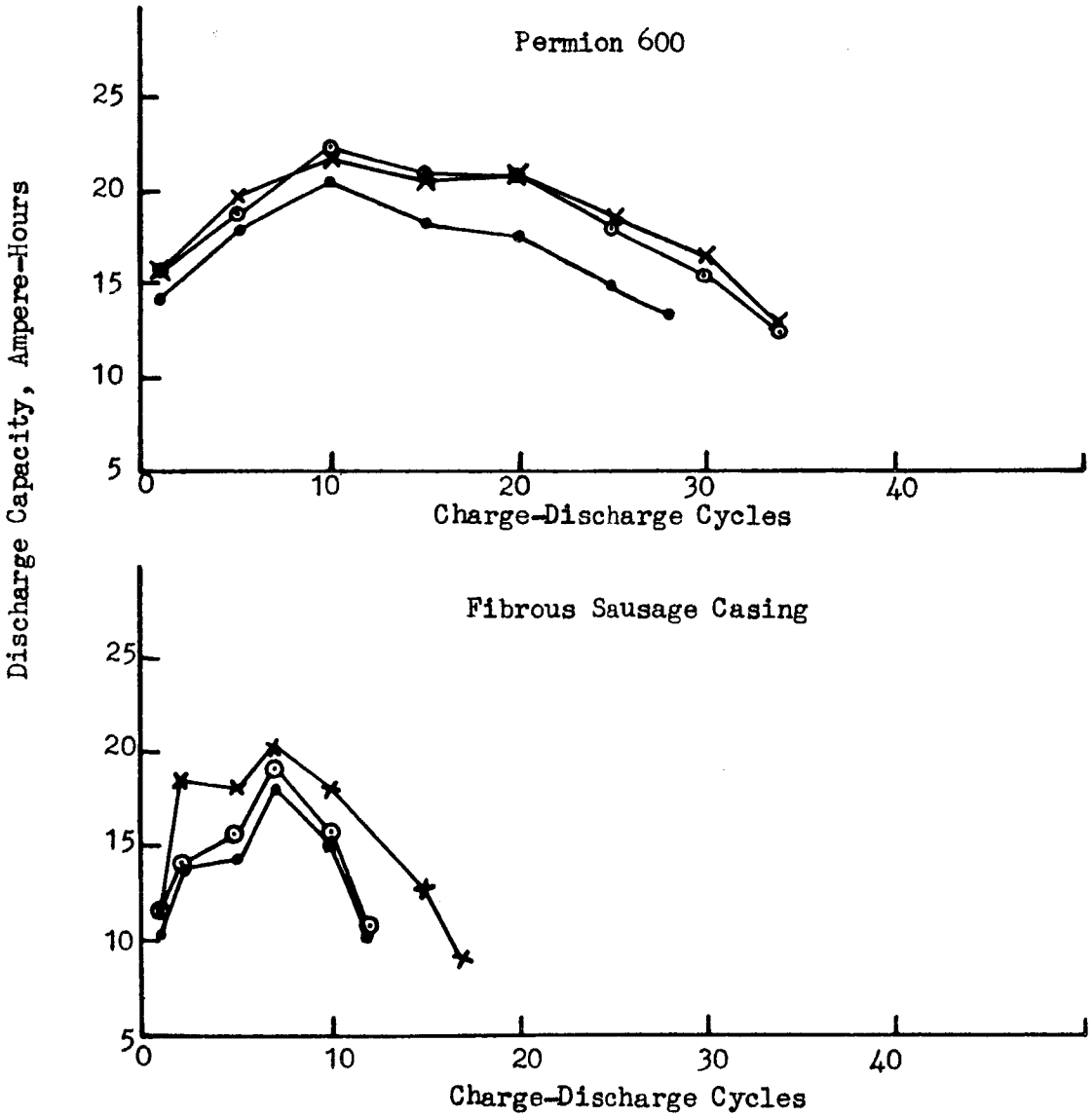


FIGURE 12

Discharge Curves of Standard Cells Filled with Liquor from Fibrous Sausage Casing Sterilized at 145°C. and 135°C.

Data for Each Curve is the Average of 3 Cells Discharged at 9 Amperes at Room Temperature

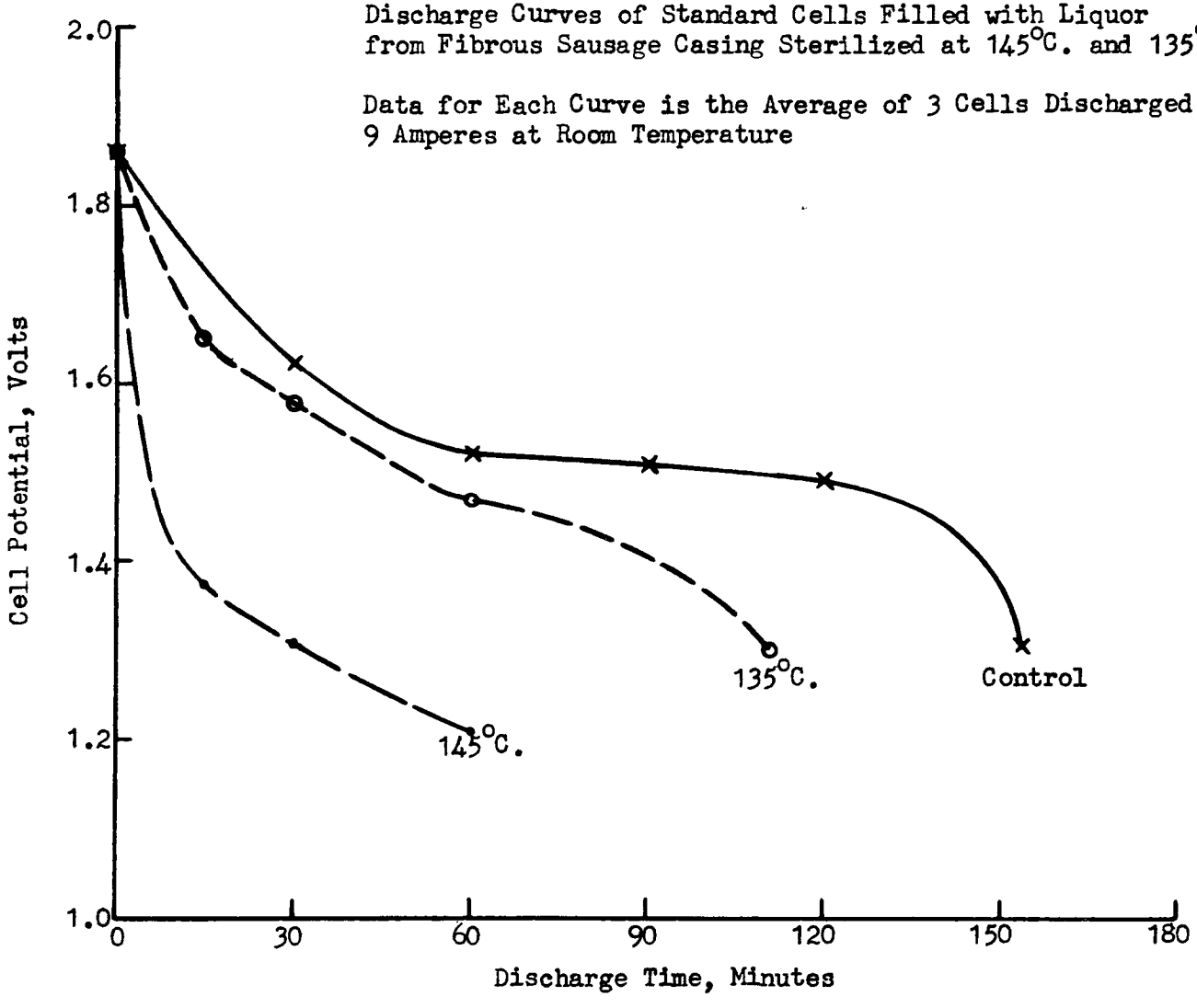


FIGURE 13

Test Cup and Holding Fixture

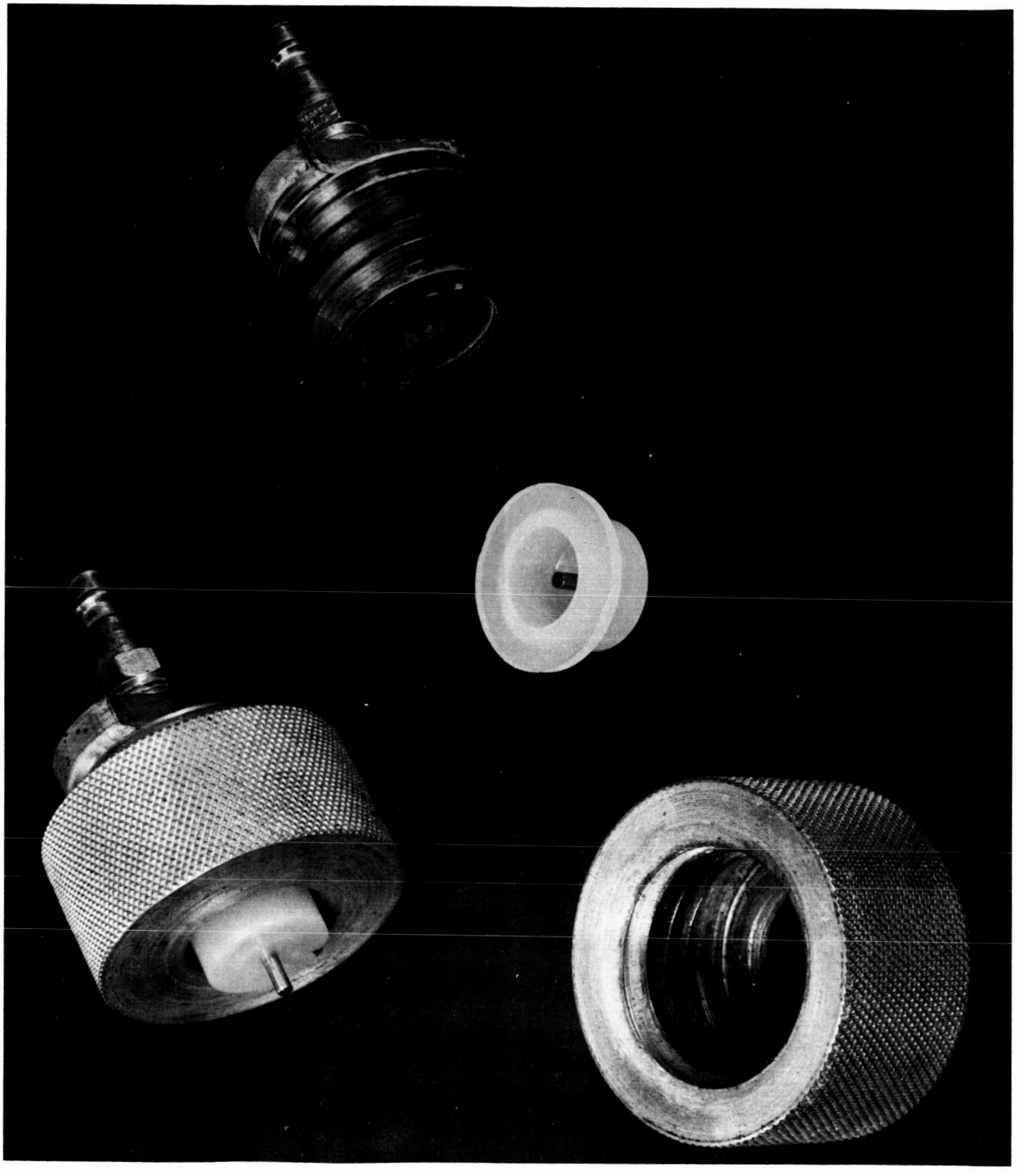


FIGURE 14

Apparatus For Terminal-to-Cover Seal Evaluation

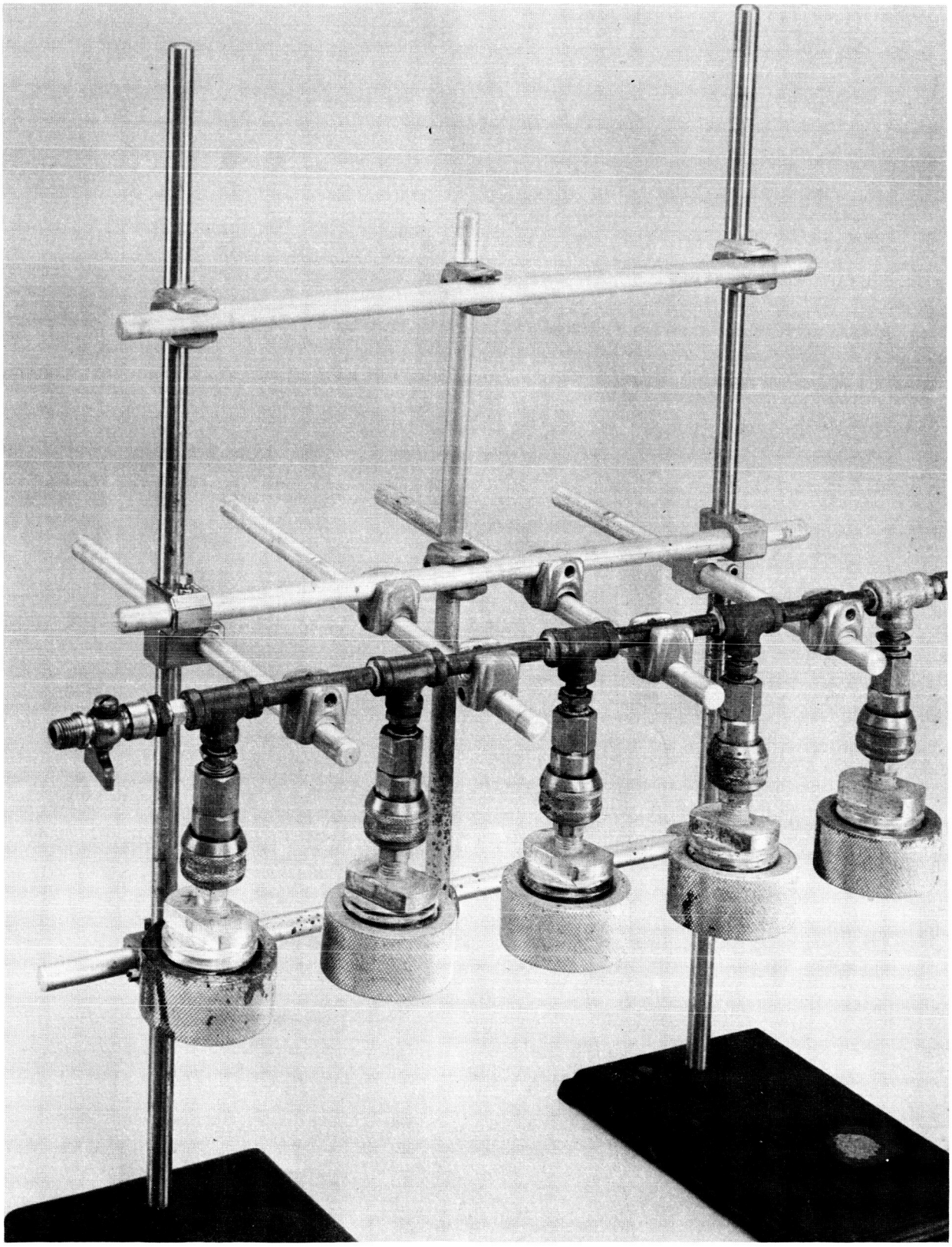
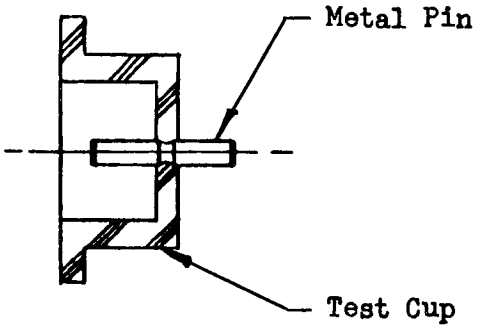
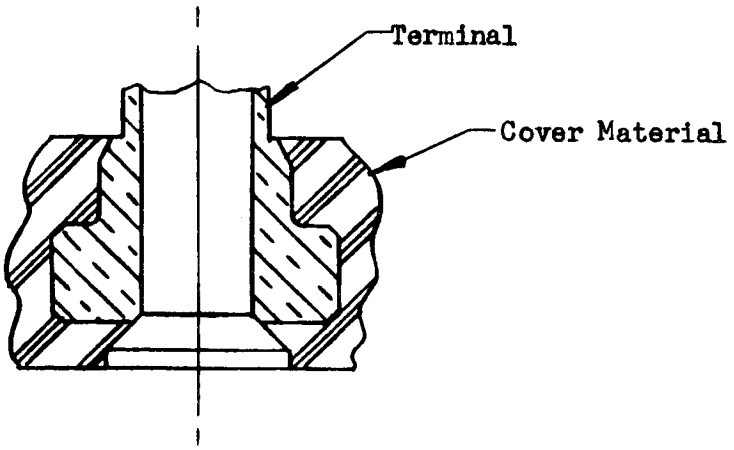


FIGURE 15

Cross Section of Test Cup and Terminal Design



Cross Section of Insert-Test Cup



Cross Section of Terminal in Cover

FIGURE 16

Cover and Holding Fixtures - Terminal Seal

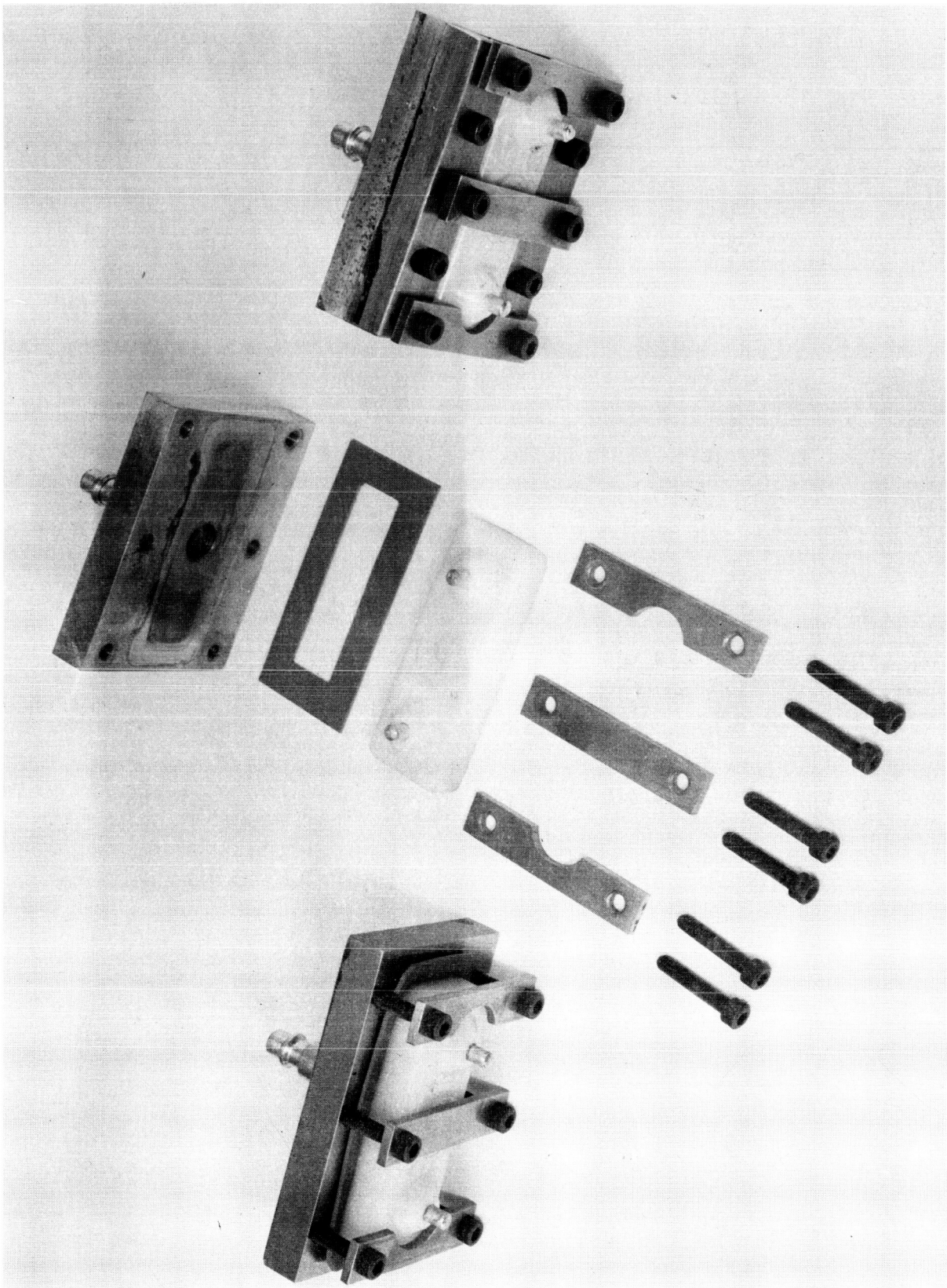


FIGURE 17

Prototype Case and Cover For Seal Evaluation

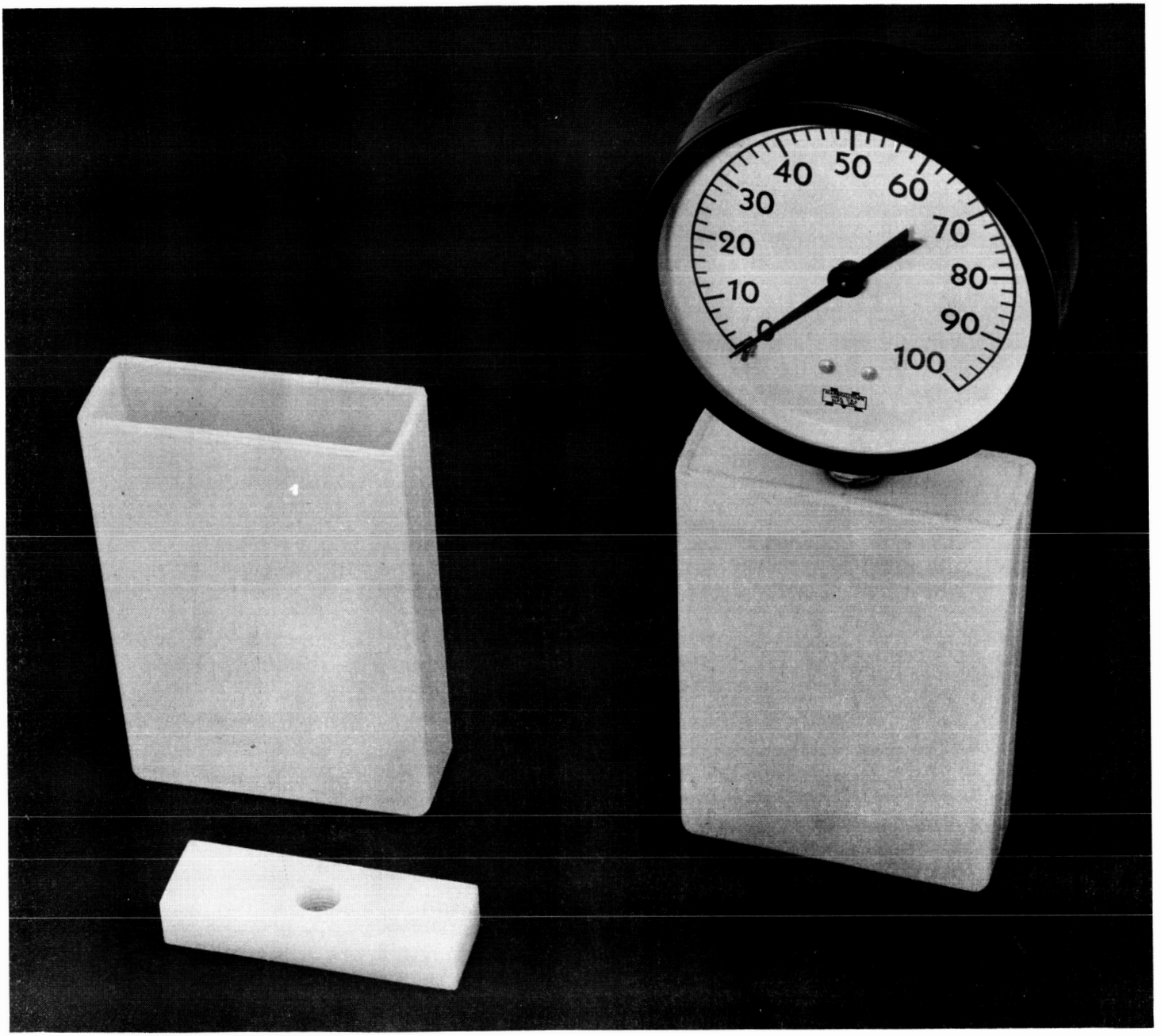


FIGURE 18

Old Case and Cover

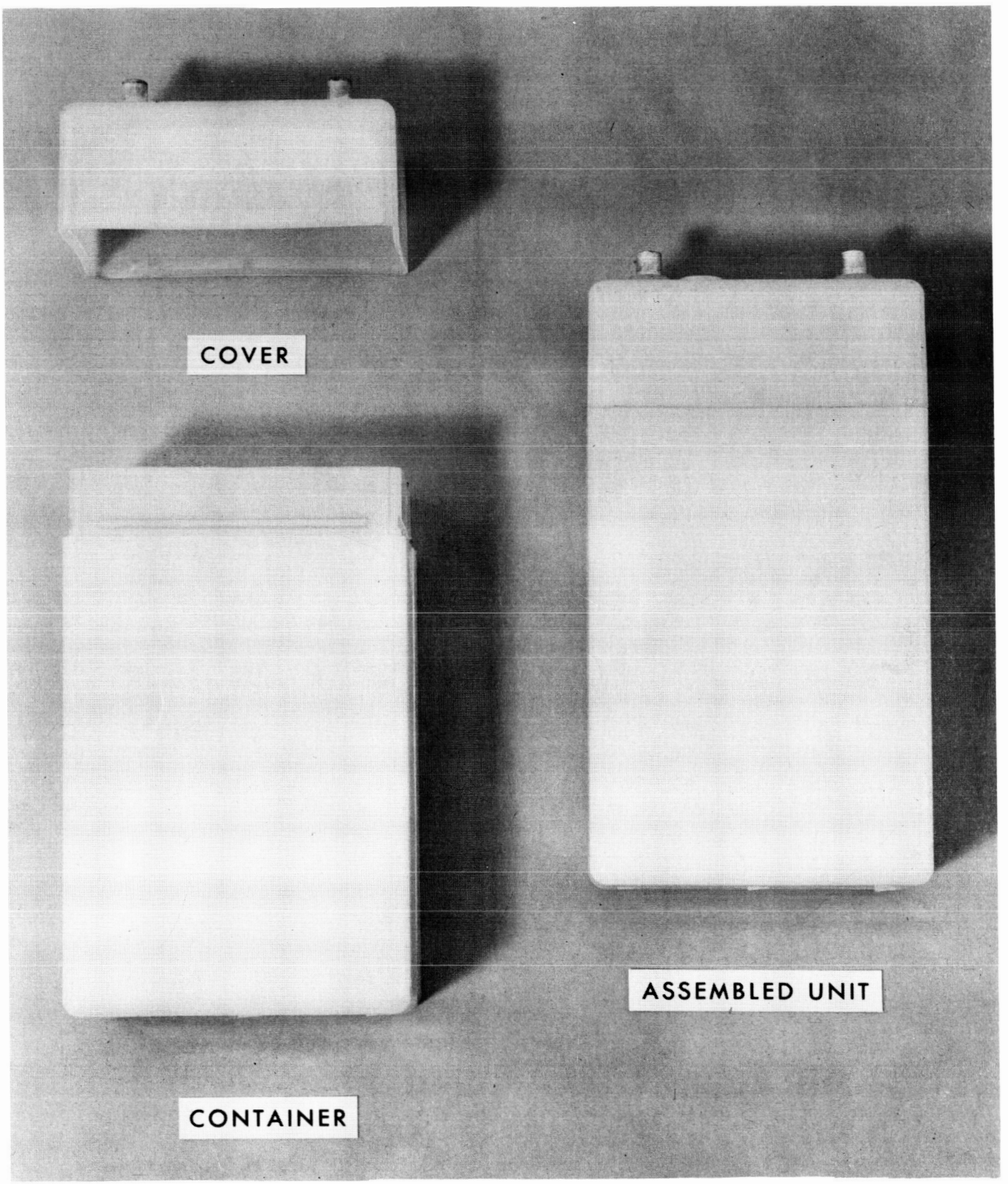


FIGURE 19

New Case and Cover

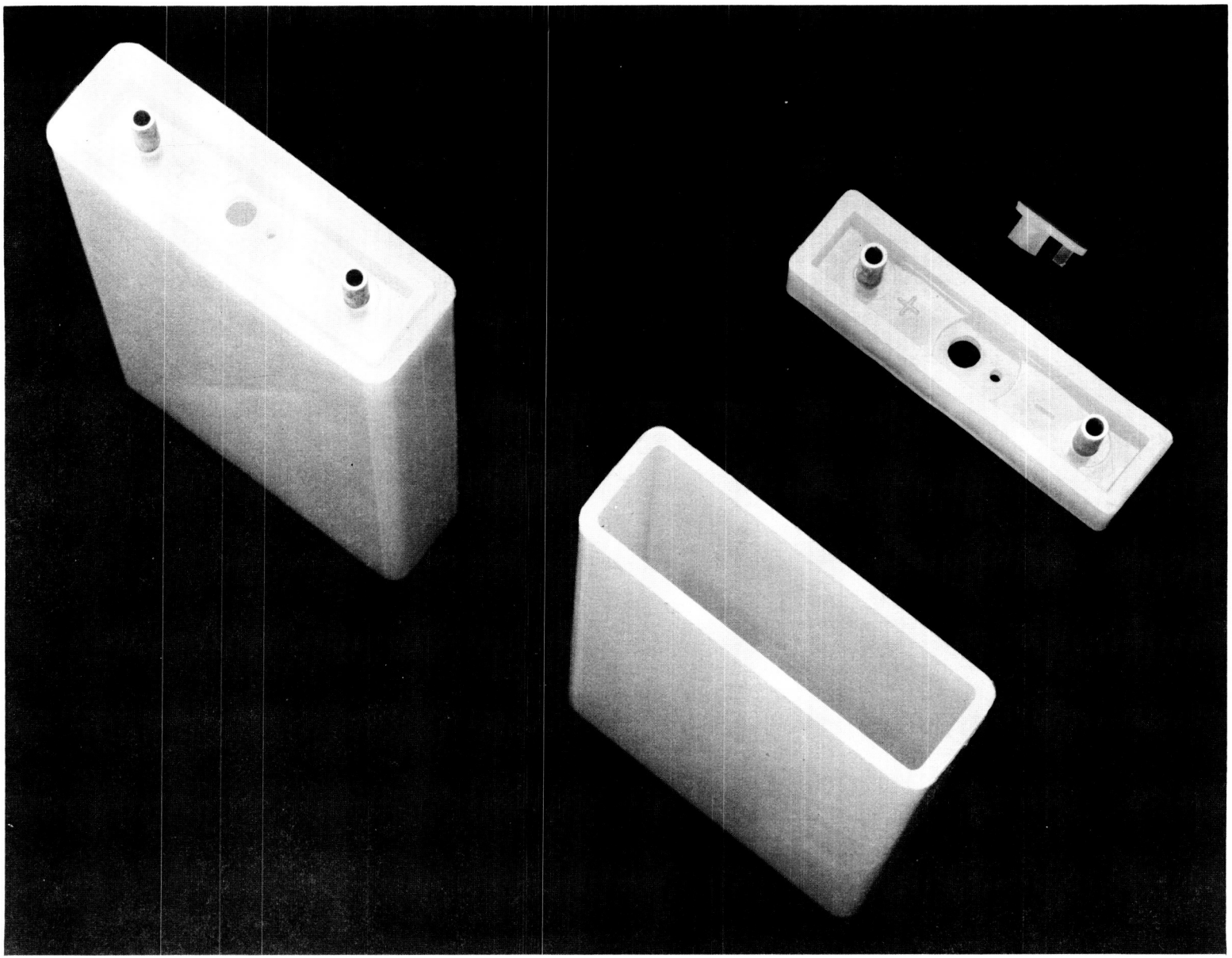


FIGURE 20

Clamping Fixture For Case-to-Cover Seal

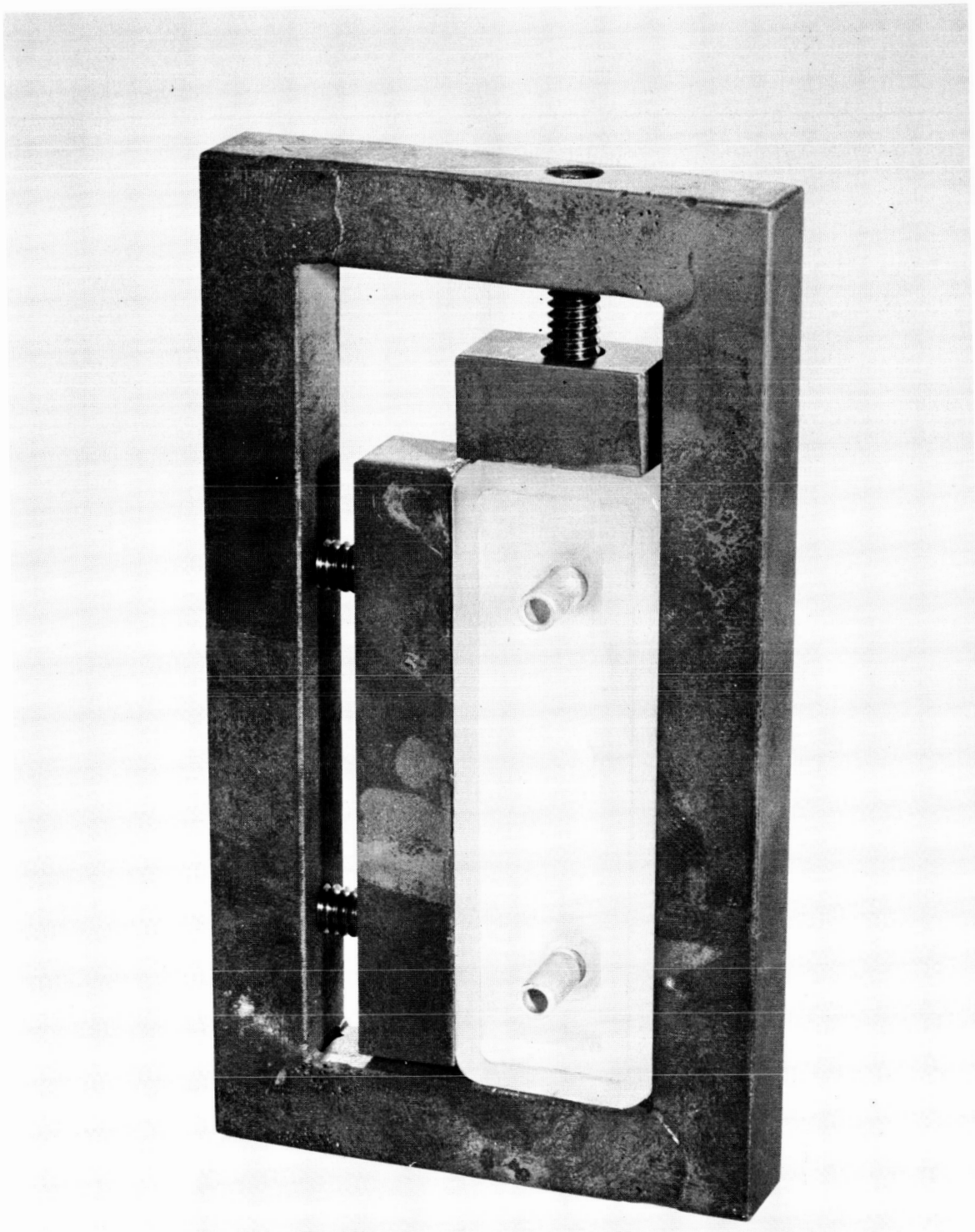


FIGURE 21

Case Pressure Tested at 90 psi after 36 Hours at 145° C

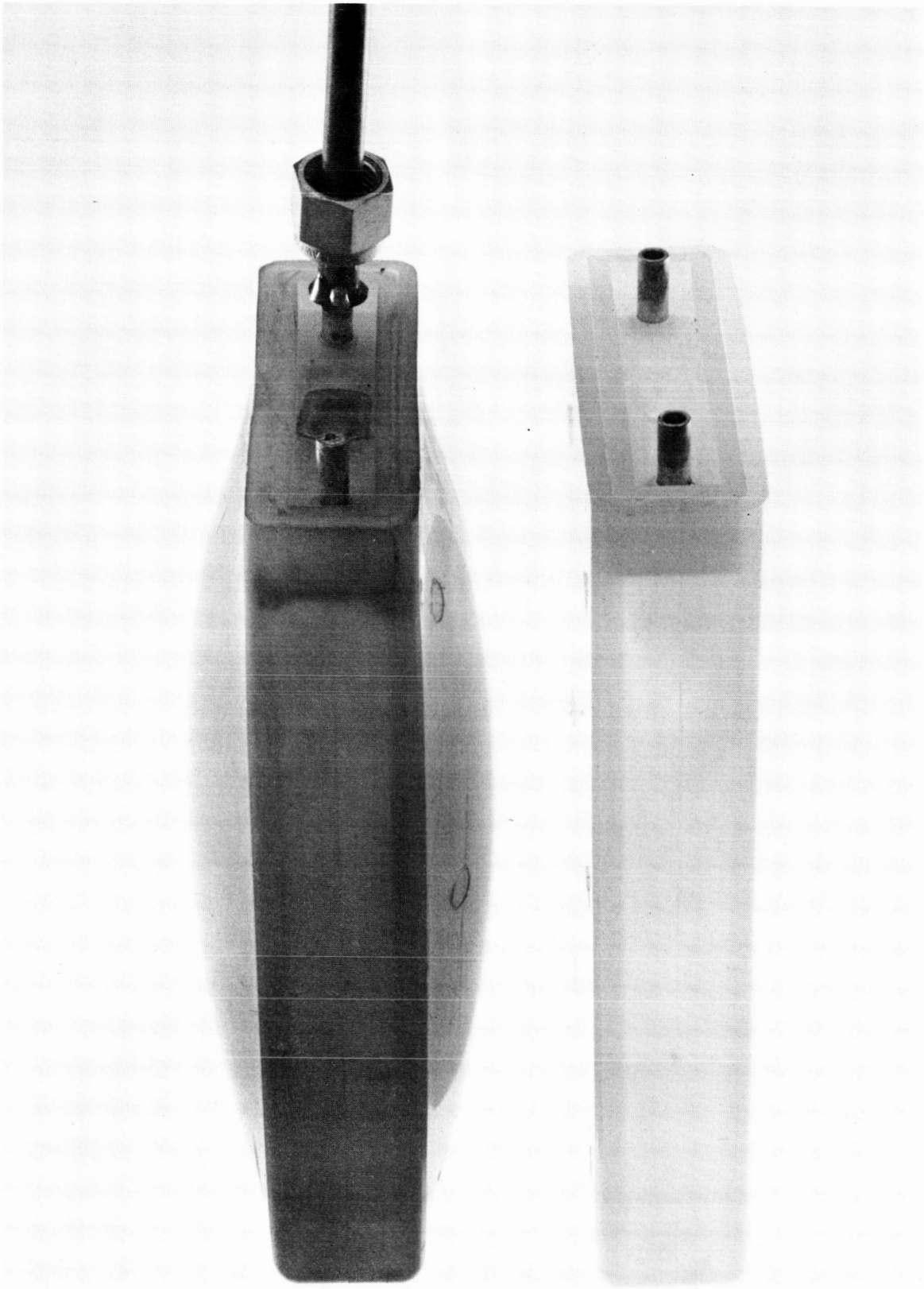


FIGURE 22

Photograph of Case Mold

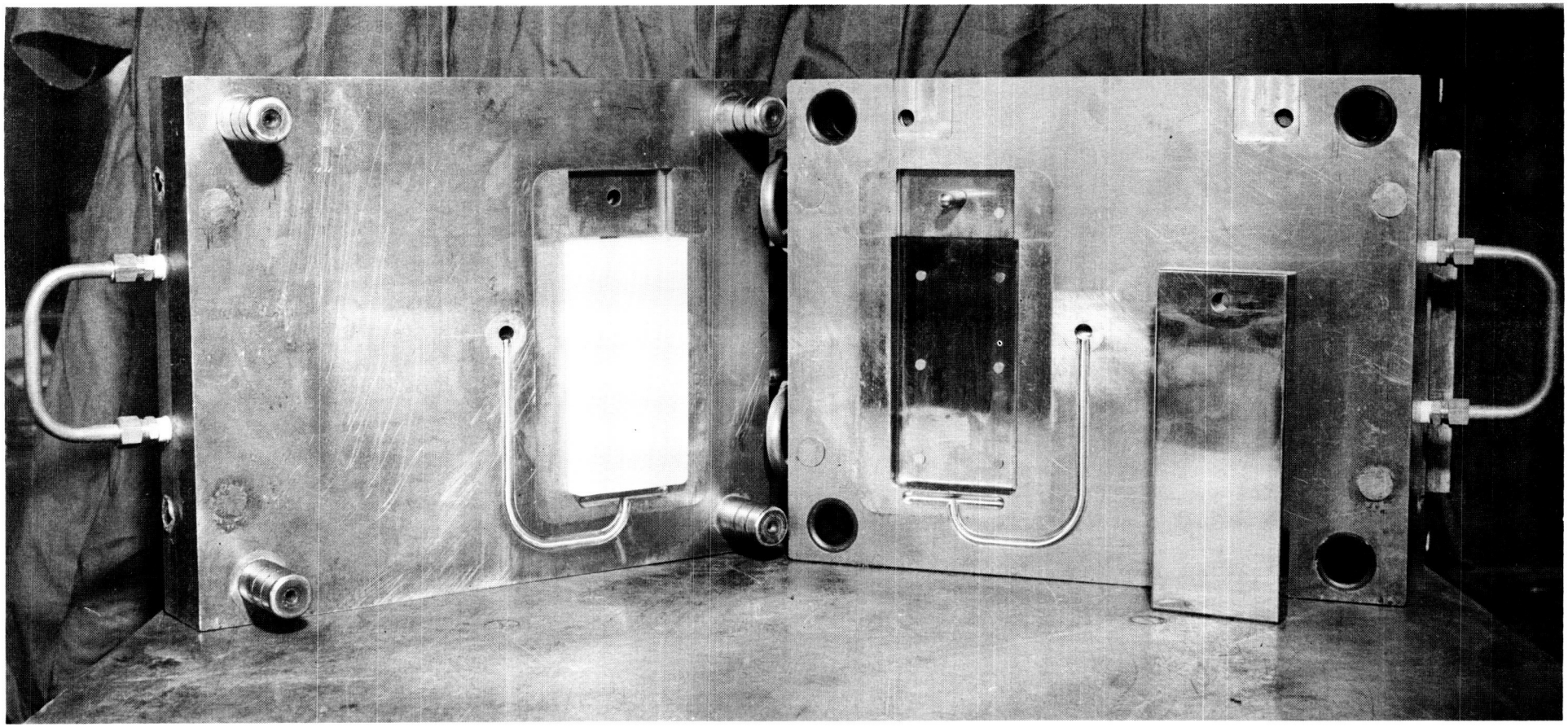


FIGURE 23

Photograph of Cover Mold

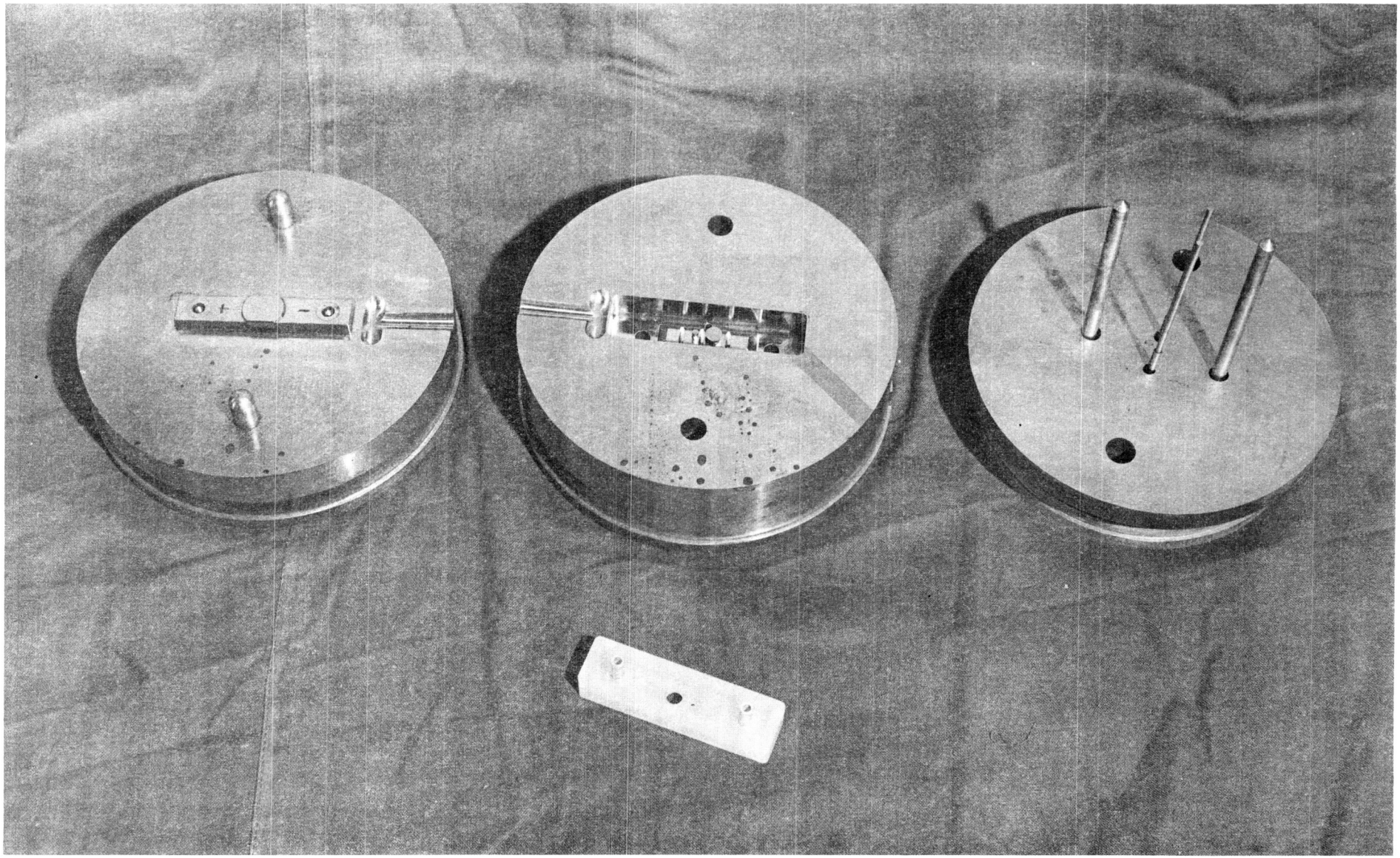
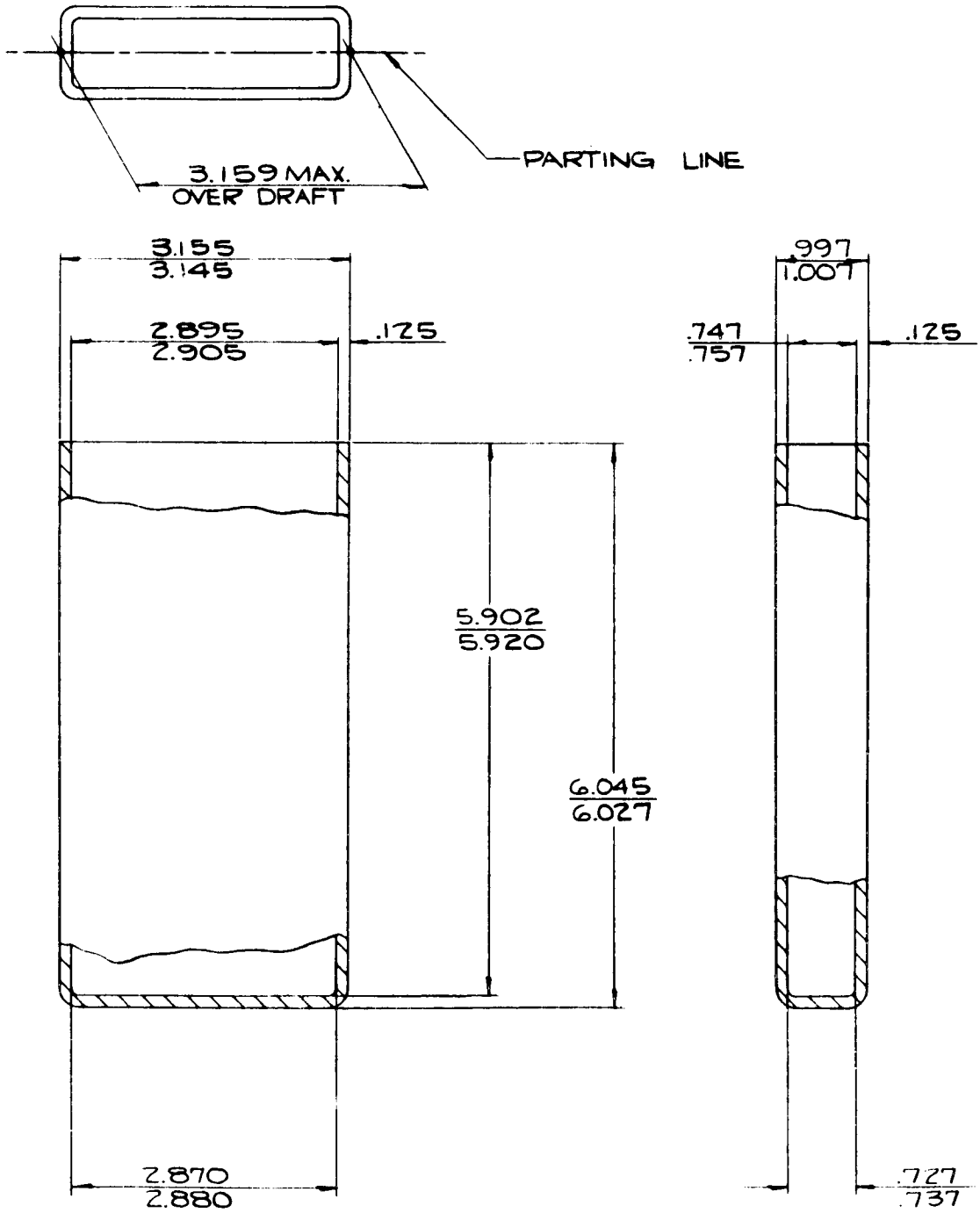


FIGURE 24

New Cell Case Design

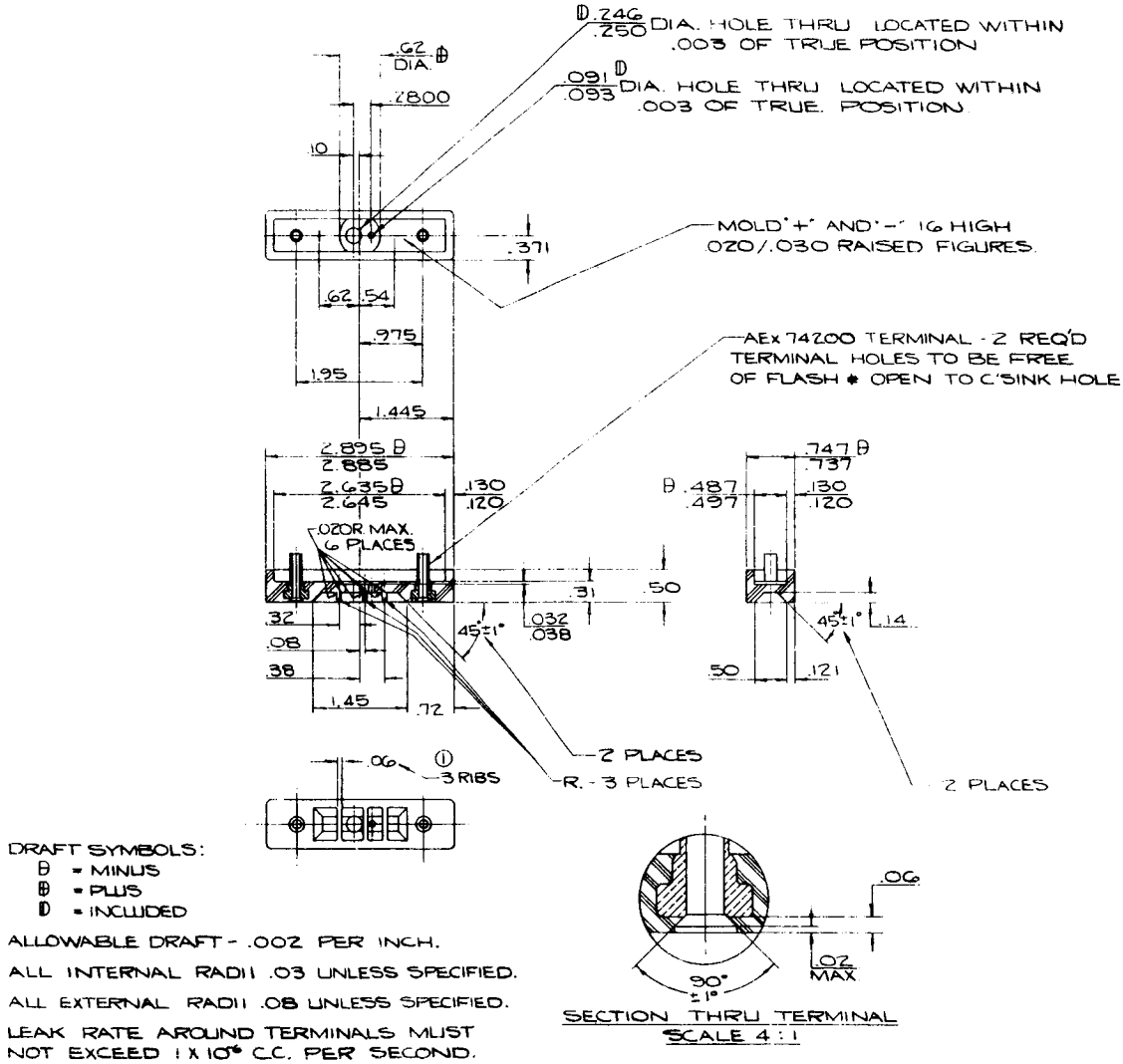


ALL INTERNAL RADII .08 UNLESS OTHERWISE SPECIFIED.

ALL EXTERNAL RADII .20 UNLESS OTHERWISE SPECIFIED.

FIGURE 25

New Cover Design



DRAFT SYMBOLS:
- Θ = MINUS
- Ⓟ = PLUS
- Ⓓ = INCLUDED

ALLOWABLE DRAFT - .002 PER INCH.

ALL INTERNAL RADII .03 UNLESS SPECIFIED.

ALL EXTERNAL RADII .08 UNLESS SPECIFIED.

LEAK RATE AROUND TERMINALS MUST NOT EXCEED 1×10^{-6} C.C. PER SECOND.

SECTION THRU TERMINAL
SCALE 4 : 1

FIGURE 26

Discharge Curves of 9 Plate Cells With C19-300 Separators

Discharged at 9 amperes at Room Temperature

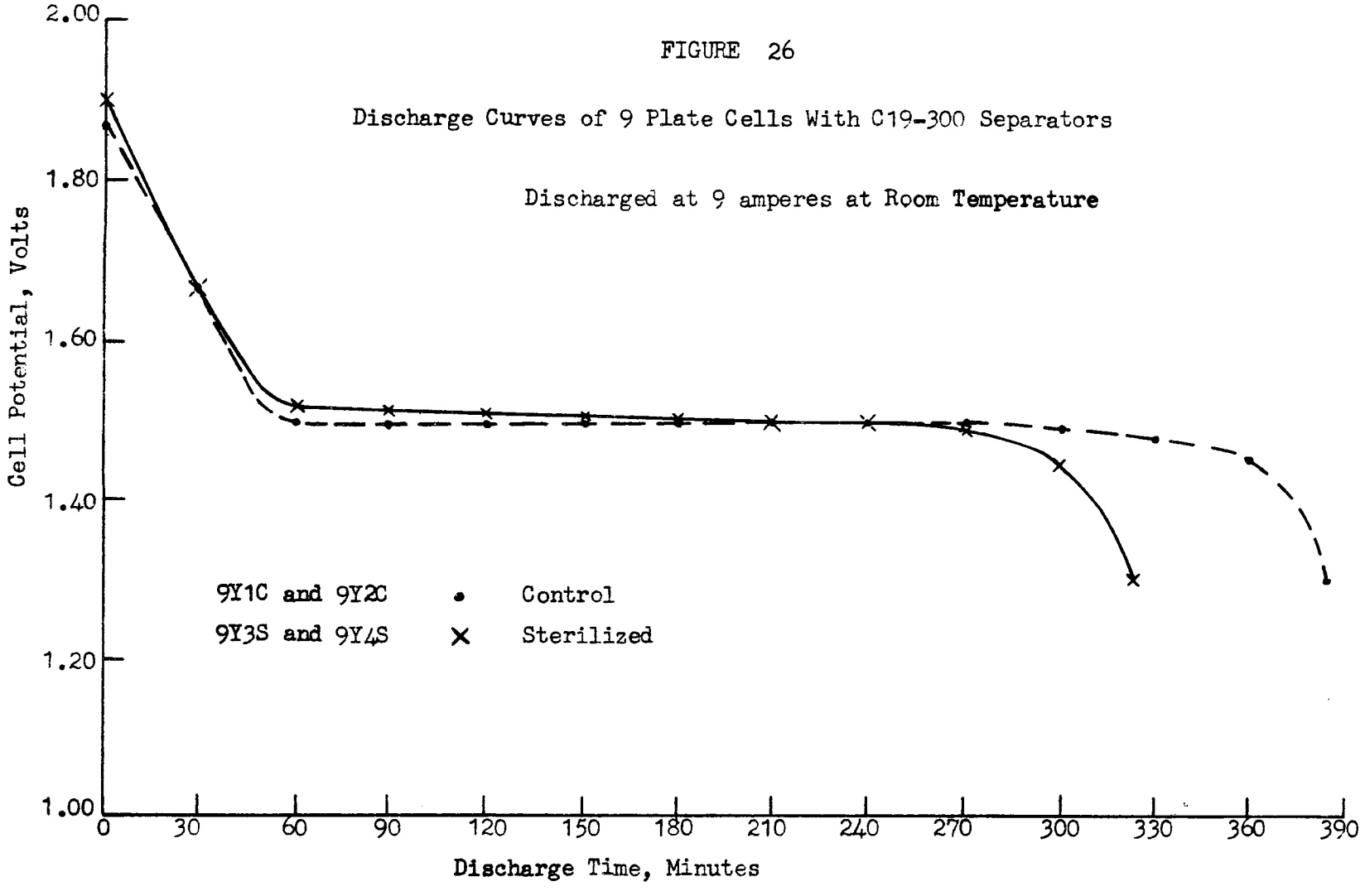


FIGURE 27

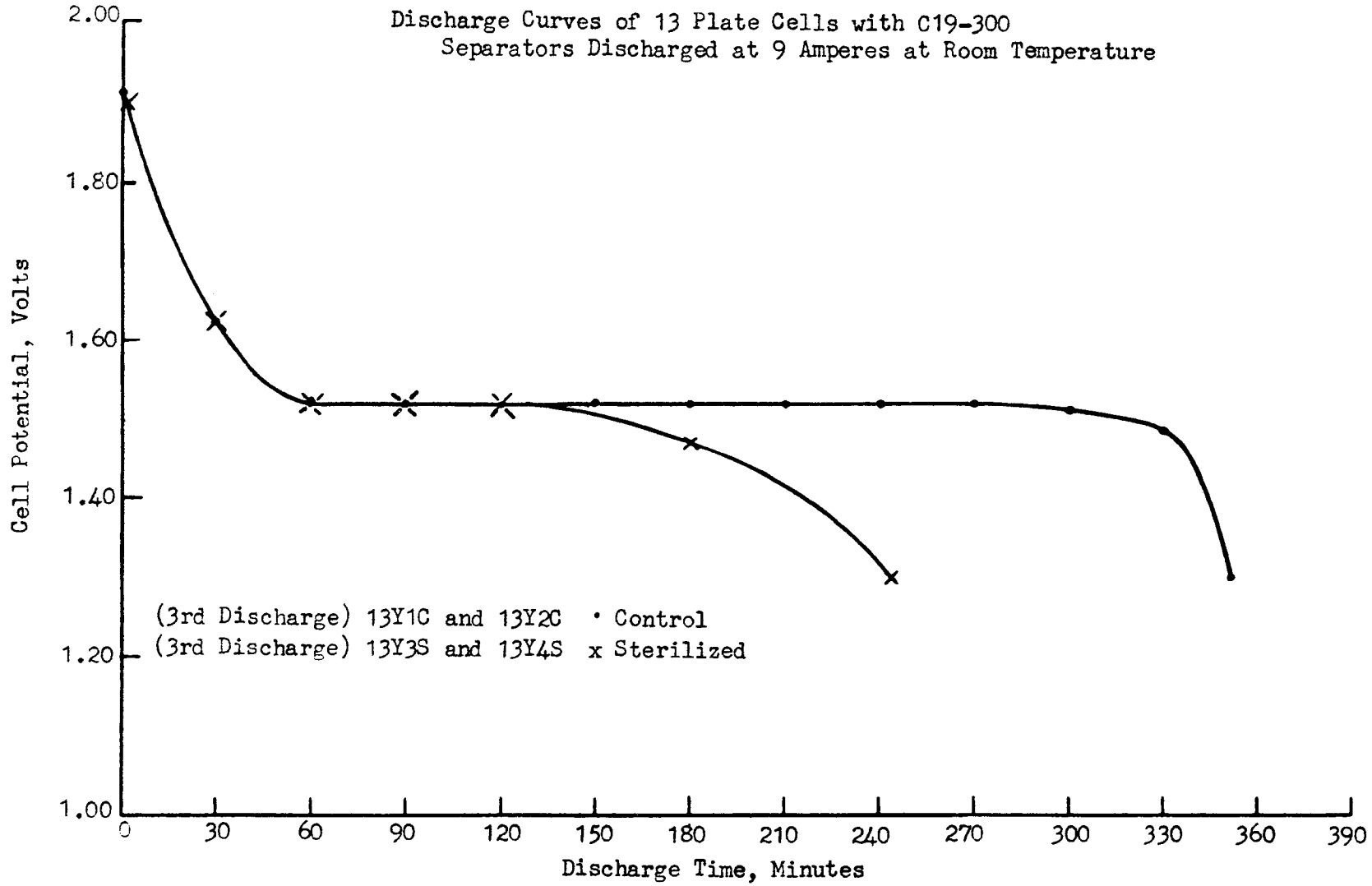

Discharge Curves of 13 Plate Cells with C19-300
Separators Discharged at 9 Amperes at Room Temperature
2.00
1.80
1.60
1.40
1.20
1.00
Cell Potential, Volts
(3rd Discharge) 13Y1C and 13Y2C • Control
(3rd Discharge) 13Y3S and 13Y4S x Sterilized
0
30
60
90
120
150
180
210
240
270
300
330
360
390
Discharge Time, Minutes

FIGURE 28

Discharge Curves for 9 and 13 Plate Cells with FSC Separators

Cells Sterilized at 145°C. after a Preformation Charge and Discharge

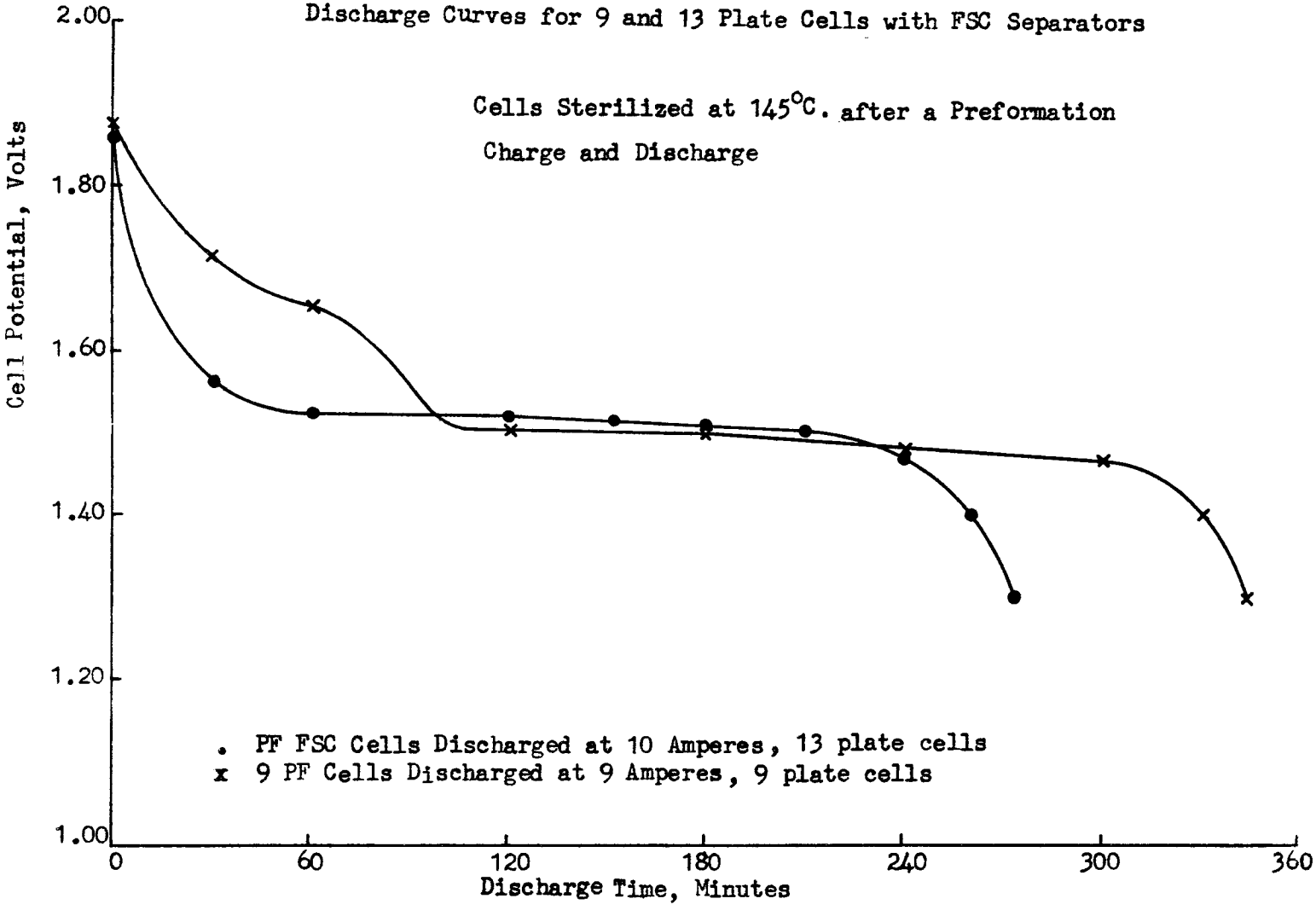


FIGURE 29

Plate Thickness Study

Charge and Material Efficiencies as a Function of Positive Plate Thickness-
Curves Based on Data from First Five Cycles

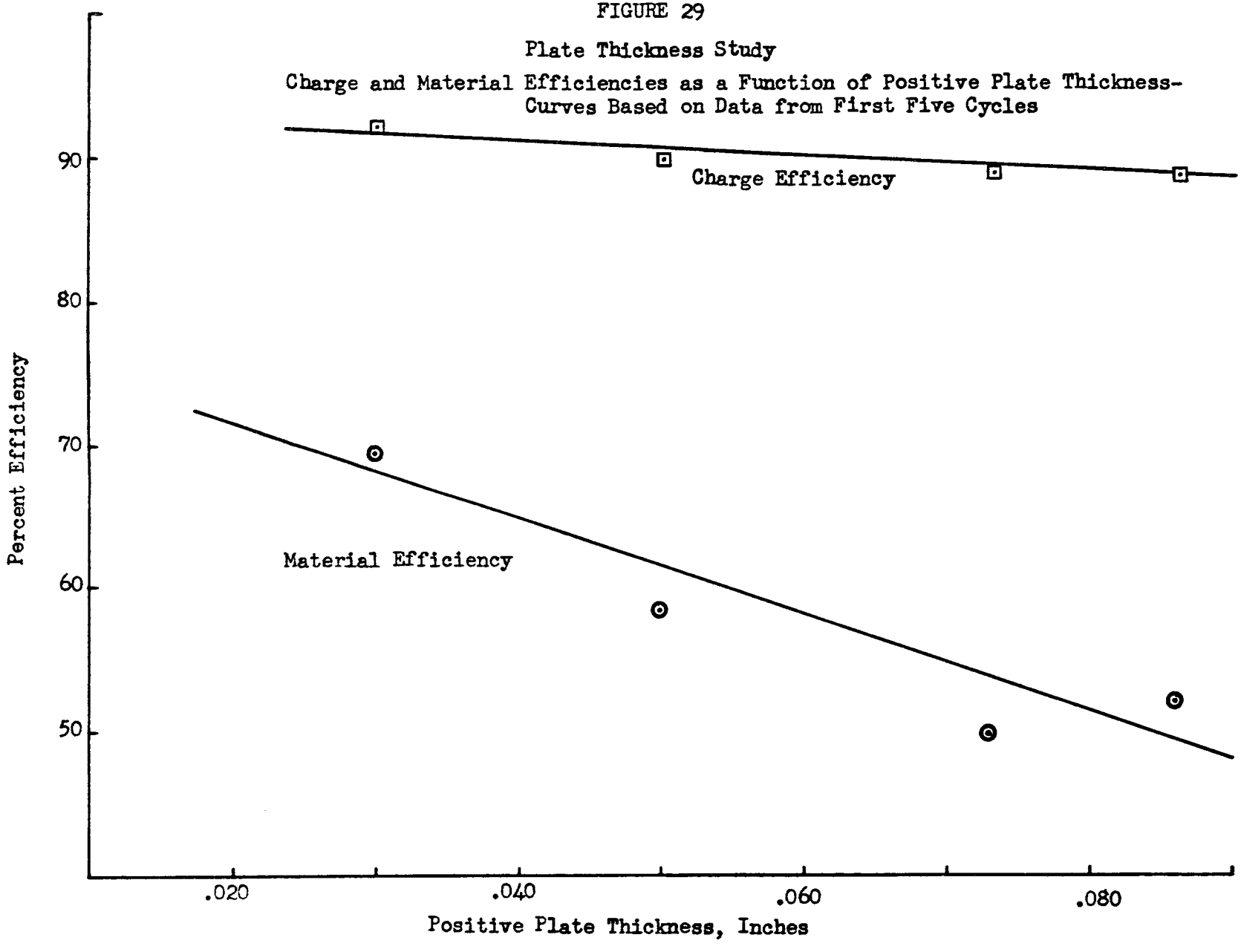


FIGURE 30

Plate Thickness Study

2 Ampere Discharge at 75°F.
13th Cycle

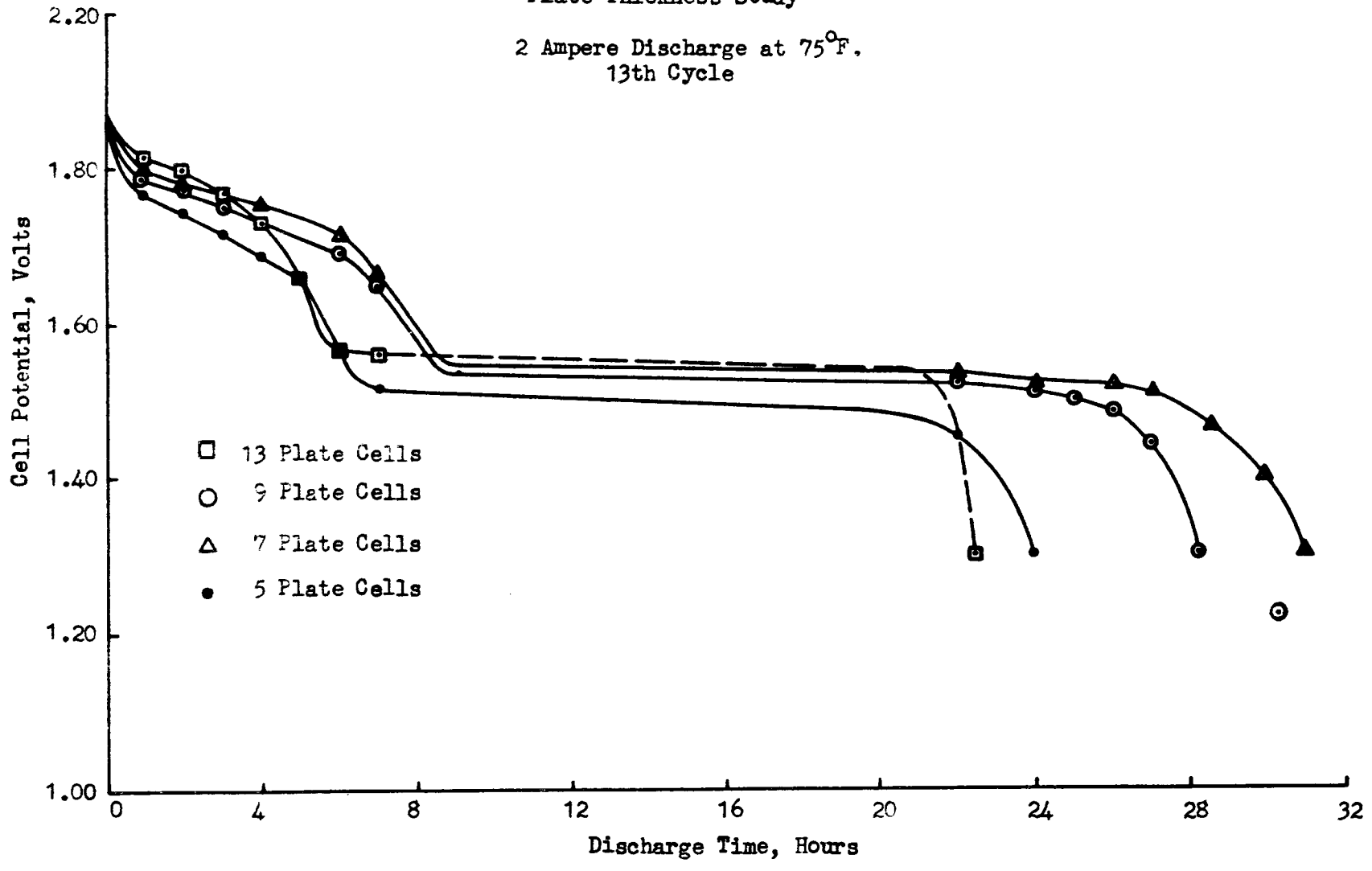


FIGURE 31

Plate Thickness Study

5 Ampere Discharge at 75°F.
8th Cycle

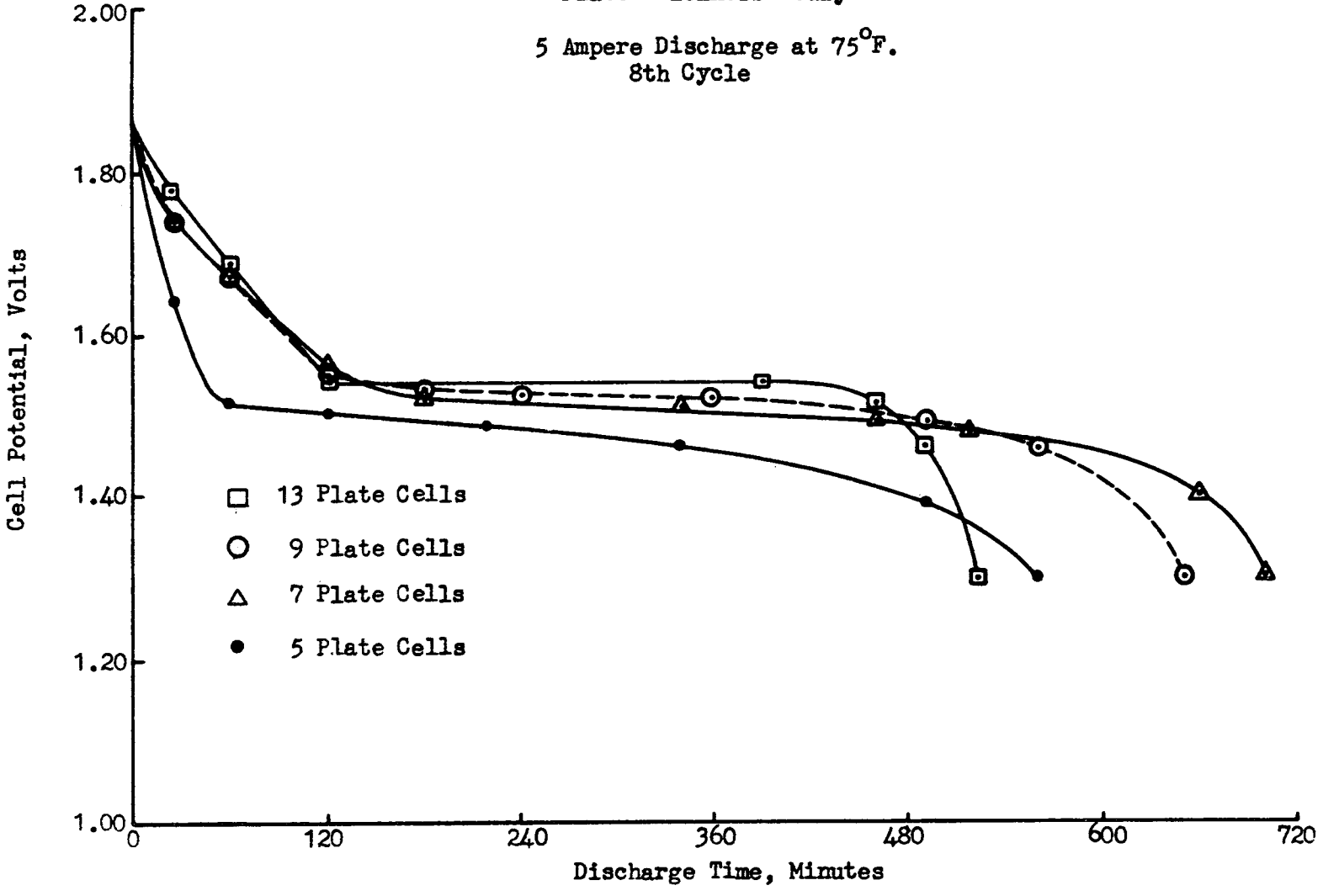


FIGURE 32

Plate Thickness Study

9 Ampere Discharge at 75°F.
5th Cycle

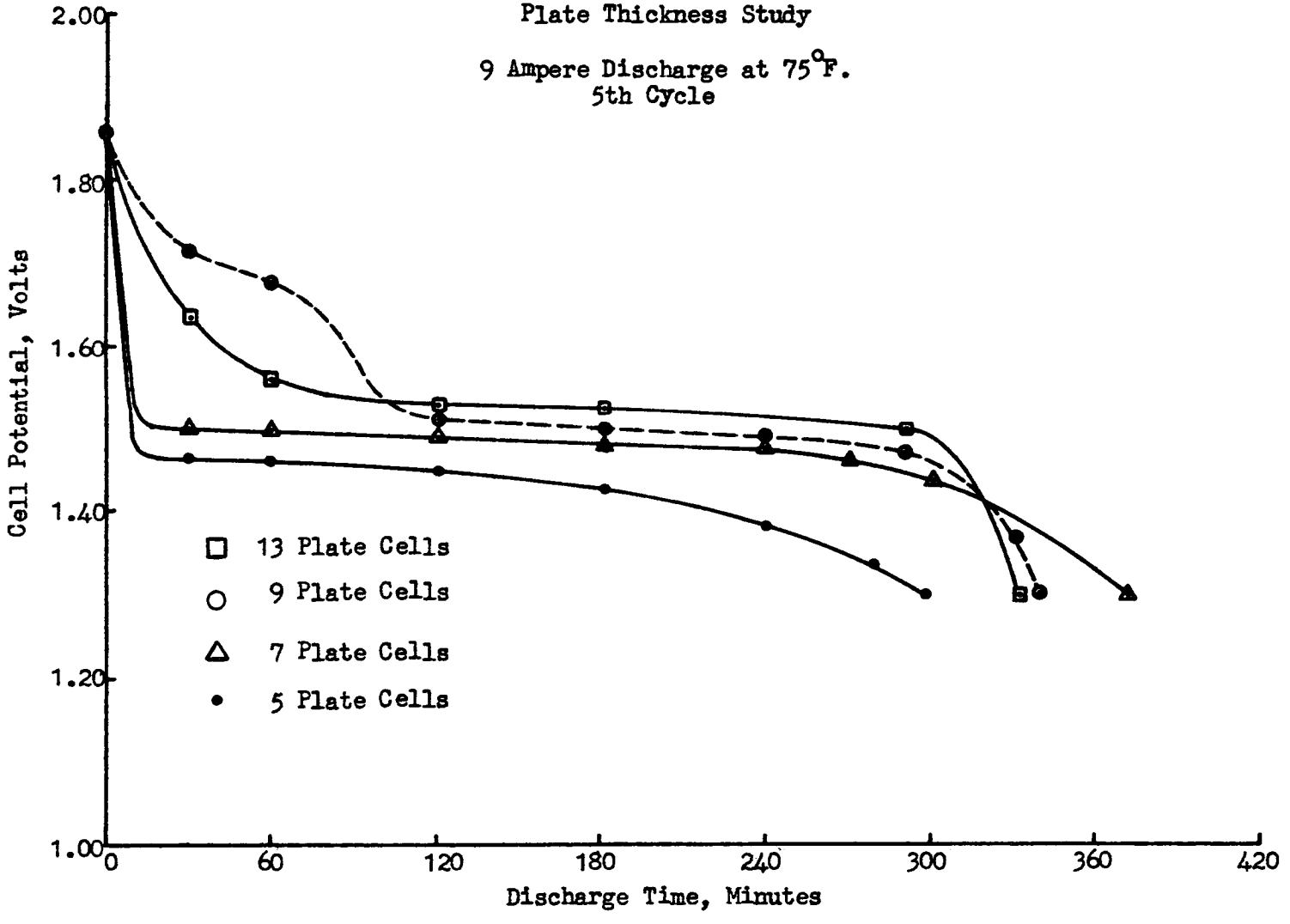


FIGURE 33

Plate Thickness Study

25 Ampere Discharge at 75°F.
7th Cycle

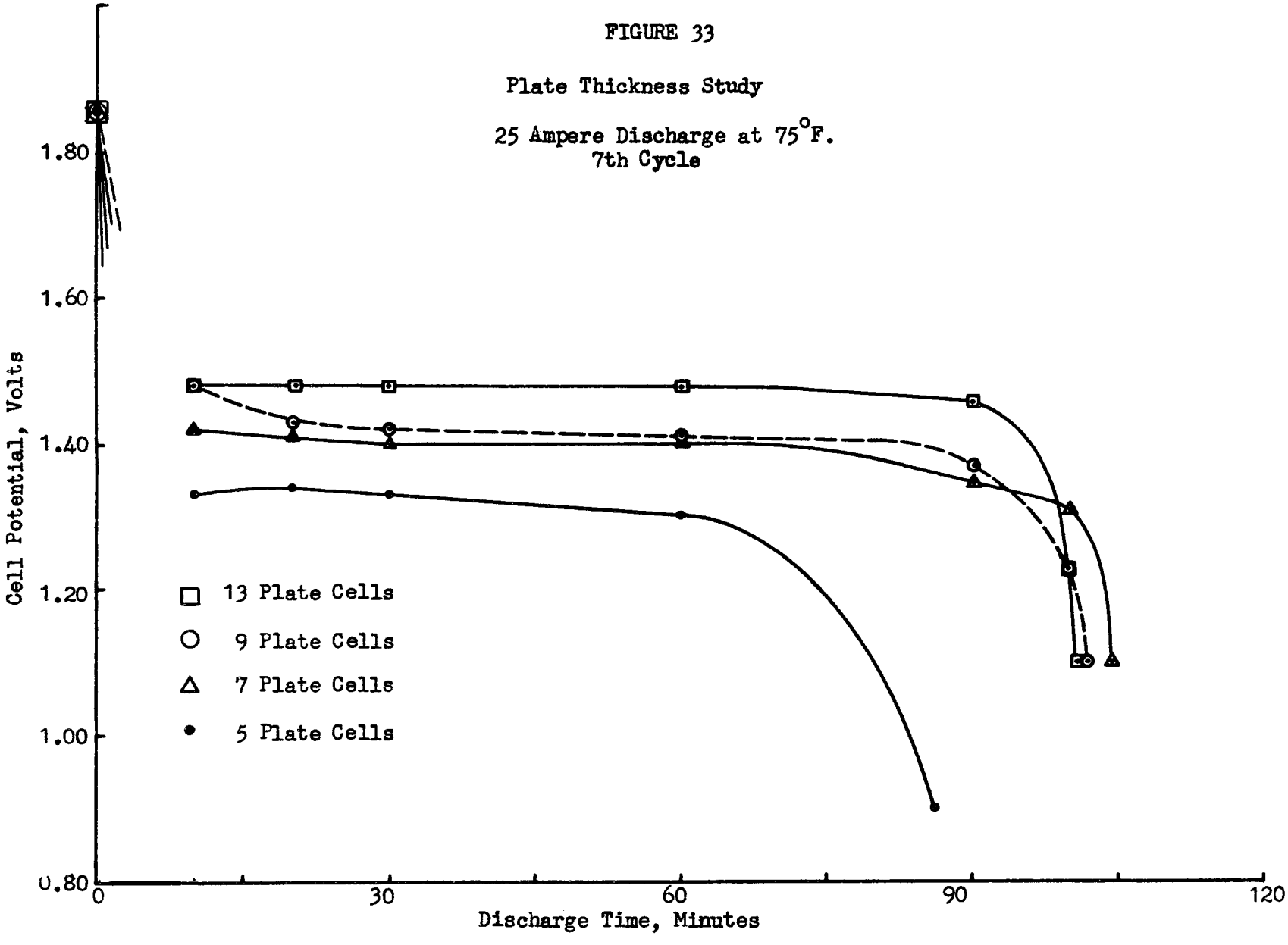


FIGURE 34

Plate Thickness Study

50 Ampere Discharge at 75°F.
6th Cycle

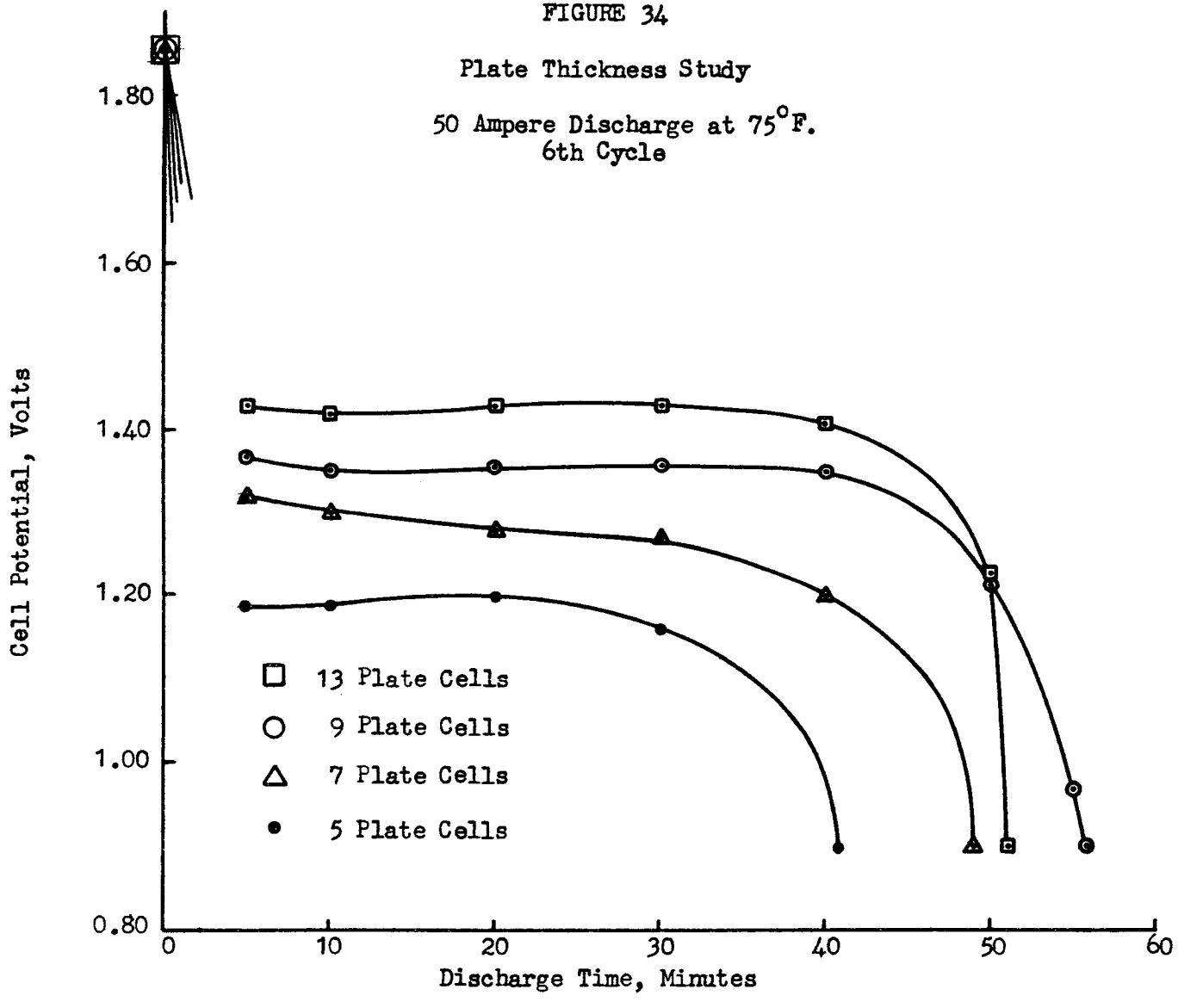


FIGURE 35

Plate Thickness Study

2 Ampere Discharge at 100°F.
17th Cycle

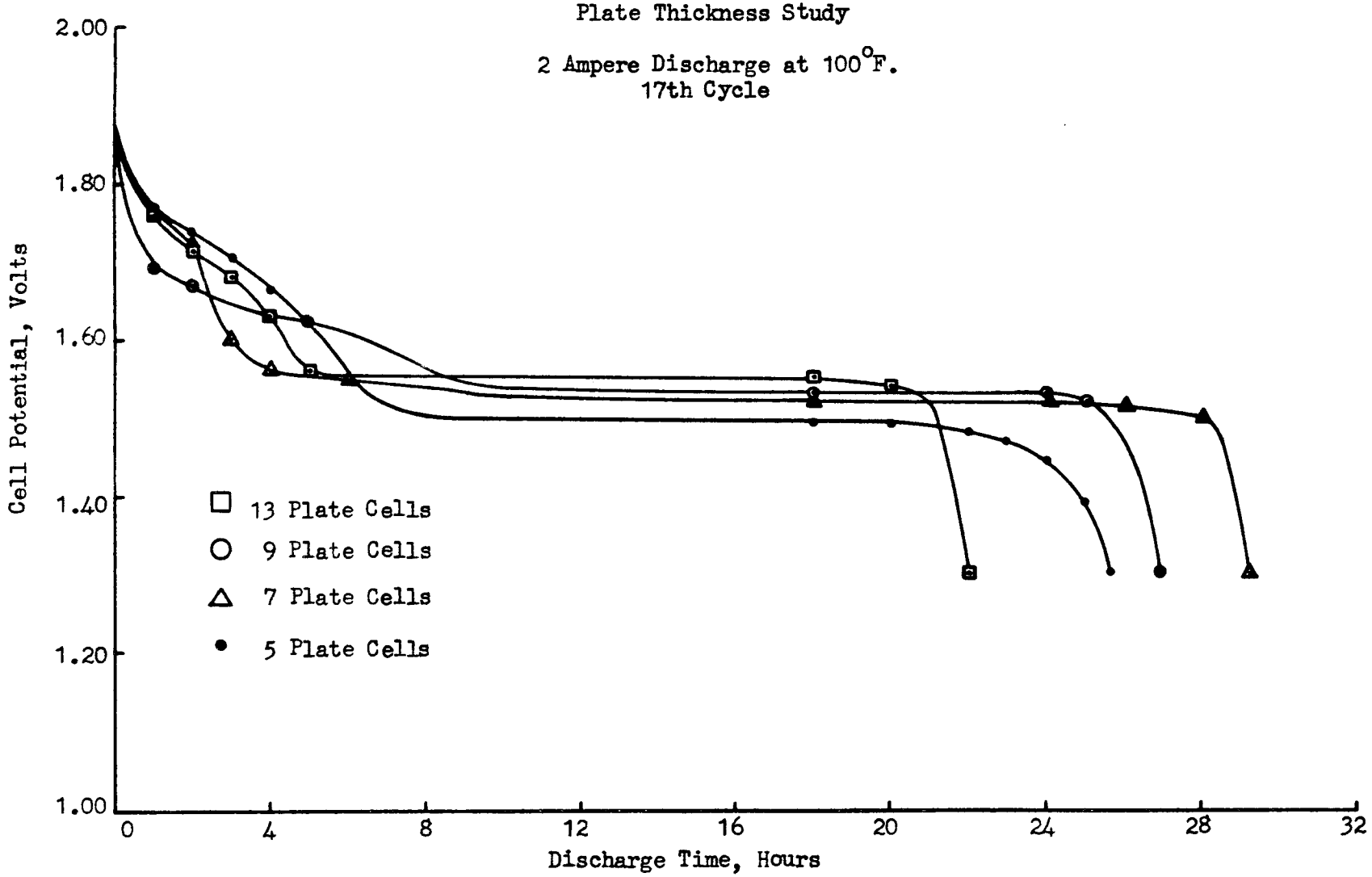


FIGURE 36

Plate Thickness Study

5 Ampere Discharge at 100°F.
16th Cycle

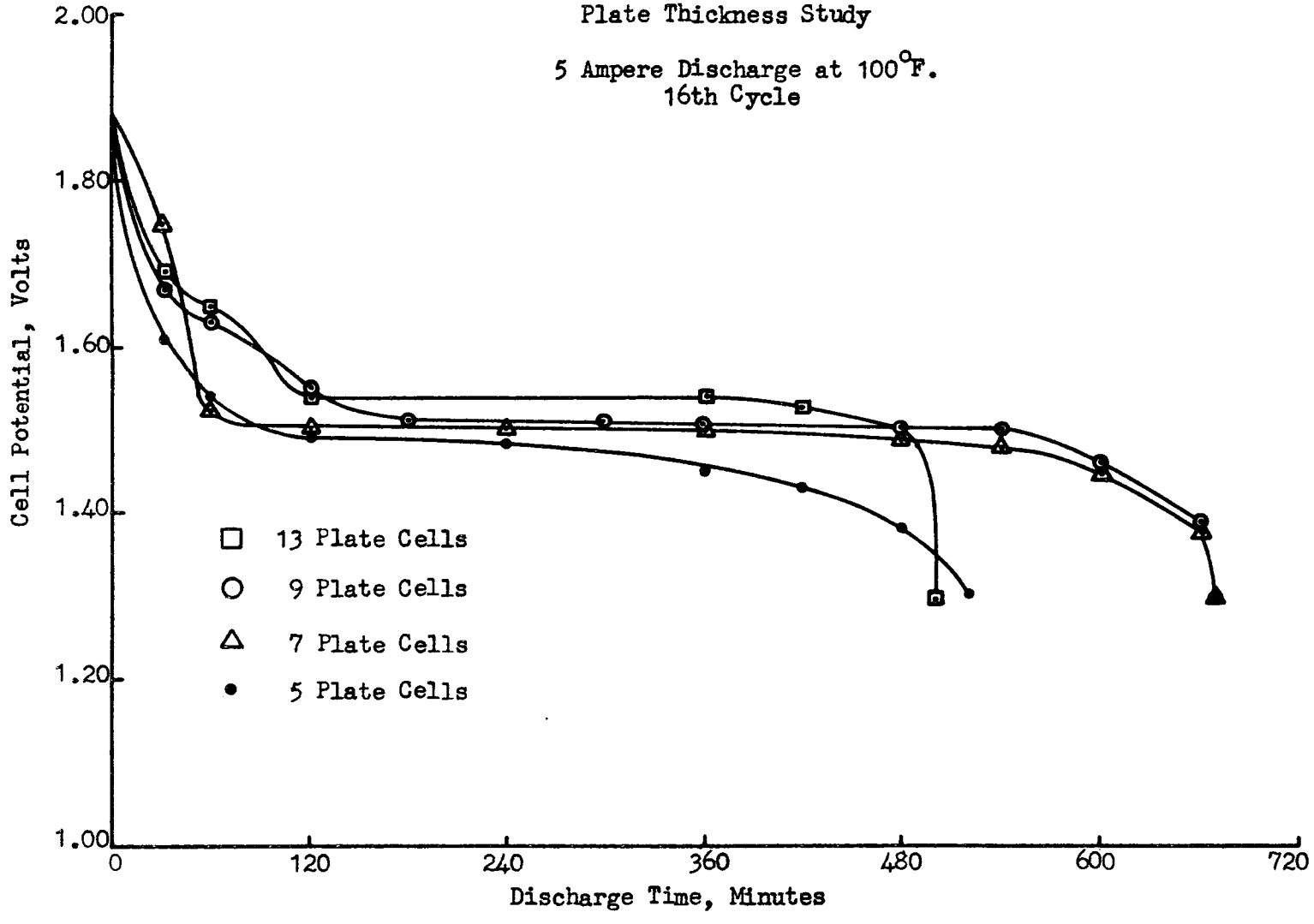


FIGURE 37

Plate Thickness Study

50 Ampere Discharge at 100°F.
10th Cycle

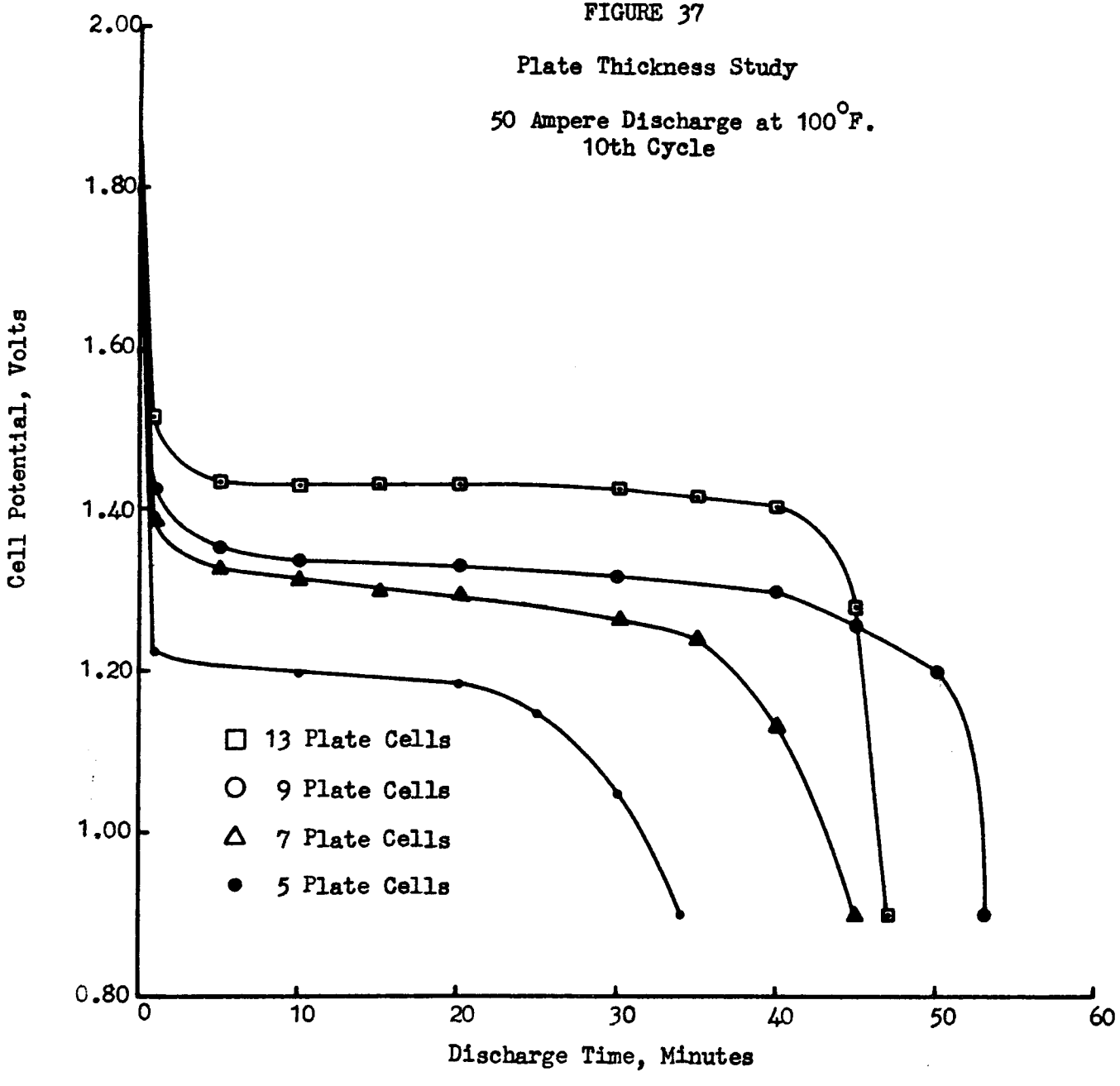


FIGURE 38

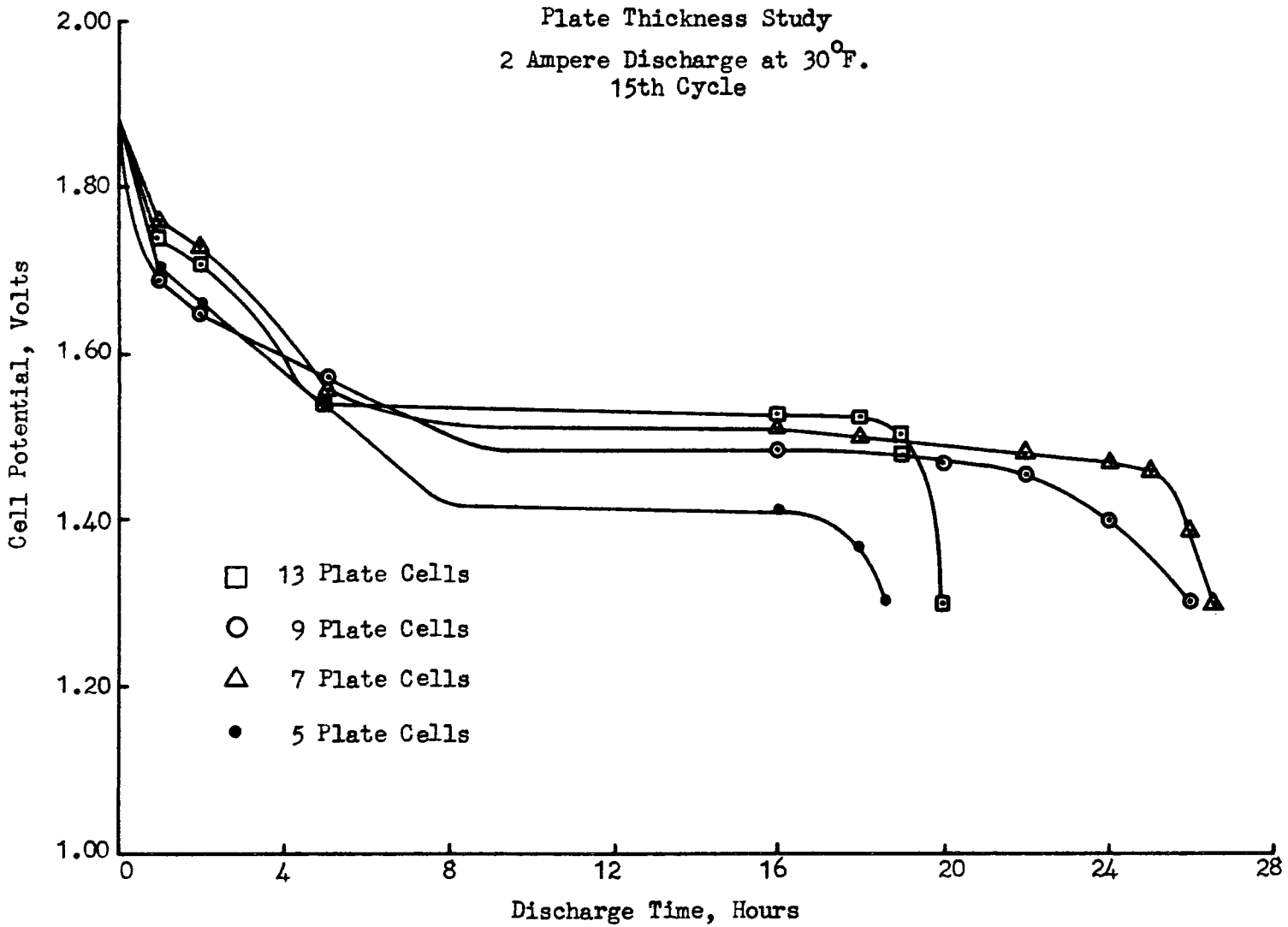


Plate Thickness Study
2 Ampere Discharge at 30°F.
15th Cycle
Cell Potential, Volts
2.00
1.80
1.60
1.40
1.20
1.00
0
4
8
12
16
20
24
28
Discharge Time, Hours
13 Plate Cells
9 Plate Cells
7 Plate Cells
5 Plate Cells

FIGURE 39

Plate Thickness Study

9 Ampere Discharge at 30°F.
11th Cycle

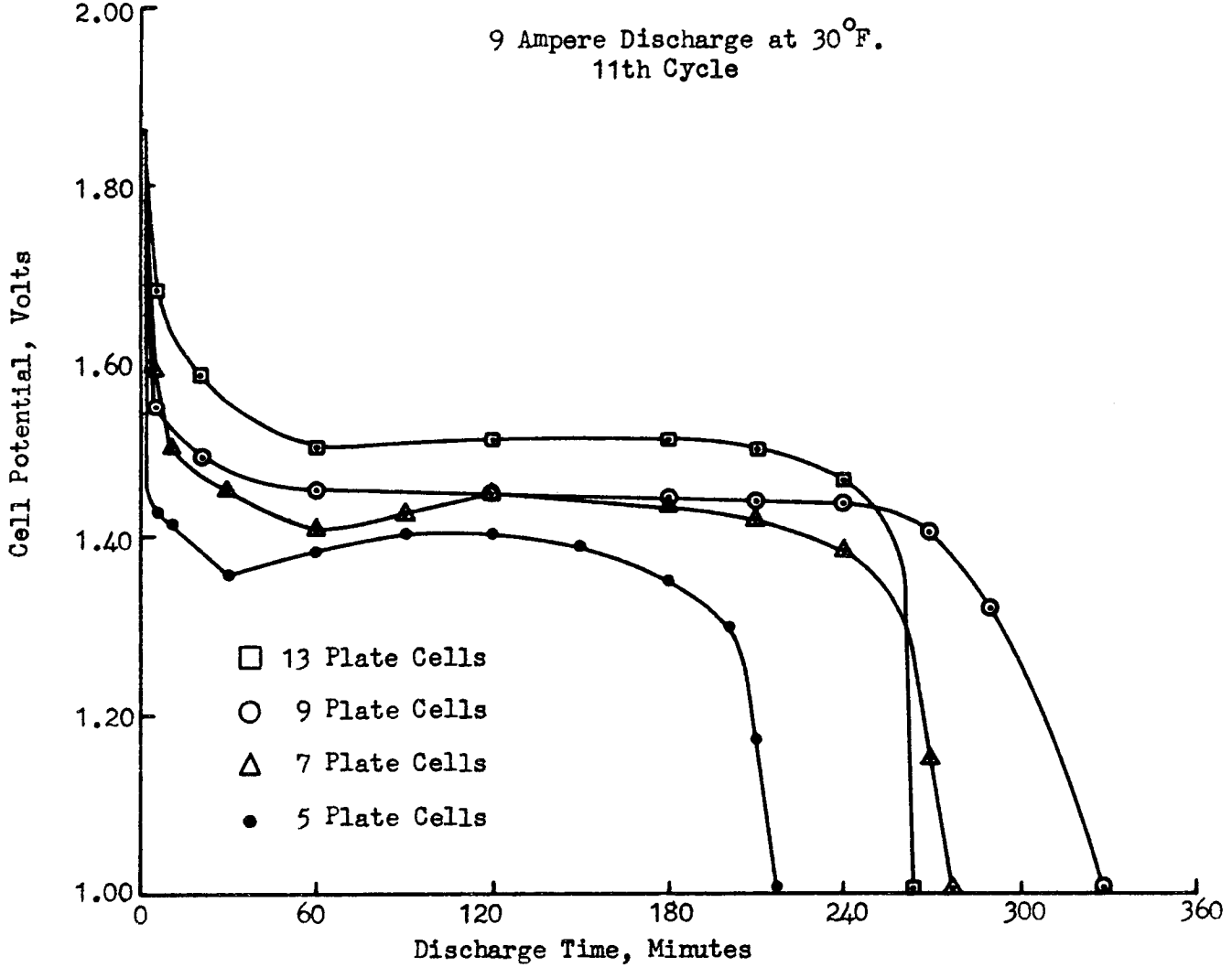


FIGURE 40

Plate Thickness Study

50 Ampere Discharge at 30°F.
14th Cycle

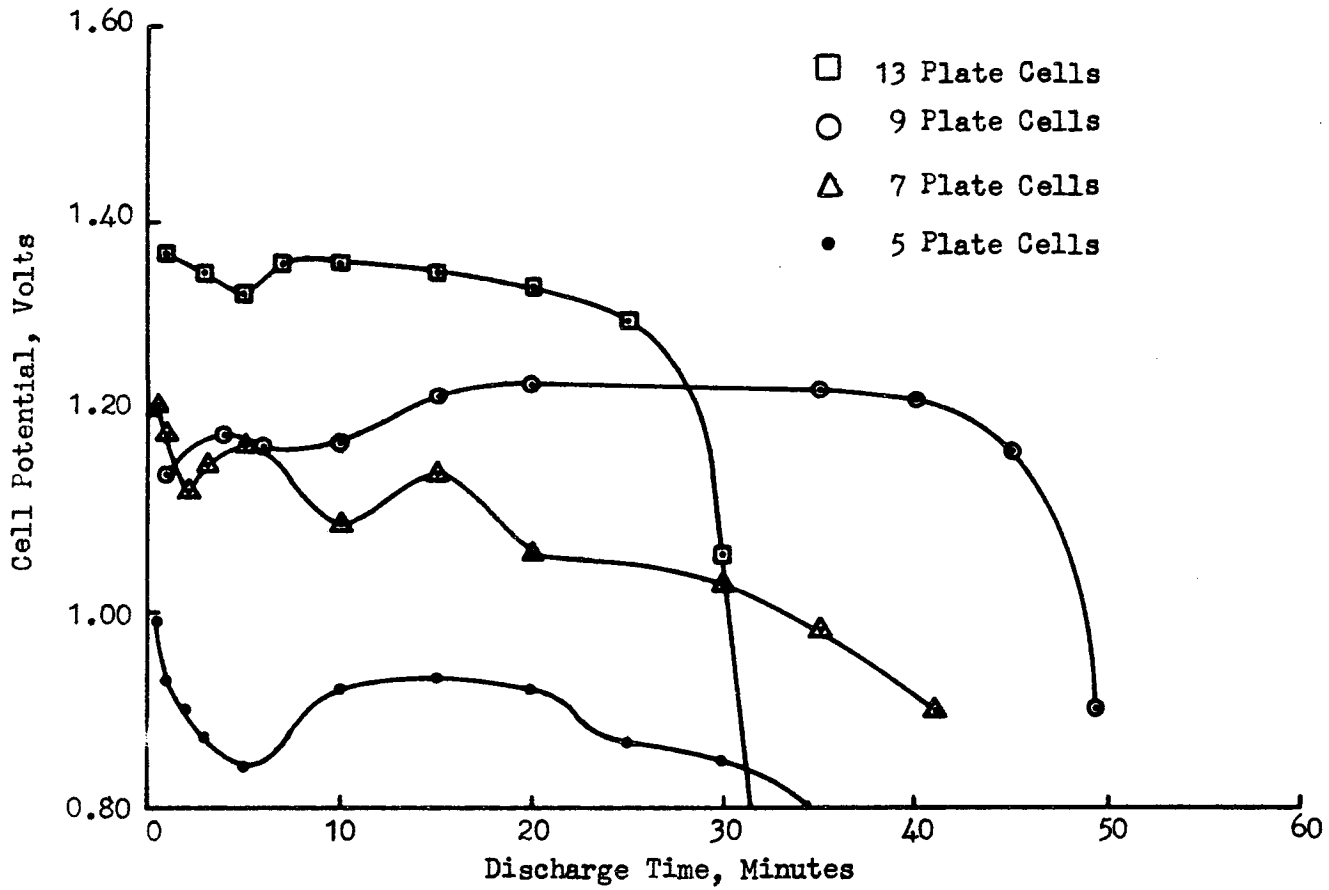


FIGURE 41

Plate Thickness Study

Plateau Voltage vs. Discharge Rate at 75°F.

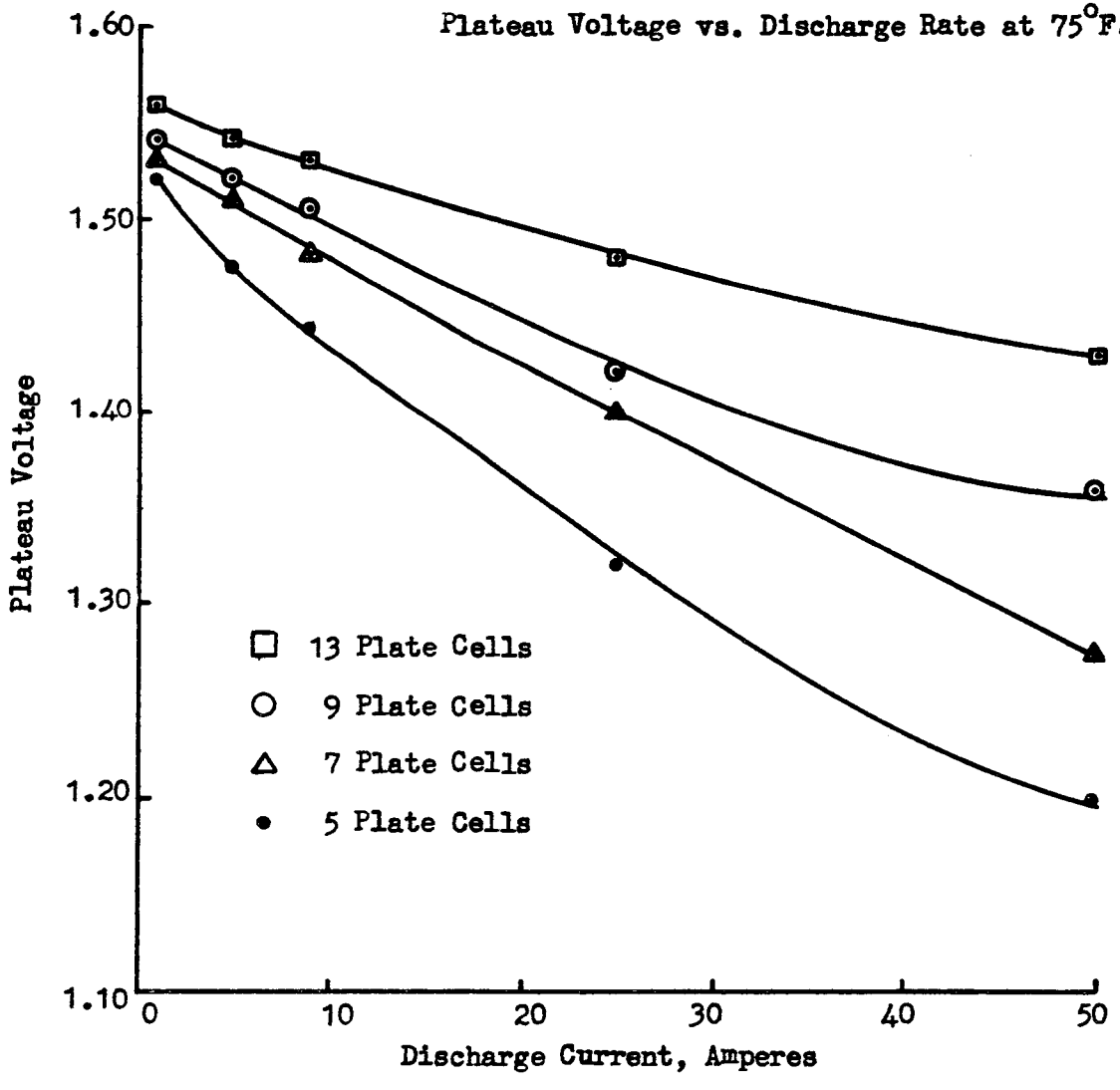


FIGURE 42

Plate Thickness Study

Energy Yield Per Pound of Element Weight Versus
Discharge Rate at 75°F.

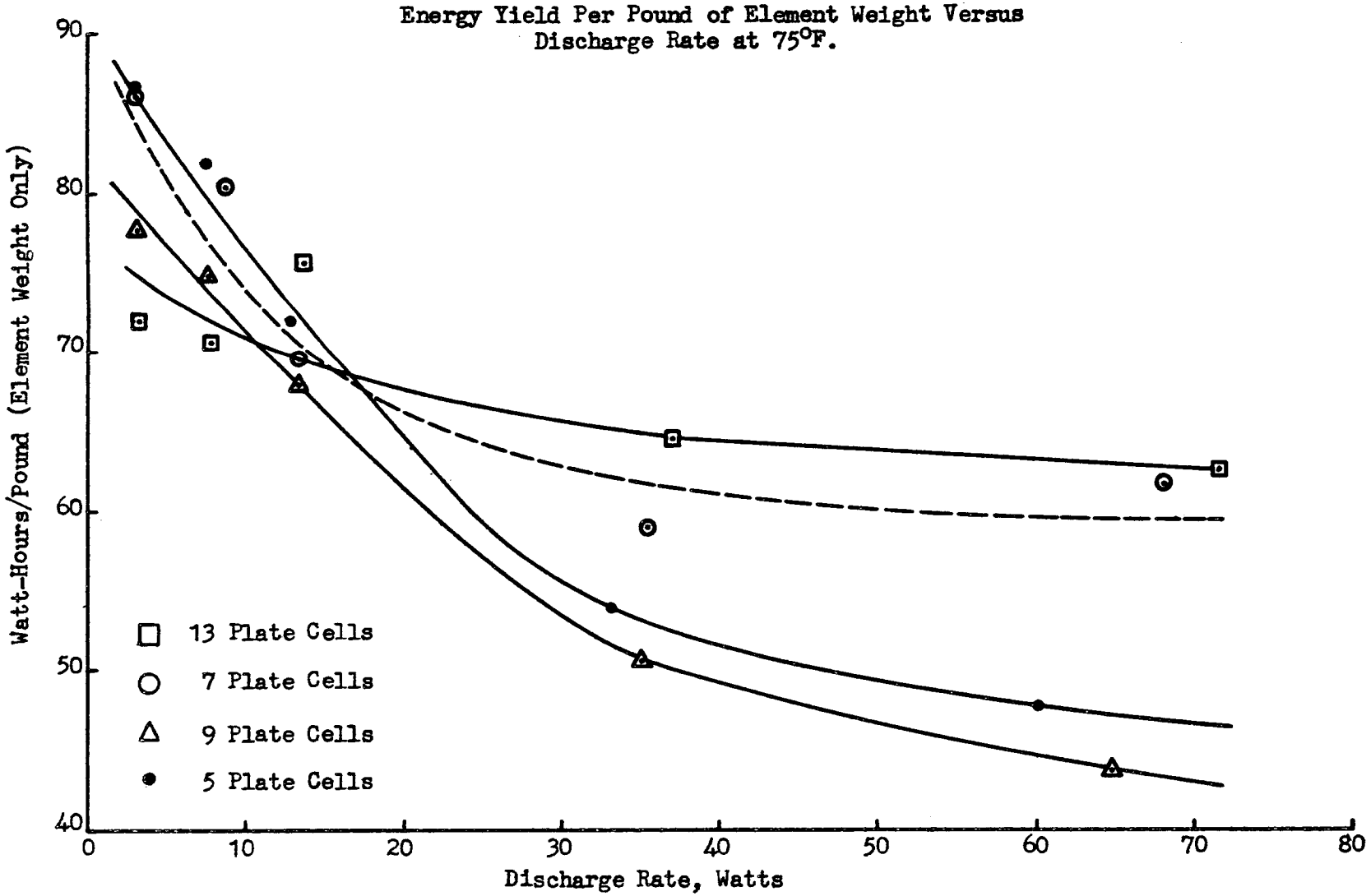


FIGURE 43

Plate Thickness Study

Energy Yield Per Cubic Inch of Element Versus Discharge Rate at 75° F.

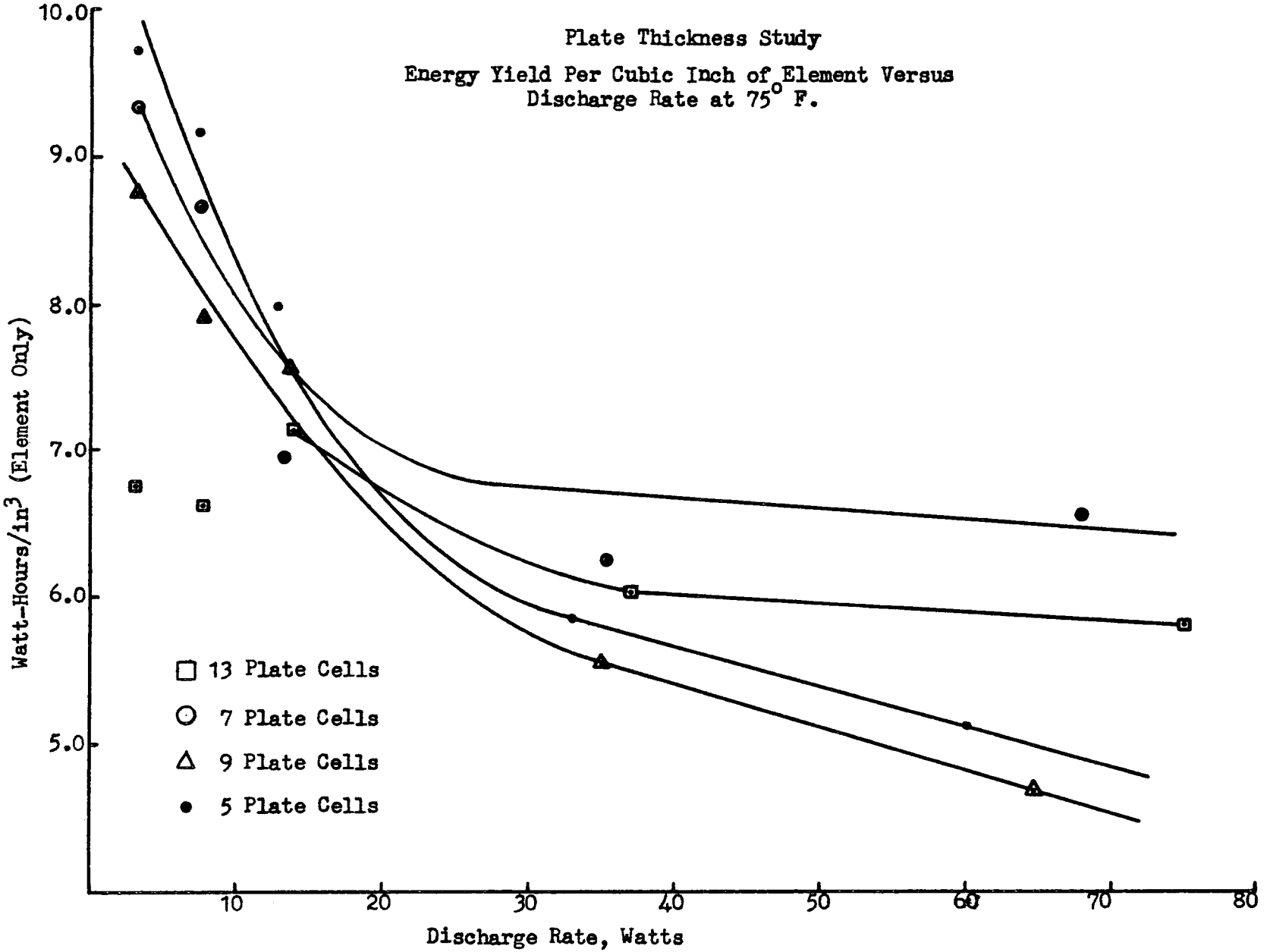


FIGURE 44

Plate Thickness Study

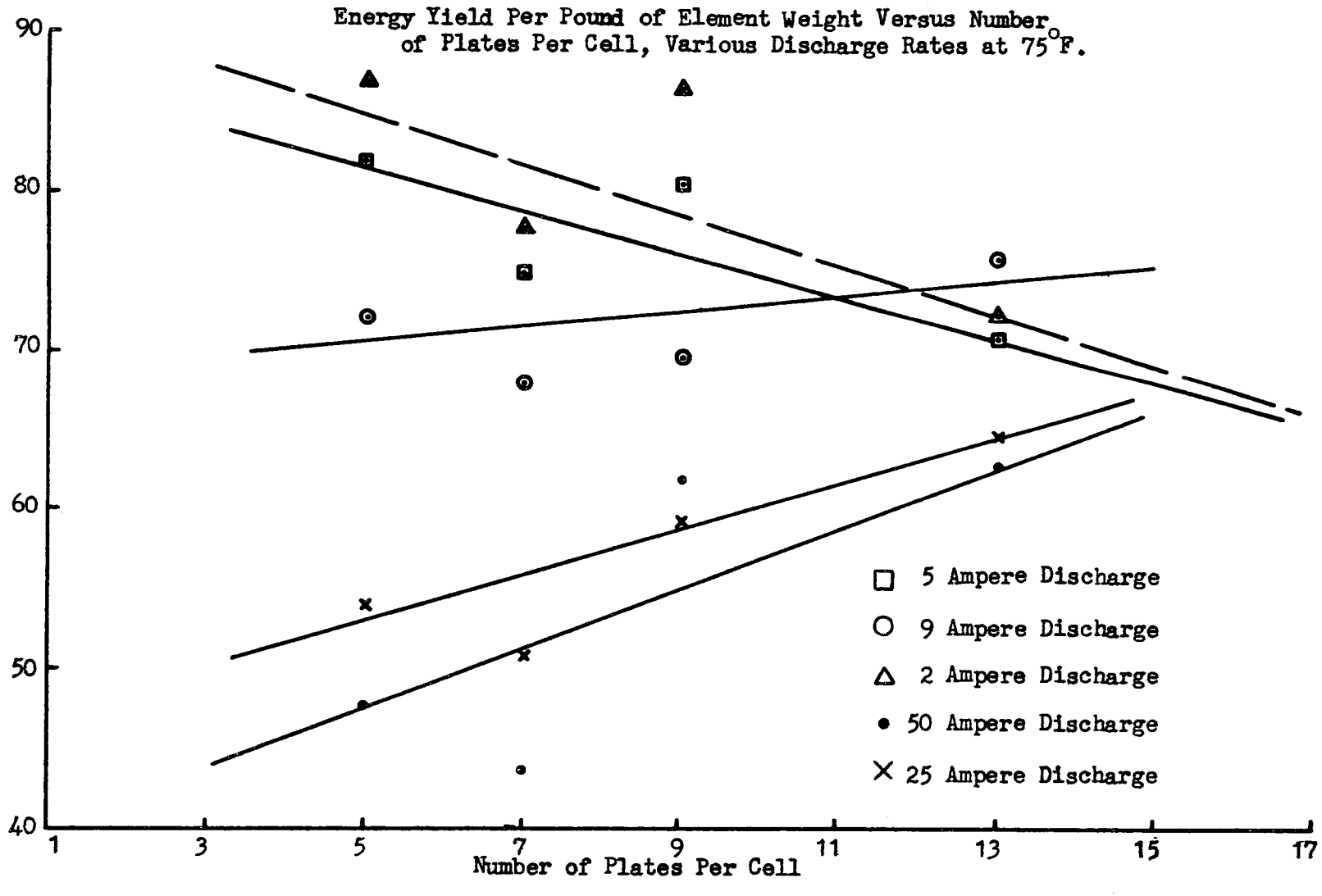


FIGURE 45

Plate Thickness Study

Cell Voltage as a Function For Various Plate Thicknesses and Discharge Rates

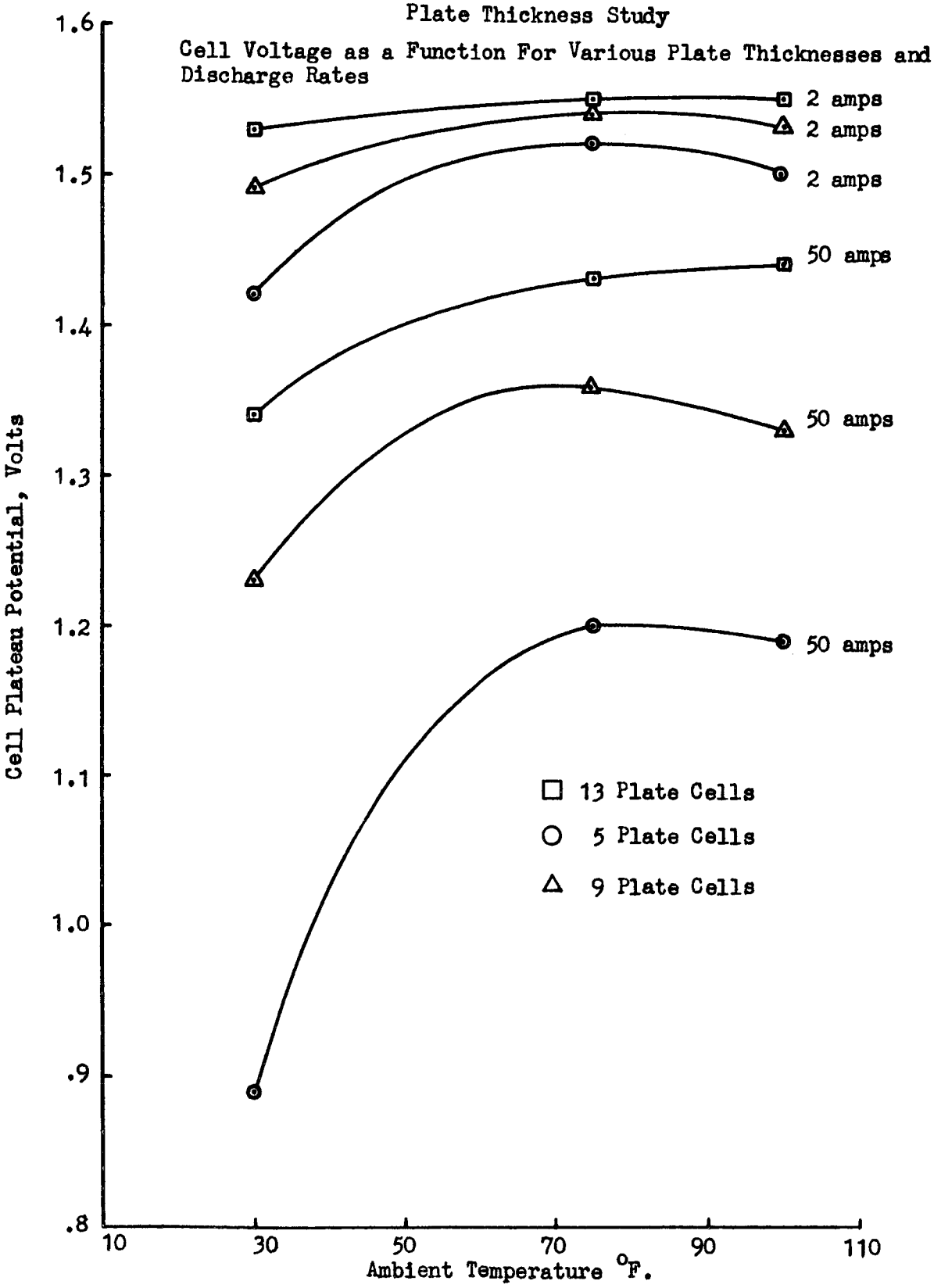
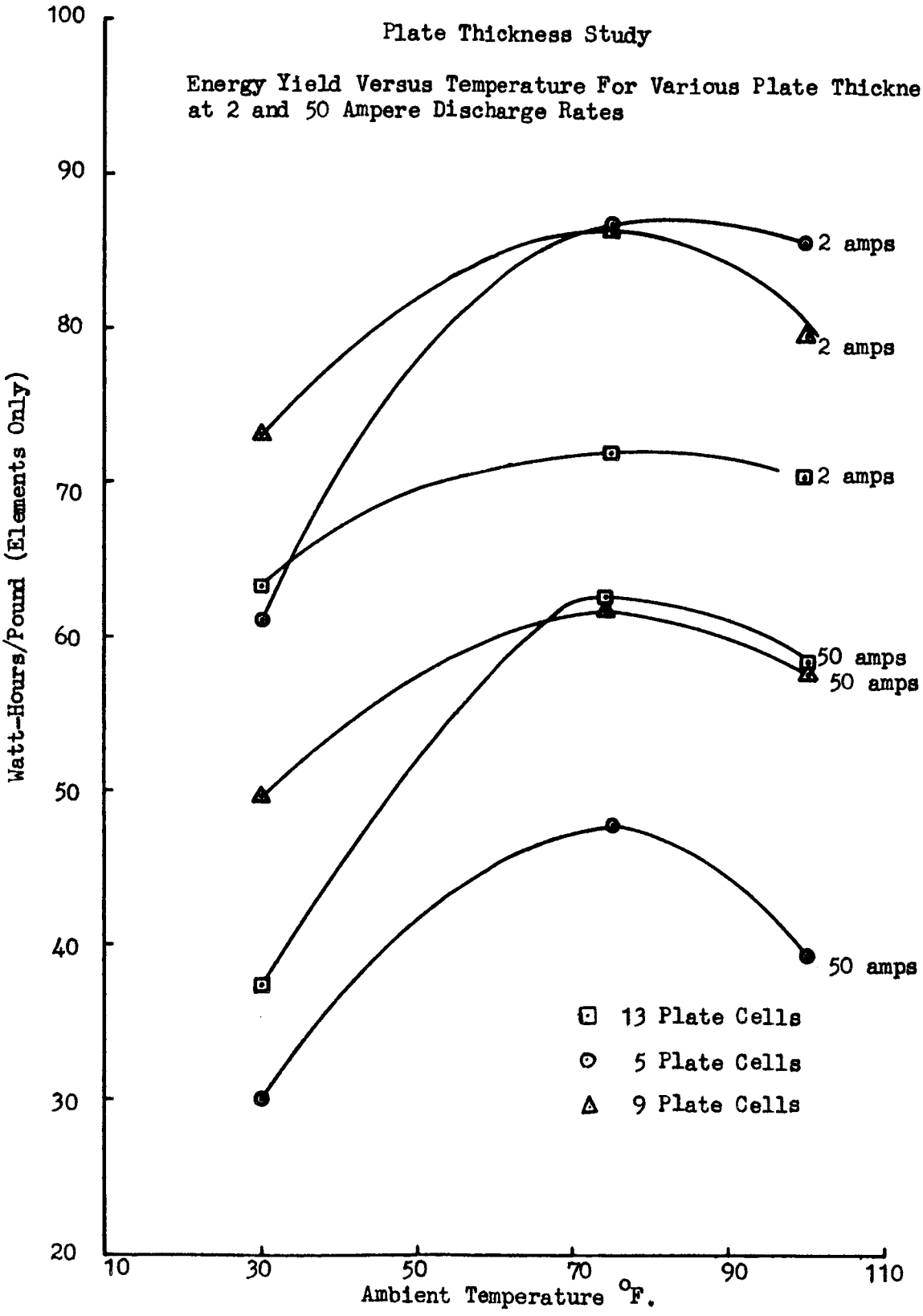


FIGURE 46

Plate Thickness Study

Energy Yield Versus Temperature For Various Plate Thicknesses at 2 and 50 Ampere Discharge Rates



APPENDIX I

SEPARATOR SCREENING TESTS

I. Separator Screening Tests

The development of procedures for determining resistivity, potassium hydroxide diffusion, and zinc dendrite growth through separator membranes were discussed in detail in Delco-Remy Report No. 4480-X, which was forwarded to J.P.L. with the proposal for the instant program; therefore, only brief explanations of these procedures are presented here. The results of screening tests performed on several types of membranes are discussed in detail in the Second Quarterly Progress Report of Delco-Remy's Air Force Contract[1].

A. Resistance Measurement in KOH

The resistance measuring cell and associated equipment are shown in Figure 1. The resistance cell consists of two lucite cells which were bolted together. A 1/8 inch diameter hole was in each of the half cells and the sample membrane was securely clamped between the half cells over the 1/8 inch holes. The cell was flooded with electrolyte from a plastic bottle through tubes in back of the cell. A current of 0.02 amperes was passed through the cell between cadmium "working" electrodes at opposite ends of the cell from an external D.C. power supply. The voltage drop between two standard reference electrodes (mercury/mercuric oxide) positioned via plastic tubes on each side of the membrane was measured with and without the membrane in place. Readings in millivolts were recorded with a Rubicon potentiometer. The blank reading was subtracted from the reading with the membrane in place and the resistance was calculated from differences in readings using ohm's law as in the following equation:

$$R = \frac{E_M - E_B}{I} \times A = \text{milliohms in}^2$$

where E_M = millivolts with membrane in place

(1) J. J. Lander, et al., Applied Research Investigation of Sealed Silver-Zinc Batteries, Contract Nr. AF33(657)-10463, Project Nr. 8173, Task Nr. 817304-21, November 19, 1963

E_B = millivolts blank reading

I = current in amperes

A = area of diffusion hole in^2

B. Diffusion of KOH Through Membranes

The apparatus used for determining the diffusion of KOH through membranes is shown in Figure 2. The diffusion of KOH through sample membranes was based on the rate of mass transfer through the membrane due to a high concentration gradient.

After soaking the membrane overnight in deionized water, the membrane was placed between 1/8 inch diameter orifices in the center of the flanges of the two cylindrical lucite cells, and the cells were bolted securely together. Approximately 230 milliliters of deionized water was placed in the left cell, and 230 milliliters of 45% KOH was added in the right cell. The cell was positioned over a magnetic stirrer and glass and calomel electrodes were inserted in the entry ports on the water side of the cell. The change in concentration of the deionized water was measured with a pH meter and recorded at five minute intervals for the first 20 minutes, then every ten minutes for 50 minutes additional. When the concentration is plotted versus time, a straight line results. Typical curves are shown in Figure 3. The slope of the curve is represented by $M = \frac{\Delta C}{\Delta t}$. Since the volume is known and the change in volume is negligible, the quantity of KOH passing through the membrane can be represented by $V \frac{\Delta C}{\Delta t} = \frac{\Delta M}{\Delta t}$, and since the area is known, the mass transfer per unit time and area is given by:

$$A \frac{\Delta M}{\Delta t} = \frac{\Delta C}{\Delta t} \times \frac{V}{A} = \text{moles KOH per square inch minute}$$

where M = moles KOH

t = time in minutes

C = concentration in moles/liter

V = volume of water in liters

A = area of diffusion orifice in square inches

C. Diffusion of Zincate Ions Through Membranes

The procedure for determining the diffusion of zincate ions through membranes was similar to the determination of KOH diffusion except the change in concentration of the zinc ion was measured potentiometrically, based on the fact that the electrode potential of the zinc/zinc ion couple at constant hydroxyl ion concentration varies by .0295 volts for every ten-fold change in zincate ion concentration.

The diffusion apparatus is illustrated in Figure 4. A disc of the membrane to be measured was cut and soaked in water for several minutes to swell the membrane. The sample was placed between the flanges of the cylindrical lucite cells with diffusion orifices of 2.33 in^2. The cell was bolted together and mounted on a magnetic stirring unit. Zincate free potassium hydroxide was added to the right side of the cell. A Hildebrand half cell for the mercury/mercuric oxide reference electrode and an amalgamated zinc indicator electrode were inserted in the entry port in the zincate-free side of the cell. Propane gas was used to blanket the cell to keep air out. The potential between the reference and the indicator electrode was observed a few minutes on a Sargent recorder on the 250 millivolt scale to see that the system was operating correctly. When the starting voltage was found to be steady, a standard one molar zinc oxide in 45% potassium hydroxide solution was added to the left side of the cell. Diffusion time was measured from the time at which the voltage trace on the recorder began to descend. Since the calibration curve for the potential readings was in moles per liter, the diffusion of zincate ion is given by:

$$M = \frac{C_1 - C_2}{t \times A} \cdot V$$

where M = moles in^{-2} min^{-1}

C_1 = initial concentration of zincate ion in moles/liter

C_2 = final concentration of zincate ion in moles/liter

t = time in minutes

V = volume in liters

A = area in square inches

D. Zinc Dendrite Penetration of Separator Materials

Since cell failure is often the result of short circuits due to the growth of zinc dendrites through the separator, an accelerated test was developed in an effort to qualitatively measure a separator material's resistance to penetration by zinc dendrites. A Hull cell manufactured by the R. O. Hull Company, Rocky River, Ohio was used in this study in order to evaluate a sample over a current density range on one test. The Hull cell was primarily designed to study the effect of current density in electroplating. The geometric configuration of the cathode end of the cell is such that when a current of one ampere flows through the cell, a current density range of 3.5 to 280 milliamperes is obtained across the face of the cathode. In the zinc dendrite test, both the anode and cathode were cut from .010 inch rolled zinc sheet. The separator material under test was wrapped around the zinc cathode and fastened on the back side with scotch tape. The cell was filled with a 45% solution of potassium hydroxide saturated with zinc oxide.

The test results were determined by visually observing the time of penetration of zinc dendrites through the separator material and the current density range. The maximum time the test was run was arbitrarily set at four hours. Qualitatively the most easily penetrated separator materials would be expected to fail first in cells because of shorts.

The Hull cell is shown in Figure 5.

Figure 1 Apparatus for Measurement of Membrane Resistance

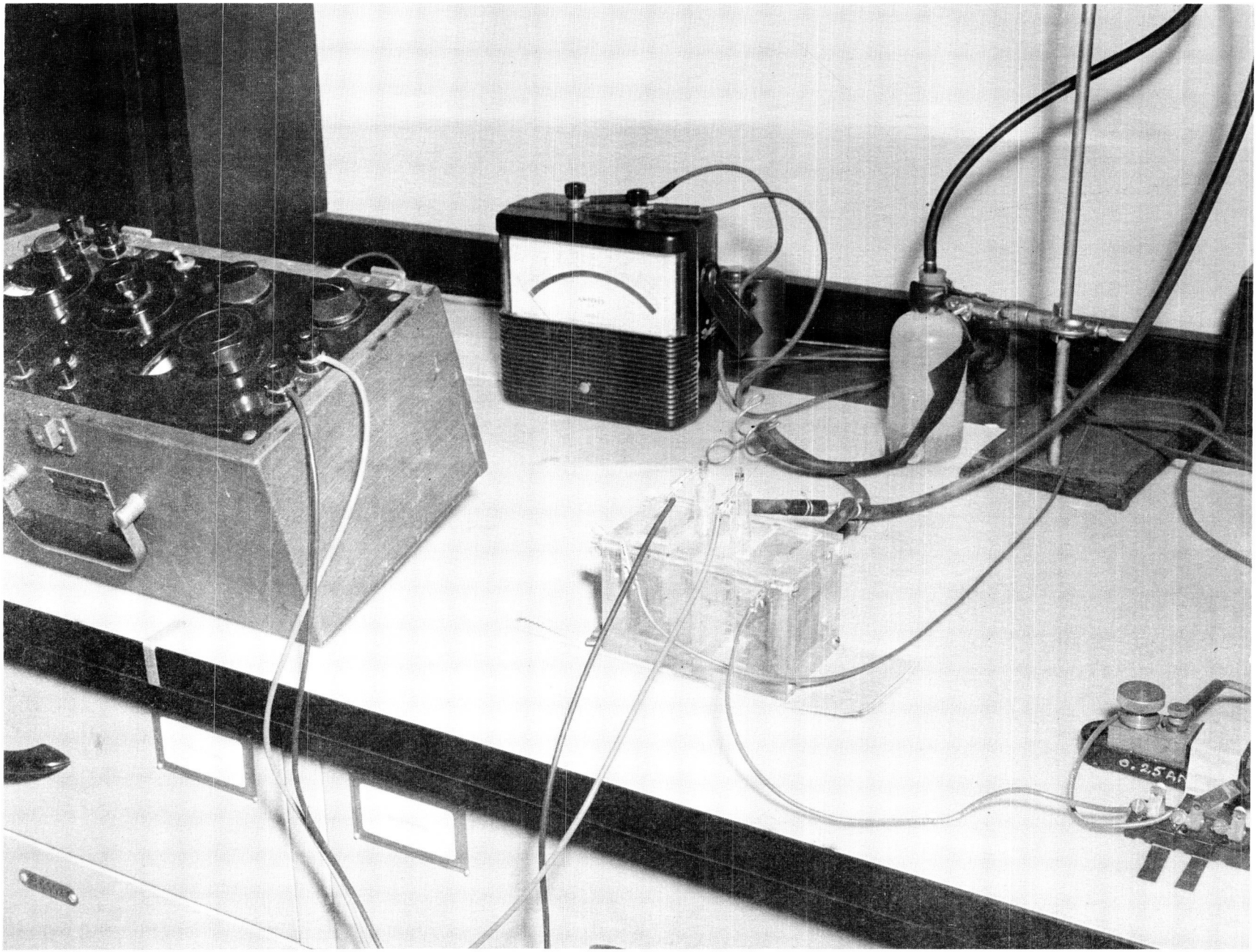


Figure 2 Apparatus for Measurement of KOH Diffusion

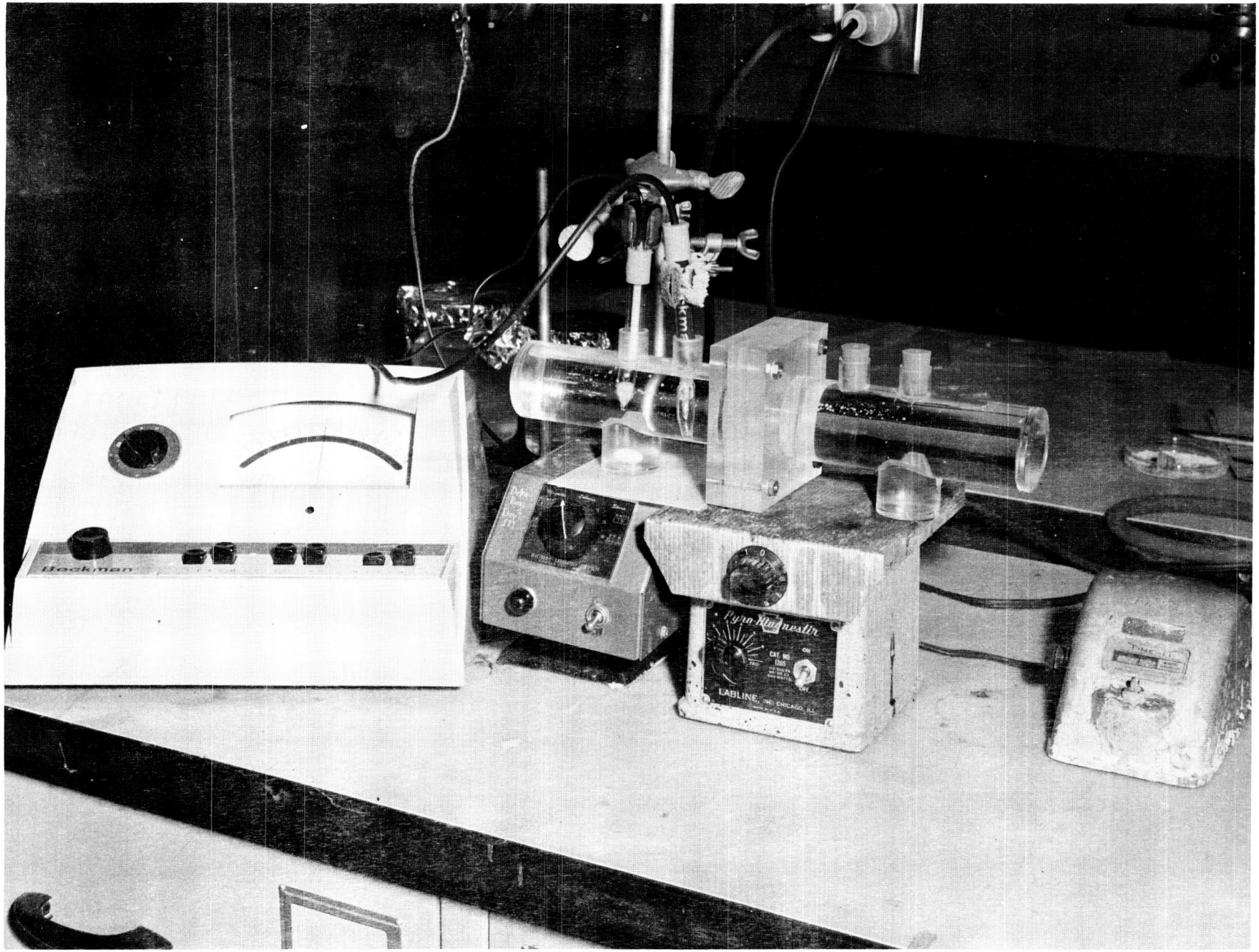


FIGURE 3

KOH Diffusion Curves

TFE-Acrylic Acid Graft

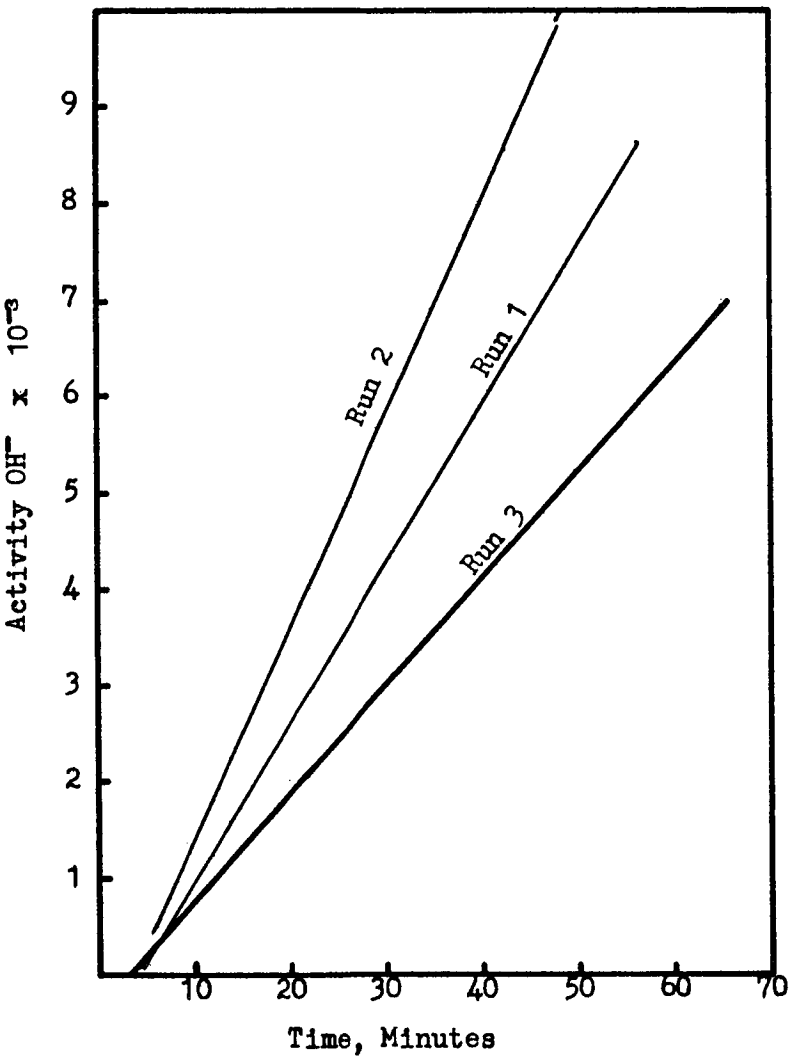


Figure 4 Apparatus for Measurement of $ZnO_2^{=}$ Diffusion

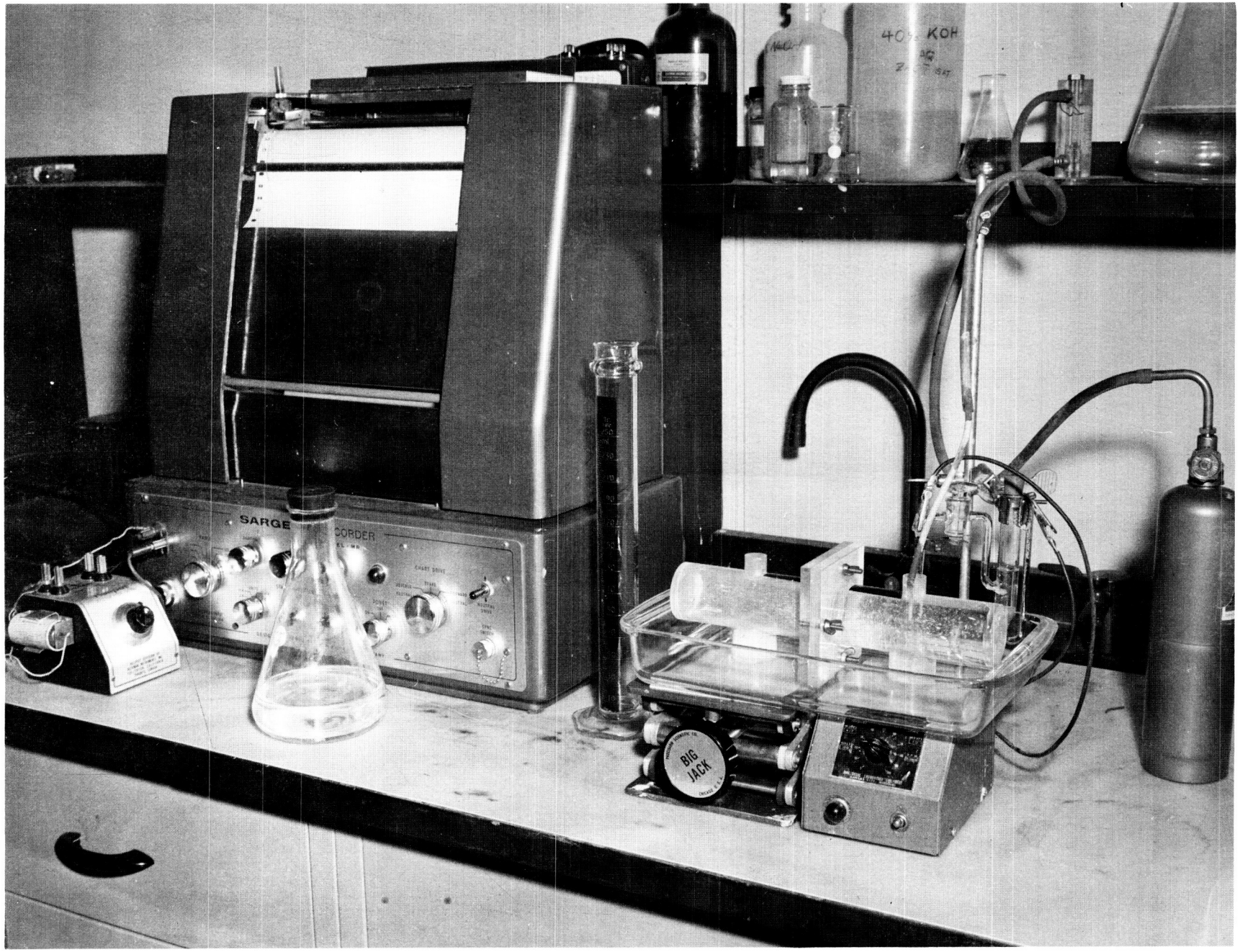
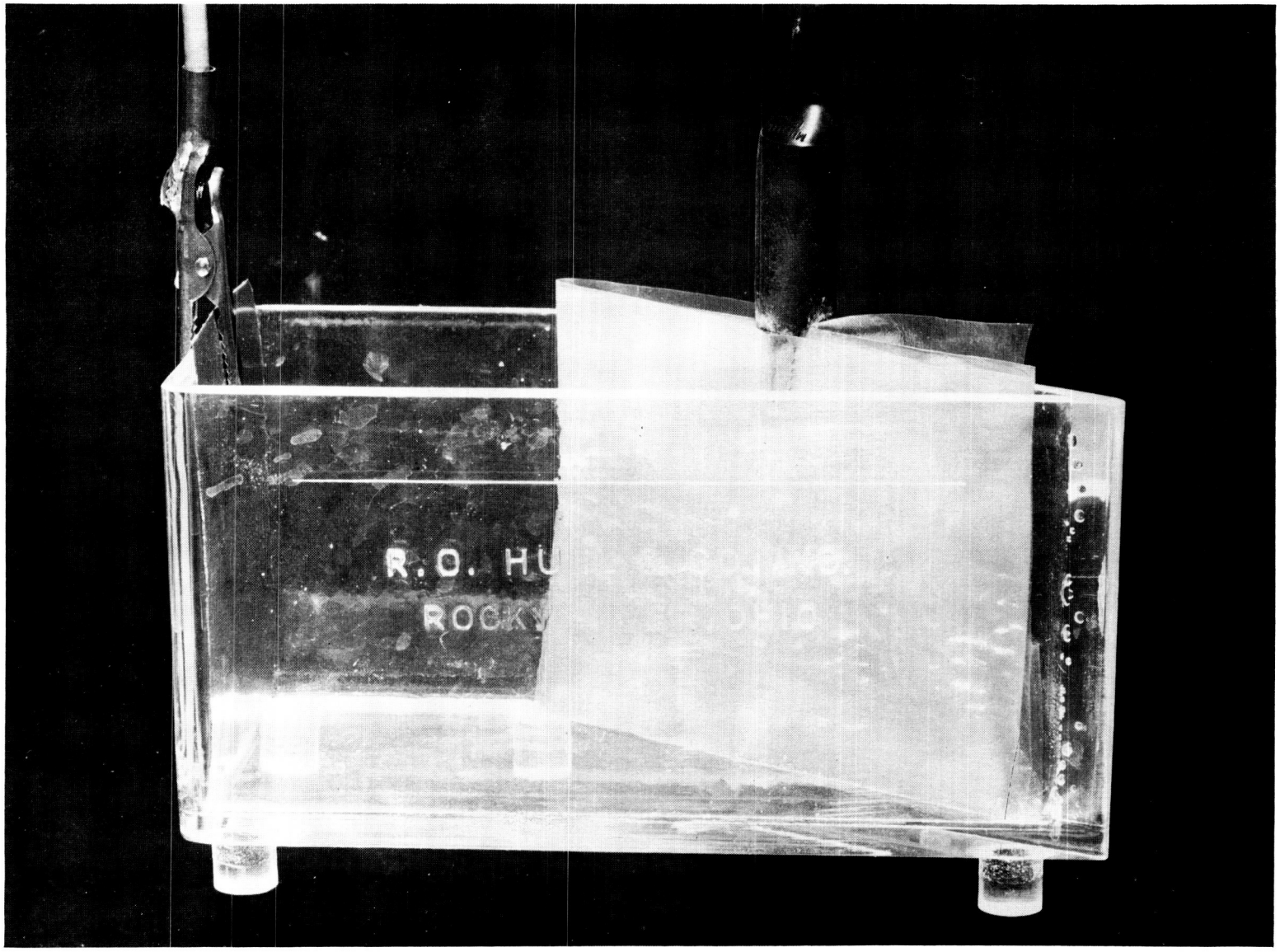


Figure 5

Hull Cell Used for Zinc Dendrite Penetration Tests



APPENDIX II

THE DEVELOPMENT OF SILVER-ZINC BATTERY SEPARATORS RESISTANT TO STERILIZATION TEMPERATURES

FINAL REPORT

Dated

July 10, 1964

The Development of Silver-Zinc Battery Separators Resistant to Sterilization Temperatures

DR-335423

JPL Study Contract 950364
Subcontract under NASA Contract NAS7-100

Prepared by:

Paul Scardaville
Radiation Applications Incorporated
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ABSTRACT

Five small screening sample membranes were prepared. Three of these samples were based upon Teflon TFE while two were based upon crosslinked high density polyethylene.

Methacrylic acid grafts and acrylic acid grafts of both the Teflon and polyethylene were prepared. Additionally, a sulfonated styrene graft based upon Teflon was prepared.

The electrical resistances, tensile strengths and exchange capacities of the membranes were measured both before and after a simulated sterilization. An infrared curve of each membrane also was taken before and after the sterilization.

All samples showed slight to moderate decreases in exchange capacity. Four samples showed slight to moderate decreases in electrical resistance but one sample, the methacrylic acid graft on crosslinked high density polyethylene, demonstrated an apparent increase in resistance.

No qualitative change was observed in the infrared curve of any sample.

Only one sample, the sulfonated styrene graft on Teflon TFE, became too brittle to handle after sterilization.

As a result of Delco-Remy's evaluation of these

screening samples, two 120 ft.^{2} samples were submitted. The materials selected by Delco-Remy for these samples were the two crosslinked polyethylene based samples.

1.0 INTRODUCTION

This report covers the first two phases of our program to develop silver-zinc battery separators capable of withstanding sterilization temperatures.

Using a radiation induced graft copolymerization technique to prepare samples, an attempt was made to determine the optimum membrane composition.

The base polymers studied were Teflon(TFE), chosen for its known temperature stability, and crosslinked high density polyethylene. The latter polymer, chosen because of its relatively high melting point, was additionally crosslinked to provide further dimensional stability at high temperature.

Three monomer systems were chosen. Methacrylic acid and acrylic acid were selected in order to discover which method of degradation, depolymerization or oxidation, might be the more critical under the sterilization conditions. Methacrylic acid, having a methyl group in place of the alpha hydrogen of acrylic acid is the more oxidation resistant. It is, however, more prone to thermal depolymerization than acrylic acid.

The third monomer selected was styrene. This monomer was grafted only to a Teflon base polymer. Sulfonation after grafting converts the polystyrene to polystyrene sulfonic acid yielding an ion conductive membrane.

This type of film was included because of the possibility that the weak acid membranes would be decarboxylated under the sterilization conditions. If the styrene sulfonic acid were desulfonated as well, it was anticipated that the product would be polyvinylphenol, which would have still provided a conductive membrane.

2.0 EXPERIMENTAL PROGRAM - PHASE I

2.1 Membrane Preparation

The preparative procedures developed to produce the required screening samples are listed in detail on the following pages.

Acrylic Acid Graft on Crosslinked High Density Polyethylene
(Sample #157-87)

Preparative Procedure

Materials:

A. 0.9 mil high density polyethylene (0.96 density)

B. Glacial acrylic acid

C. Toluene, benzene or xylene

D. Carbon tetrachloride

E. Paper toweling

Procedure:

1. Irradiate A under the beam of a 2 Mev Van de Graaff accelerator using 2 Mr/pass, until a total dose of 30 Mrads is accumulated.
2. Roll the irradiated A film in E.
3. Prepare a mixture of B, C, and D such that B = 25 pts., D = 10 pts., and C = 65 pts. by volume.
4. Immerse roll A - E in solution B - C - D.
5. Irradiate at 27,000 r/hr. for 72 hours.
6. Wash the film free of clinging homopolymer with 5% KOH, rinse in water and dry at 40°C. for 4 hours.

Methacrylic Acid Graft on
Crosslinked High Density Polyethylene
(Sample # 157-92)

Preparative Procedure

Materials:

A. 0.9 mil high density (0.96) polyethylene film

B. Glacial methacrylic acid

C. Toluene, benzene or xylene

D. Carbon tetrachloride

E. Paper toweling

Procedure:

1. Irradiate A under the beam of a 2 Mev Van de Graaff accelerator using 2 Mr/pass, until a total dose of 30 Mrads is accumulated.
2. Roll the irradiated A film in E.
3. Prepare a mixture of B, C, and D such that B = 30 pts., C = 60 pts. and D = 10 pts. by volume.
4. Immerse roll A - E in solution B - C - D.
5. Irradiate at 36,500 r/hr. for 72 hours.
6. Wash the film free of clinging homopolymer with 5% KOH, rinse in water and dry at 40°C. for 4 hours.

Acrylic Acid Graft on Teflon(TFE)
(Sample # 155-79-3)

Preparative Procedure

Materials:

A. Acrylic acid (glacial)

B. Toluene

C. 1 mil fusion cast Teflon(TFE) film

D. Paper toweling

Procedure:

1. Roll up C in D.
2. Prepare a solution of A in B such that the ratio is 18% A to 82% B by volume.
3. Immerse roll C - D in solution A - B.
4. Irradiate twenty-four hours at 42,900 r/hr.
5. Wash the film in 5% KOH to remove clinging homopolymer, rinse with water and dry at 40°C. for 2 hours.

Methacrylic Acid on Teflon(TFE)
(Sample # 155-85)

Preparative Procedure

Materials:

A. Glacial methacrylic acid

B. Toluene

C. 1 mil fusion cast Teflon(TFE) film

D. Paper toweling

Procedure:

1. Roll up C in D
2. Prepare a solution of A in B such that the ratio is 30 parts A to 70 parts B by volume.
3. Immerse roll C - D in solution A - B.
4. Irradiate 20 hours at 36,500 r/hr.
5. Wash in 5% KOH to remove clinging homopolymer and dry at 40°C. for 2 hours.

Sulfonated Styrene on Teflon(TFE)
(Sample # 155-79-5)

Preparative Procedure

Materials:

A. Polymer grade styrene monomer

B. Toluene

C. Methanol

D. 1 mil fusion cast Teflon film

E. Paper toweling

F. Chlorosulfonic acid

G. Chloroform

Procedure:

1. Roll up D in E
2. Prepare a solution of A, B, and C such that the ratios are 30% A:35% B:35% C by volume.
3. Immerse roll D - E in solution A - B - C.
4. Irradiate at 31,100 r/hr. for 24 hours.
5. Wash in benzene.
6. Repeat steps 1. through 5.
7. Prepare a 20% solution of F in G.
8. Treat the grafted film in solution F - G at 50°C. for 8 hours.
9. Wash in benzene, then in water and dry at room temperature.

2.2 Sample Testing

The effects of sterilization on the membranes were followed by measuring the electrical resistance, exchange capacity, tensile strength and physical dimensions before and after sterilization. The infra-red absorption curve of each sample was also taken before and after sterilization.

2.3 Sterilization

The sterilizations were performed in Teflon containers which in turn, were enclosed in stainless steel bombs.

The containers were filled with 45% KOH, the samples immersed and the bombs sealed. The bombs were then placed in an oven set at 145°C. for 48 hours.

2.4 Exchange Capacity

The exchange capacities of the samples were determined by the following procedure.

The test sample was first equilibrated 24 hours in a large volume of 0.1N HCl. The sample was then rinsed in deionized water and dried. The dry sample was then equilibrated 24 hours in a measured volume of standardized NaOH.

An aliquot of the NaOH solution in which the sample was equilibrated was then titrated with a known HCl solution. The decrease in the NaOH content of the solution is taken as equivalent to the number of exchange sites

on the sample.

The exchange capacity is expressed as:

$$\text{Exchange Capacity} = \frac{\Delta N_{NaOH} \times V_{NaOH}}{\text{dry wgt. of film}} = \text{meq/gm.}$$

2.5 Tensile Measurements

The tensile strengths of the samples were determined after 24 hour equilibration in 40% KOH. Dog-bone shaped samples, 3" x 1/2" in the neck area, were cut after the samples were equilibrated and the tensile strength measured on a Dillon Tester. The jaw speed used was 2"/minute.

2.6 Dimensional Changes

The areas of the samples equilibrated with 40% KOH were simply measured with a steel rule graduated in millimeters.

The results of these tests are listed in Table 1.

Table 1

Effects of the 48 hour Soak in 145°C. 45% KOH on Membrane Properties

Sample Composition	Resistance in 40% KOH milliohms-in^2 Before	After	Exchange Capacity meq/gm. Before	After	Tensile Data (Wet with 40% KOH) psi Before	After	Dimensional Changes cm. Before	After	Visual Changes
Methacrylic acid on TFE	40	35	2.7	2.5	2800	1100	3.0x3.0	3.2x2.5	None
Methacrylic acid on cross-linked high density Polyethylene	30	40	5.8	3.5	2600	2900	3.0x4.5	3.2x3.9	To opaque white
Acrylic acid on TFE	40	30	2.7	2.3	1250	900	13.0x3.9	12.5x3.9	None
Acrylic acid on cross-linked high density Polyethylene	70	60	4.1	3.7	5600	5000	3.0x3.0	3.0x3.0	To opaque white
Sulfonated styrene on TFE	60	40	1.3	0.9	2400	2000	3.0x4.0	3.0x4.0	To very brittle

Note: No qualitative changes in the I.R. curve were found in any instance

3.0 SUMMARY OF PHASE I

All samples show a decrease in exchange capacity. A decrease in resistance was found in all but one case. The probable result is that the effective pore size increases slightly due to fragmenting off of portions of the grafted chains.

The Teflon samples all exhibited significant losses in physical properties. The sulfonated styrene graft on Teflon showed the most drastic loss of elasticity. This is probably due to degradation during the radiation grafting step. Small, grafted, (poly)-tetrafluoroethylene chain fragments are probably leached out during sterilization.

As a result of these data and their own evaluation, Delco-Remy selected the acrylic and methacrylic acid grafts on crosslinked high density polyethylene for further evaluation.

These were reproduced as 120 $ft.^2$ samples. The test data for these samples are presented in Section 4.0.

4.0 PHASE II - PREPARATION AND TESTING OF THE 120 FT.^{2} SAMPLES

Procedures 157-87 and 157-92 (Section 2.0) were adapted to large scale production procedures.

The membranes were tested by taking samples from either end of the membrane, prior to washing and drying. These were then washed and dried along with the larger samples.

The pieces taken from either end of the long samples were then tested using the same procedures as described in Section 2.0 of this report. These data are presented in Table 2.

5.0 SUMMARY - PHASE II

The large scale samples were reasonable reproductions of the smaller samples.

Table 2

Effects of 48 Hour Soak in 45% KOH at 145°C. - 120 Square Foot Samples

Sample Composition	Resistance in 40% KOH milliohms-in^2 Before	After	Exchange Capacity meq/gm. Before	After	Tensile Data psi Before	After	Visual Changes	Changes in I.R.
Methacrylic acid on cross-linked high density Polyethylene	75	45	5.0	3.0	3700	3900	Became opaque white	No qualitative change
Acrylic acid on cross-linked high density Polyethylene	55	25	4.8	4.2	4700	3200	Became opaque white	No qualitative change