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NICKEL-CADMIUM GUIDED MISSILE BATTERIES

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In discussing the performance characteristics under various operating conditions of sintered plate nickel-cadmium batteries of the Nike and Corporal types, I would like to start with the Nike battery, since its development predates that of the Corporal battery.

In March 1951, under a Signal Corps contract with the Sonotone Corporation, an investigation was undertaken to develop a battery which would serve as the power supply for the Nike guided missile. This battery was to be capable of 15 minutes of operation within the voltage range of 28 V $\pm$10% when discharged through 2.8 ohms. This performance was to be obtained under severe conditions of shock and acceleration and at high altitudes, as well as after long periods of discharged storage and float. As with most guided missile components, the reliability requirement for the battery was very high, since no more than one missile failure in a thousand could be tolerated. It was felt by the Signal Corps that the sintered plate nickel-cadmium system could best meet the high reliability and long float charge requirements on the Nike battery and therefore this system was selected for development.

In January 1952, ten months after the start of the development contract, regular production of the battery was initiated by the Sonotone Corporation. For several months thereafter (approximately January thru May 1952), both development and production models were produced. The battery, bearing Signal Corps nomenclature BB-401/U, is presently being produced by both the Sonotone Corporation and the Eagle-Picher Company. It consists of 24 cells connected in series, each cell having a nominal capacity of about 3.5 - 4.0 ampere hours at the 5 hour discharge rate.

The cell cases are molded from Bakelite C-11, a transparent plastic, and are assembled in a steel case which has been made corrosion resistant by the application of a special paint. A transparent plastic protective shield above the cells, and slots or windows cut in the sides of the battery allow for some inspection of the individual cells. With the exception of the upper post terminal nuts, which are nickel-plated steel, all the battery hardware, such as plate straps, terminal posts and inter-cell connectors, are made of pure nickel. This was done to minimize the presence of iron within the cells which might prove harmful. Each cell contains nine plates, 5 positive and 4 negative, all the plates having a thickness of approximately .025". The separator used is a combination of one sheet of cellophane sandwiched between two sheets of nylon parachute cloth and the over-all separator thickness is approximately .010". The electrolyte is a solution of potassium hydroxide having a specific gravity of about 1.300.

Since 1952, when production of the Nike battery began, the Signal Corps Engineering Laboratories have tested approximately 200 sample batteries to

determine their ability to meet specification requirements. The test procedure involves a series of 5 initial tests followed by two delayed tests. All sample batteries are given the initial tests and then half of each sample lot are placed on a 2 year discharged storage test and the other half on a 1 year float test. The initial tests are started within 30 days and completed within 60 days after their receipt at these Laboratories. The series of initial tests is as follows:

a. VISUAL AND MECHANICAL INSPECTION

This test is run to determine that the dimensions, markings and workmanship are in accordance with specification requirements.

b. FULL CHARGE CAPACITY DISCHARGE

In this test, the batteries are charged at 37.4 ±1% V. (1.55 V/cell) for 8-16 hours at room temperature. By the way, all charges with the exception of the float charge, are carried out in this manner. After the charge, the batteries are discharged thru a fixed resistance of 2.8 ohms to a cut-off voltage of 25.2 volts. No difficulties have been encountered in the batteries meeting the requirement of 15 minutes discharge time under this test.

c. SIMULATED ALTITUDE TEST

After the batteries are charged, they are placed in a chamber, half of them upright and half in an inverted position. The chamber is then evacuated to a pressure simulating altitude of 100,000 feet. The batteries are then discharged at the reduced pressure. Although virtually all the free electrolyte drains out of the inverted batteries, both the upright and inverted batteries have always met the 15 minute specification requirement.

d. HIGH TEMPERATURE TEST

After charge, the batteries are allowed to stand at 125 ±2°F for 12 hours and then discharged at this temperature. Here again, half the batteries are discharged in the inverted position. The batteries have had no difficulty passing this test.

e. SHOCK AND ACCELERATION

After charge, the batteries are subjected to the following series of shocks and accelerations:

(1) A 50 g acceleration for 3 seconds, followed by a 3 g acceleration for 26 seconds, followed by a 100 g shock for 6.5 milliseconds all along the axis perpendicular to the ends of the battery.

(2) A 10 g acceleration for 150 seconds followed by a 100 g shock for 6.5 milliseconds along the axis perpendicular to the sides of the battery.

(3) A spin at 600 rpm for 10 seconds about the axis perpendicular to the top of the battery.

Following this sequence of shocks and accelerations, the batteries are given the normal discharge through 2.8 ohms. Although all the batteries have

met the 15 minute requirement on this test, many cell cases cracked, due to the shocks imposed and consequently most of the free electrolyte was lost from these cells during the spin test. When cracked cells occurred, the delayed tests could not be performed on the batteries and therefore, the shock and acceleration test was moved to the end of the test program. This occurrence of cracked cases has since been greatly reduced by increasing the length and width of the steel case and by inserting a neoprene rubber liner between the cells and the walls of the steel battery case.

f. DELAYED TESTS

(1) The first delayed test is a 2 year discharged storage test. The batteries are first discharged through 2.8 ohms to 0 volts and then stored for varying periods at temperatures ranging from -80°F to +160°F.

Following storage, the batteries are given the normal charge and discharge. No failures have resulted from this test.

(2) The other delayed test is a one year float test. After a normal charge, the batteries are floated at 33.6 ±.3 V (1.4 V/cell) at 75 ±7°F and 50 ±5% R. H. for 1 year. Every 3 months cell electrolyte levels are checked and if the levels are low, they are adjusted with distilled water to the bottom edge of the windows in the battery case. Following the float period, the batteries are given the normal discharge. Many of the early production batteries failed this test, due to the development of one or more internally shorted cells during the float period. These shorts were caused by contamination of the cells with copper and/or silver. Early in the production of the batteries, it was found that copper inclusions were getting into the sintered nickel plaques during manufacture, and steps were taken to prevent this. Following this, however, copper and silver appeared as contaminants as a result of welding with electrodes of these materials. In the batteries presently manufactured, nickel or nickel-plated electrodes are being used for welding and the occurrence of shorted cells has been practically eliminated.

In 1952, a test program was set up at SCEL to obtain data which would help to establish the performance to be expected from Battery BB-401/U immediately prior to actual missile use, that is, after manufacture, shipment, preparation and maintenance for use. Approximately, 440 batteries manufactured between July 1952 and June 1953 were obtained for this test. The batteries were tested under the following conditions:

(a) Shock
(b) Acceleration
(c) Vibration
(d) Charged Storage
(e) Discharged Storage
(f) Float

In this program, the battery was again given a shock of 100 g for 6.5 milliseconds. However, each battery was subjected to 9 of these shocks, 3 each along each of the three mutually perpendicular axes. The battery was discharged for one minute before the first shock, for one minute after the first 8 shocks and following the last shock, the discharge was continued to the cut-off voltage of 25.2 volts. The acceleration on each battery test consisted of a 50 g acceleration for 3 minutes, along each of three mutually perpendicular axes.

The battery was discharged during, and subsequent to the 9 minutes of acceleration. In the vibration test, each battery was given a horizontal vibration for 5 minutes along each of the three axes. The vibration frequency was uniformly varied from 10 to 50 to 10 cps every 2.5 minutes and the axial excursion was 0.060". The batteries were discharged throughout the course of the vibration period. During the shock and vibration tests, the batteries were in the metal battery box in which they are housed in the missile. Of the 36 batteries subjected to the shock test, all passed the specification requirement of 15 minutes, with the average discharge time being 18.9 minutes. Twelve batteries were subjected to the acceleration test and all but one battery, which gave 12 minutes, passed the test. The average discharge time was 18.8 minutes. In the vibration test, all 13 batteries passed and the average discharge time was 18.8 minutes. The data for the three mechanical tests was sufficiently consistent and reproducible to conclude that no battery failures which would affect missile performance would be anticipated under the conditions of these tests.

Discharged storage tests were run from 1 week to 3 months at -40°F, for 6 months at 0°F, for 9 months at 32°F, for 6 to 24 months at 80°F, for 1 week to 3 months at 125°F, for 1 week to 3 months at a temperature varying between -80 and +80°F, and for 1 week to 3 months at a temperature varying between +80 and +160°F. Out of 46 batteries tested under these varying conditions of discharged storage, all but one met the specification requirement and the average discharge time was 19.4 minutes. The one failure gave 14.5 minutes. It is therefore evident that storing the batteries in a discharged condition prior to use should not cause any battery failures.

Charged storage tests were conducted for periods up to 12 months at 0°F, 32°F, and 80°F, and up to 1 month at 125°F. Of a total of 34 batteries given the charged storage tests, only 13 passed the 15 minute specification requirement. The results were inconsistent and the retention of charge vs. time at any temperature did not seem to follow the expected pattern. Though the reasons for this are not definitely known, it is believed that they were not associated with the basic electro-chemistry of the system, but rather with mechanical faults in the battery construction which can, and in most cases have been, corrected.

Float tests at 33.6 $\pm$ .3 volts were conducted for periods up to 9 months at 32°F, up to 24 months at 80°F, up to 18 months at 100°F and to 12 months at 125°F. Out of 139 batteries tested here, 71 gave less than 15 minutes discharge time. However, 52 of these failures occurred at 100 and 125°F where difficulties were encountered in controlling the temperature of the cabinets in which these tests were conducted. In many cases fusion of the cell containers was observed, indicating that the temperature of the cabinets reached 200°F or higher. As with the specification testing previously described, many failures were due to shorted cells resulting from copper and silver contamination.

In summarizing the results of the test program conducted at SCEL, it is apparent that the incidence of battery failure is much greater for charged storage and float tests than for discharged storage and mechanical tests. It appears that these two conditions permit battery faults such as internal shorting and cracked cases to become overt. Elimination of the causes of these faults have improved the battery reliability during charged storage and float.

The battery for the Corporal missile power supply was designed in the early part of 1954 under an Ordnance missile contract. SCEL was given the responsibility of preparing the specification and procuring the battery. The battery

was required to give 6 minutes of operation when discharged at 18 amperes to a cut-off voltage of 18.3 volts and the voltage was not to exceed 20 volts after 2 minutes. The missile power supply actually consists of six of these batteries connected in series so that the nominal voltage is 115 volts. Four of the batteries are designated as BB-406/U and the other two as BB-407/U, the only difference being that the brackets used for mounting the batteries in the missile are placed in a different position on the steel outer battery case. Production of the batteries was started by the Sonotone Corporation in July 1954 and by the Nickel Cadmium Battery Corporation in January 1955.

The battery consists of 16 cells whose internal construction is essentially the same as that of the Nike cell except that each cell contains 21 plates and has a nominal capacity of about 5 ampere hours. The cells are housed in a steel battery case and cover. Felt pads are cemented to the inside surfaces of the case and cover to cushion the cells and also to absorb any electrolyte which may leak from the cells. The first felt pads were made of cotton but were changed to nylon which is much more alkali-resistant. Unlike the Nike battery which has a heater wrapped around the outside of the battery case, the heater forms an integral part of the Corporal battery and is embedded in the felt padding inside the battery case. It maintains the battery at a temperature of about 100°F, whereas the Nike heater is used to keep the battery above 40°F. The Corporal heater was originally made of aluminum, but this was changed to stainless steel because the aluminum was not resistant to the potassium hydroxide electrolyte.

The Corporal battery is required to be charged in two hours. In the field, six batteries are charged in series. The charger used charges the batteries essentially at a constant current of 3 to 4 amperes until a potential of 138 volts is reached. At this point, the charge current drops rapidly until a cut-off voltage of between 142 and 145 volts is reached. After cut-off, the charging current remains at about 100 milliamperes. The batteries are not maintained at full charge in the missile by continuous floating as is done with the Nike battery because the high current of 100 milliamperes, particularly at a temperature of 100 F would rapidly dry out the battery. Instead the batteries are booster charged while in the missile every 4 days for a period not to exceed 60 days. If the missile is not fired in this time, the batteries are removed for any conditioning and maintenance that may be necessary. Subsequent to this, they may be returned to a missile.

One of the early major problems encountered with the Corporal battery was the high occurrence of electrolyte leakage and cracked cells during shipment. It was found that one of the main causes of the leakage and cracked cells was the fact that the batteries were shipped in a shorted condition by the insertion of a shorting plug in the cannon connector on the outside of the battery case. In shorting the battery, some of the cells were reversed, causing gassing. The gassing built up excessive pressures within these cells, resulting in the electrolyte being forced out and, in some instances, the expansion and cracking of cell cases. Cell cracking was most prevalent in the front row of four cells which were not as well supported as the other two rows of six cells. The placing of a steel band around the row of 4 cells greatly reduced the occurrence of cracked cases during shipment and operation. The removal of shorting plugs and the replacement of vent plugs with shipping screws during shipment has essentially eliminated leakage problems.

Another problem which was very prevalent in the field was the occurrence of excessive electrolyte spewage during charge, the spewage resulting in shorted

batteries, due to leakage paths across the top of the cells. An investigation at SCEL showed that after dumping all the free electrolyte from the cells, the batteries could be cycled at least 50 times and still meet the specification requirement of six minutes discharge time. It was therefore decided to dump the cells prior to charge. However, it was found that the cells did not readily dump because air locks developed in the narrow vent openings when the battery was inverted. To overcome this, SCEL designed a dumping tool to facilitate electrolyte removal.

In the specification testing of production batteries at SCEL, it has been found that acceleration, vibration and reduced pressure equivalent to 150,000 feet elevation do not affect battery performance. A high temperature, high humidity test, where the batteries are exposed to a temperature of 120°F and a 95% relative humidity has caused many battery failures, particularly with one manufacturer's batteries. In this test, the temperature and relative humidity are uniformly raised over an eight hour period to 120±5°F and 95±5% R.H., respectively. After soaking for 6 hours, the temperature is reduced uniformly over an eight hour period to 70±10°F, at which temperature they remain for an additional 2 hours. This cycle is repeated 3 times, after which the battery is discharged. Apparently, the high temperature, rather than the high humidity causes the battery failure because when the test is run at low relative humidity, the batteries still fail. The test conditions affect the battery voltage rather than the capacity since the batteries give their normal discharge time, but most of the capacity is obtained below the required cut-off voltage of 18.3 volts. The manufacturer is of the opinion that lowering the electrolyte specific gravity from 1.300 to 1.200 will overcome this deficiency and this point is being checked.

Most of the problems which have been encountered with production batteries for the Nike and Corporal missiles are in a large measure attributable to the extremely short time that was available for their development and production. This left no time for a pilot plant stage, at which point most of these difficulties would have normally been discovered and corrected. In spite of this, most of the causes for malfunctions have now been eliminated and present production models are giving very satisfactory performance under all operating conditions.

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PLASTIC CONTAINERS FOR LEAD-ACID STORAGE BATTERIES

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Complaints are continually coming in on damaged automotive storage battery containers although a very good grade of hard rubber is used in the manufacture of both the cases and covers. A recent survey and discussions with battery men in the field indicate that many batteries are damaged in removing the battery terminal while changing batteries. The heel of the wrench strikes the cover and in the operator's anxiety to remove the terminals, puts sufficient pressure on the cover to break it. Cases are further damaged by tightening the hold-down clamps too tight and by careless handling.

During 1952, discussions with plastic suppliers and fabricators revealed that it seemed that the art had advanced to the state where it was worthwhile to investigate its possibilities for use as an injection molded container. It was further decided that instead of experimenting with cases only, that the contract be awarded to a battery manufacturer who would be responsible for the design of the case, the battery and its operation. A contract was accordingly awarded, early in 1953, to the Electric Storage Battery Company. This contract contained some very severe requirements as far as impact strength, heat dislocation, low acid absorption and light weight were concerned. The requirements were set as a challenge to the plastic industry. As an example, it was specified that the case and cover should be capable of withstanding an impact resistance of 4.65 lbs. weight when tested on a prescribed impact tester at the following distances at these temperatures:

TEMPERATURE	DISTANCE DROP
-65°F	30"
80°F	48"

With the cases assembled into a battery, it shall be capable of being dropped, at room temperature, from a height of five feet on a concrete floor. The drop to be repeated four (4) times, all without damage, with:

(1) Battery hitting on one of its bottom corners.
(2) On a diagonal opposite bottom corner.
(3) On one of its top corners.
(4) On the diagonal opposite top corner.

The contractor contacted all major plastic suppliers and was advised that there was no plastic commercially available to meet these specifications. Several of these plastic suppliers worked with the contractor to develop a new plastic. Of thirty-five (35) of the original plastics investigated, five (5) were eliminated due to poor acid test; twelve (12) were not given any further consideration due to poor impact resistance; one (1) presented a molding problem; one (1) heat distortion was unsatisfactory, and the remaining sixteen (16) were re-evaluated. About this time, plastic suppliers came up with these recommendations:

(1) Bakelite suggested their QMS-152 and QMS-155.
(2) Monsanto suggested Lustrex LT.
(3) Dow suggested Q-764, a blend of styron 700 and styron 475. They also suggested nylon.
(4) Naugatuck Chemical Company suggested their Kralastic "J".
(5) The American Hard Rubber Company suggested:
    a. Koppers MC-185.
    b. Styron 700.
    c. Bakelite C-11.
    d. Kralastic "H".

Since Dow and Naugatuck did not include Styron 700 or Kralastic "H", these materials were eliminated from the American suggestion.

(6) Goodyear Rubber Company stated that they would not recommend their Plio-Tuf.
(7) GATX recommended Koppers MC-409.
(8) Mack Moulding furnished data on fiberglass filled with P-8 polystyrene.

In addition to the above, the contractor also evaluated Koppers HIP-249; Naugatuck Kralastic-2163; Hard Rubber Resin Rubber #1; Richardson's Implast; American Hard Rubber ACE-TUF "C"; and the Standard Ordnance hard rubber compound as a comparison.

Of all these materials, the most favorable were Bakelite QMS-155 and Naugatuck, Kralastic "J". Of these two, Kralastic "J" had the better impact resistance over a wider temperature range and came nearer meeting the contract requirements. The heat distortion of Kralastic "J" is not quite as good as Bakelite QMS-155 and does not meet the specified 200°F, but the container was so designed as to overcome this problem.

Upon selection of a material, the contract sub-contracted with Mack Moulding Company, Arlington, Vt., for the production of a mold and a quantity of 2HN containers and covers. The Prolon Company, Florence, Mass., was given the task of furnishing a mold and cases for the type 6TN battery.

Upon receipt of containers and covers, the contractor assembled batteries and conducted drop tests. It was found that the type 2HN battery could meet the prescribed requirements, but the 6TN, being twice the weight, caused heavy indentation in the case and the elements were damaged. These tests demonstrated that a perfect seal could be accomplished using Kralastic-Methyl Ethyl Ketone plastic to plastic seal and that the type 6TN battery requires a reinforcement at the corners to withstand the five foot drop test; also that the interior would be as rugged as the case.

The contract with Electric Storage Battery Company was, therefore, extended to improve the interior construction and reinforce the corners. At this point, there was considerable delay as Exide moved their operations from Fairfield, Connecticut, to the Willard plant in Cleveland, Ohio. There was further delay in procuring an envelope type plastic separator from England which will permit elimination of the bridge at the bottom of the cell and form a compact unit giving it the advantage of the Varley separator.

Sample batteries have been completed and are on test at the Detroit Arsenal Laboratories and the Willard Company, Cleveland, Ohio. Samples of both the 2HN and 6TN have been shipped to Rossford Ordnance Depot, Packaging Depot, for rough handling test and determination of the minimum packaging requirements for shipment and handling. Samples have also been furnished for climatic tests at Yuma and Churchill, as well as CONARC, Board #2, Fort Knox.

Complementary to the plastic battery case development, there is a project to determine the feasibility of packaging battery electrolyte in plastic containers and in packing the electrolyte in the same package with the battery.

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THE SILVER OXIDE-ZINC-ALKALINE SECONDARY TORPEDO PROPULSION BATTERY *

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This paper deals with the characteristics exhibited by the silver oxide-zinc alkaline secondary torpedo propulsion battery in both field and laboratory evaluation.

Before discussing the characteristics of the system, it is of interest to very briefly trace the history of electric torpedo batteries in this country and compare the ratio of energy to weight of the several electrochemical systems presently being used to provide propulsion power for torpedoes.

Work was initiated in this country on the development of the first electric torpedo in 1915. However, it was not until after the outbreak of World War II that intensive development finally culminated in the Torpedo Mark 18, which was the first electric torpedo released to the fleet. Power for this torpedo was provided by a lead-acid secondary battery, the Mark 2 Mod 0, which weighed 1220 pounds and supplied 720 amperes at an average voltage of 120 volts for 4 minutes. The battery thus provided 4.7 watt-hours per pound. During the next few years a series of lead-acid secondary batteries was developed which gave a slightly higher watt-hour per pound output but did not differ markedly from the original design. The rather low ratio of energy to weight obtainable was the principal shortcoming of electric torpedoes as it was approximately one-third of that obtainable from conventional steam torpedoes. With the advent of the longer running homing torpedo this low energy to weight ratio became an even more acute problem. The first real improvement in this regard came towards the end of World War II when a silver chloride-magnesium-sea water torpedo battery was developed. This primary battery delivered 38 watt-hours per pound which was approximately 8 times the energy per unit weight obtainable from the lead-acid Battery Mark 2 Mod 0. However, the high cost of this battery caused further development to be directed towards a lower cost primary battery for war shot use and a high energy secondary battery for exercise and ranging purposes. In the period between 1949 and 1953, the Electric Storage Battery Company developed what they termed their "SR" series of lead-acid secondary batteries. Through the use of

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*This paper has been prepared for official use of the Department of Defense. No information concerning the performance of any item mentioned herein should be disclosed to any manufacturer or his representative.

electrolyte-retaining separators, high gravity acid, thin plates and finally lead plated copper screen grids, the energy per unit weight output of the lead-acid system was increased from 4.7 to 7.9 watt-hours per pound in the Battery Mark 32 Mod 3. This appears to be the practical limitation of the lead-acid system at the discharge rates used for torpedo propulsion.

Since the introduction of the Andre silver oxide-zinc cell in this country, it has been possible to obtain a marked increase in energy per unit weight and volume for secondary torpedo batteries. The first torpedo propulsion batteries utilizing this system were manufactured in 1951. One of these, the Battery Mark 37 Mod 0, weighed 390 pounds and supplied 470 amperes at an average voltage of 140 volts for 5 minutes. This battery thus provided 14.1 watt-hours per pound. Concurrent with this improvement in secondary battery performance, a silver oxide-zinc-alkaline primary battery was developed which gave approximately 30 watt-hours per pound at about two-thirds the cost of the original sea water battery design. More recent improvements in the manufacture of the sea water battery have reduced its cost so that the sea water and silver oxide primary batteries are now about equal in cost.

Figure 1 gives a comparison among the above mentioned systems on an energy per unit weight basis. It is to be noted that for the silver oxide-zinc secondary batteries a much higher watt-hour per pound output can be obtained if it is not desired to recycle the battery, as would be the case in an actual war-shot. When recycling is required the discharge of this type battery must be terminated at a time when the voltage is still above the normal minimum acceptable value in order to prevent overheating and destruction of the battery.

OPERATING CHARACTERISTICS

In discussing the operating characteristics of the silver oxide-zinc secondary torpedo battery system the maintenance which the battery requires will be described first and then the performance which has been obtained will be reviewed. Since the Yardney Electric Corporation is the only qualified supplier of this type battery at the present time, practically all the data to be presented was obtained from this manufacturer's batteries. Figures 2 through 5 are photographs of the various batteries which will be discussed.

Maintenance

Silver oxide-zinc secondary torpedo batteries are presently delivered by the manufacturer in the dry and uncharged condition. Table I illustrates the operations and time required to prepare a battery for service.

TABLE I

OPERATIONS REQUIRED TO PREPARE A SILVER OXIDE-ZINC TORPEDO BATTERY FOR SERVICE

Operation	Time Required
Fill with electrolyte	2 to 7 hours
Soak	48 hours
Initial Charge	8 to 22 hours
Discharge (high rate)	0.1 hour
Discharge (low rate)	2 hours
Stand	2 hours
Charge	8 to 20 hours

Battery is now ready for service.

If an 8 hour work day is assumed for all operations which require personnel in attendance, it requires five to ten days from the time filling is started before a battery is available for use. Field reports have indicated that this one to two week period is a handicap in the preparation of schedules for the use of torpedoes. The probable answer to this problem is to call for delivery to be made with the batteries in the charged and dry condition. Torpedo batteries have recently been manufactured in this condition and an evaluation is underway to determine the ability of these batteries to stand in the dry condition for reasonable periods of time and still give a satisfactory discharge without being charged after filling. This practice would require approximately two days for preparation.

Charging of torpedo batteries is performed at a constant current rate of about three to five amperes. Figure 6 illustrates the typical two plateau charging curves exhibited by silver oxide-zinc batteries. On the initial charge approximately 20% of the charge is made on the lower plateau. As cycling proceeds, more of the charge is given at this lower level until at the end of cycle life approximately 35% of the charge is given before the rise to the second plateau takes place.

Termination of charge is based on a battery voltage cut-off value equal to 2.02 volts multiplied by the number of cells in the battery. Termination of charge on this basis usually results in discharge to recharge efficiencies of very close to 100%. Some charges will not quite return to the battery the ampere-hours removed on the previous discharge. It is impossible to terminate charge on the basis of an input equal to say 110% of the previous output, as in field usage the ampere-hours removed from a battery during an actual torpedo run will be unknown. Further this method of termination does not take into account any loss due to self-discharge on the previous charged stand.

As the cycling of a battery progresses, the individual cells tend to become unequal in their state of charge and therefore reach the 2.02-volt value at considerably different times. This inequality is brought about by a number of factors such as differences among cells in self-discharge rate, charge acceptance, etc. Since the charging voltage curve rises rather steeply as it passes thru 2.02 volts, several high cells can cause the battery voltage to reach the cut-off value before all the cells are fully charged. A similar problem is solved in the lead-acid system by simply overcharging until the lowest cell is brought up to full charge. However, overcharge of a silver oxide-zinc battery is harmful to both the separator and negative plate. Therefore in order to equalize cells as much as possible, a low rate discharge is performed after every fourth normal high rate discharge. The low rate or equalizing discharge is made thru a constant resistance and is terminated when the battery voltage falls within the range of zero to two volts.

The manufacturer's instructions state that no water or electrolyte shall be added to the cells at any time after the cells are initially filled with electrolyte. Under normal temperature conditions no appreciable loss of water has been noted in cells which have delivered approximately 20 cycles over a five to six month period after filling.

Discharge Characteristics

The silver oxide-zinc secondary battery is used for exercise torpedo runs and is usually replaced by a primary battery for war-shots. In order to obtain optimum cycle life in exercise use, it is not possible to obtain all the usable capacity from a battery on each cycle. The discharges must be terminated at about 50 to 60% of rated capacity in order to prevent excessive overheating which will destroy the cellulosic plate separation and distort the plastic cell cases. The battery temperature after a discharge terminated at the 50% point will rise to about 140°F while it will reach temperatures well above 200°F if the battery is completely discharged.

Figure 7 shows the range of discharge voltage curves obtained during the cycling of a Battery Mark 41 Mod 1 with all discharges being terminated at the 50% point. The initial discharge curve followed a little below the upper extreme of the range. As cycling progresses, the high initial peak disappeared and the voltage was actually at its lowest during the first half minute of a discharge. The entire discharge curve became lower on each succeeding cycle and reached the lower extreme of the range on the seventh discharge after which the discharge curves became higher and the initial high peak reappeared. The voltages reached a maximum on the fifteenth discharge and then tapered off slightly until a cell failure occurred on the twenty-third cycle.

The dependence of the discharge voltage on current density at two temperatures (80°F and 32°F) is shown on Figure 8. Discharges above 80°F tend to parallel the 80°F curve at a slightly higher voltage. Discharges made at 110°F were 0.05 volt per cell higher than the 80°F discharge.

During a 32°F discharge at current densities from 0.80 to 1.2 amperes per square inch, the initial closed circuit voltage may fall slightly below 1.00 volt per cell for one or two seconds but will be at least 1.03 volts per cell at five seconds.

Reliable performance can be expected at temperatures as low as 32°F. However, performance becomes very erratic at slightly lower temperatures. Batteries which gave excellent discharges at 32°F failed to give any usable capacity when tested at 10°F and very little capacity at 20°F. It is therefore evident that a battery heater is necessary for all torpedo batteries except possibly those which are submarine launched. Through proper design and location of the heater, rapid warm-up of the battery

can be obtained using very little externally supplied power. For instance, a 100-watt heater can raise the temperature of a 63 pound battery in a 0°F ambient to a satisfactory operating temperature (50 to 60°F) in approximately two hours.

Cycle Life

Present specifications require a minimum of ten cycles within 90 days after filling a battery with electrolyte. Laboratory tests have demonstrated that over 20 cycles can be obtained in a five-month period after filling. However, the number of cycles obtained depends on several factors such as the period of time over which the cycles are obtained. Several prolonged charged stands of 30 days or more will sharply reduce the cycle life. For instance, a Battery Mark 41 Mod 1 gave 22 cycles over a five-month period. The charged stand times ranged from one to three days on all cycles except for one 30-day charged stand. A second battery of the same type delivered only nine cycles over the same five month period. However, this battery was subjected to a 30-day charged stand early in the cycling and failed on the tenth discharge which was made after a 60-day charged stand. This battery did not recover capacity on subsequent discharges which were made after overnight charged stands.

Results obtained from field usage of batteries indicate that stand in the wet and discharged condition has the same effect on decreasing cycle life and that a battery probably has a "wet life" of approximately five or six months regardless of whether it is cycled once a week or allowed to stand in either the charged or discharged condition for prolonged periods of time on each cycle. Where field usage of batteries has entailed cycling without prolonged charged or discharged storage, cycle life has been found to be equal to that obtained in laboratory tests, i.e. approximately 20 cycles. However, if the silver oxide-zinc secondary battery is used in the field as a war-shot battery, cycle life becomes of less importance. In this type of application the battery is charged, installed in a torpedo and then maintained in the charged condition throughout a war patrol. After the patrol, if the battery had not been used, it would then of course be desirable to test and recharge the battery for a second patrol. However, due to the six month wet life limitation, present instructions call for the use of only freshly filled batteries for war patrols.

Charged Stand

Torpedo battery specifications require satisfactory operation after a 30-day charged stand at room temperature. The specifications require the same capacity after a 30-day charged stand as after an overnight stand. However, as was mentioned previously, the specifications only require about 50% of the initial capability of the battery so that the battery can actually lose 50% capacity due to self-discharge during the 30 days and still meet requirements.

Laboratory tests have demonstrated that batteries give reliable performance after two months charged stand at room temperature if the stand is given in the early stages of the cycling. As the "wet age" of the battery increases, its ability to give satisfactory capacity after a prolonged charged stand diminishes. Batteries have not as yet been subjected to charged stands of more than two months in laboratory tests.

An interesting field test of the ability of batteries to give satisfactory capacity after a six-month charged stand was made in late 1954. Fourty-eight "war-shot-ready" torpedoes using the Battery Mark 42 Mod 0 were issued to certain ships which were deployed for six months in the Pacific. Because of an insufficient quantity of properly prepared batteries at the start of the test period, 18 batteries previously used for exercise purposes were installed in some of the torpedoes prior to deployment. These batteries had been in the filled condition for three to five months prior to installation. The remaining 30 batteries had been filled and prepared in the proper manner immediately prior to issue to the ships. All torpedoes were stowed on the main deck of the ships during the six-month deployment; the reported temperatures ranged from 29°F to 105°F.

After the return of the ships the 48 batteries were removed from the torpedoes for inspection and discharge. Any battery having an open circuit voltage of less than 60.0 volts (1.82 volts per cell) was given a freshening charge before being discharged.

All 18 batteries which had been used in previous exercise runs required the freshening charge and all failed to give satisfactory capacity when discharged 12 hours after the freshening charge.

At the end of the six-month period only four of the 30 new batteries required a freshening charge as determined by an open circuit voltage check. Two of these four batteries failed to give a satisfactory capacity when discharged 12 hours after the freshening charge. The remaining 26 batteries all had acceptable open circuit voltages at the end of the deployment. Twenty of these were discharged without a freshening charge and gave satisfactory capacity.

Shock

In Laboratory evaluation, torpedo batteries have been subjected to single phase shocks of 50 to 200 g's of 0.040 to 0.100 second duration. It has been found that the shock resistance of the silver oxide-zinc secondary battery is excellent in this range of shock intensities provided the individual cells of the battery are supplied adequate external support. This support involves two factors. First, the individual cells must be tightly packed within the battery case. Any shimming which is necessary due to cell case dimensional variation should be done with rigid, noncompressible material. Second, the battery case must be properly supported by its mount within the torpedo. Figure 9 is a photograph of a Battery Mark 42 Mod 0 after being subjected to a shock of 186 g's and 0.040 second duration. The battery mount in the torpedo was not adequate in that it supported only the outer periphery of the end of the wooden battery case and allowed the mass of the battery to push thru the open center area of the support.

One minor but frequent objectionable effect of shock has been the cracking of the seal of the plastic cell cover to its case. If these leaks are not repaired they can result in electrolyte leakage on recharge and more rapid self-discharge during subsequent charged stand. It would appear that this fault could be easily remedied by modification of the cover seal. However, it is a point to which most battery manufacturers apparently give very little thought.

Tests at greater intensity of shock than the 50 to 200 g shocks mentioned above have been made on single cell units. Single phase shocks of 0.050 second duration and ranging in intensity from 100 to 1000 g's have been applied without any detrimental effects. For these tests each cell was mounted in a close fitting laminated phenolic resin box which gave adequate external support to the plastic cell case.

Shock tests have not been performed at temperatures other than normal room temperature. However, since an externally powered battery heater must be supplied to ensure satisfactory capacity, no low temperature problem is involved.

No battery failures have resulted from shock in actual field usage.

Vibration

Vibration of silver oxide-zinc batteries which have been filled with electrolyte does have a detrimental effect on their performance. The active material of the negative plate, which has poor cohesion and which is held in place primarily by the tightness of the plate assembly and the paper separator in which it is enclosed, sheds from the plate during vibration. The extent of this shedding depends to a large degree on the external support supplied to the individual cell. The actual vibration applied to the torpedo is magnified if the battery case is not rigidly mounted in the weapon and the individual cells are not securely anchored in the battery case. Figure 10 illustrates the extent of shedding caused by a three hour vibration at three g's in the ten to 60 cycle per second frequency range. In this instance the cells were not adequately supported in the torpedo. The two cells on the left were not vibrated and the sediment in the bottom of the cells is the normal result of cycling. The two cells on the right were subjected to the same number of cycles in addition to which they were vibrated. It can be seen that the vibration caused a considerable increase in shedding. Sufficient data is not available to determine quantitatively what latent effects this shedding of plate material has on the cycle life or stand characteristics.

Tests were conducted on single cells to determine if the effects of vibration could be minimized by modifying the external support of the cell. Single cells which were rigidly mounted to the vibration table showed no increase in sediment when subjected to the same vibration schedule.

No reports of battery failure due to vibration have been received from field activities. However, since the effect noted in the laboratory tests is internal to the cell it is not suprising that field reports have made no mention of it. No vibration tests have been performed to simulate transportation vibration prior to filling the batteries with electrolyte.

SOURCES OF SUPPLY

As was mentioned previously, the Yardney Electric Corporation is the only qualified supplier of silver oxide-zinc secondary torpedo batteries. Four other manufacturers - - American Machine & Foundry Company, Eagle-Picher Company, Electric Storage Battery Company, and Gould National Batteries, Inc. have submitted samples for evaluation.

American Machine & Foundry Company submitted five designs of the Battery Mark 39 Mod 0 between 1952 and 1954. Their initial submission exhibited very poor electrical characteristics in regard to cycle life, charged stand, and 32°F discharge performance. However, this manufacturer made relatively rapid improvement in design, and the latest submission met all electrical requirements but failed to meet the center of gravity and weight requirements. The AM&F Co. batteries, while not quite meeting all requirements, are considered second to Yardney in performance of the type required for torpedo use.

The Electric Storage Battery Company has submitted numerous samples of various Marks and Mods from 1949 to the present time. None of these batteries met all electrical requirements. Cell unreliability and poor charged stand characteristics are the principal shortcomings at the present time.

Gould National Batteries Inc. and Eagle-Picher Company have each made one submission for evaluation in the past two years. The batteries of both these manufacturers exhibited poor charged stand and cycle life characteristics.

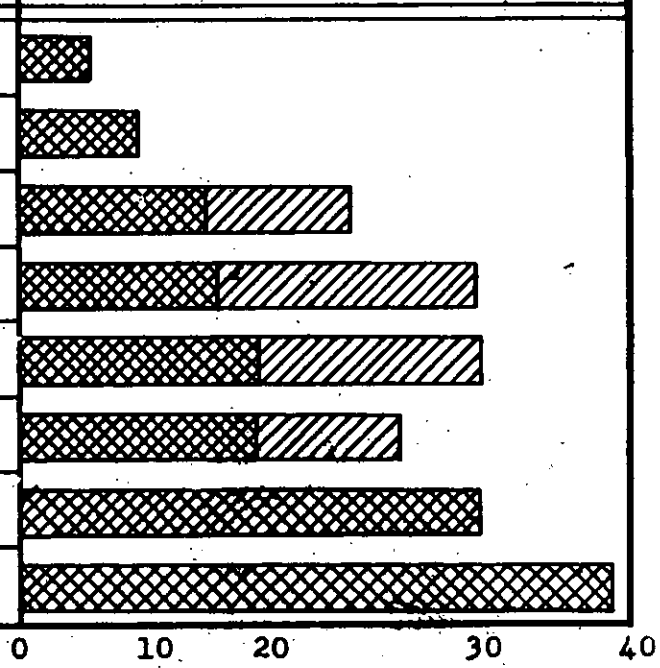
25 August 1956
(Date)

Released by the Commander, Naval Ordnance Laboratory, White Oak, Maryland, for government use only.

Mary T. Kanagy
MARY T. KANAGY
Technical Information Office

COMPARISON OF TORPEDO PROPULSION BATTERY SYSTEMS
ON THE BASIS OF ENERGY PER UNIT WEIGHT

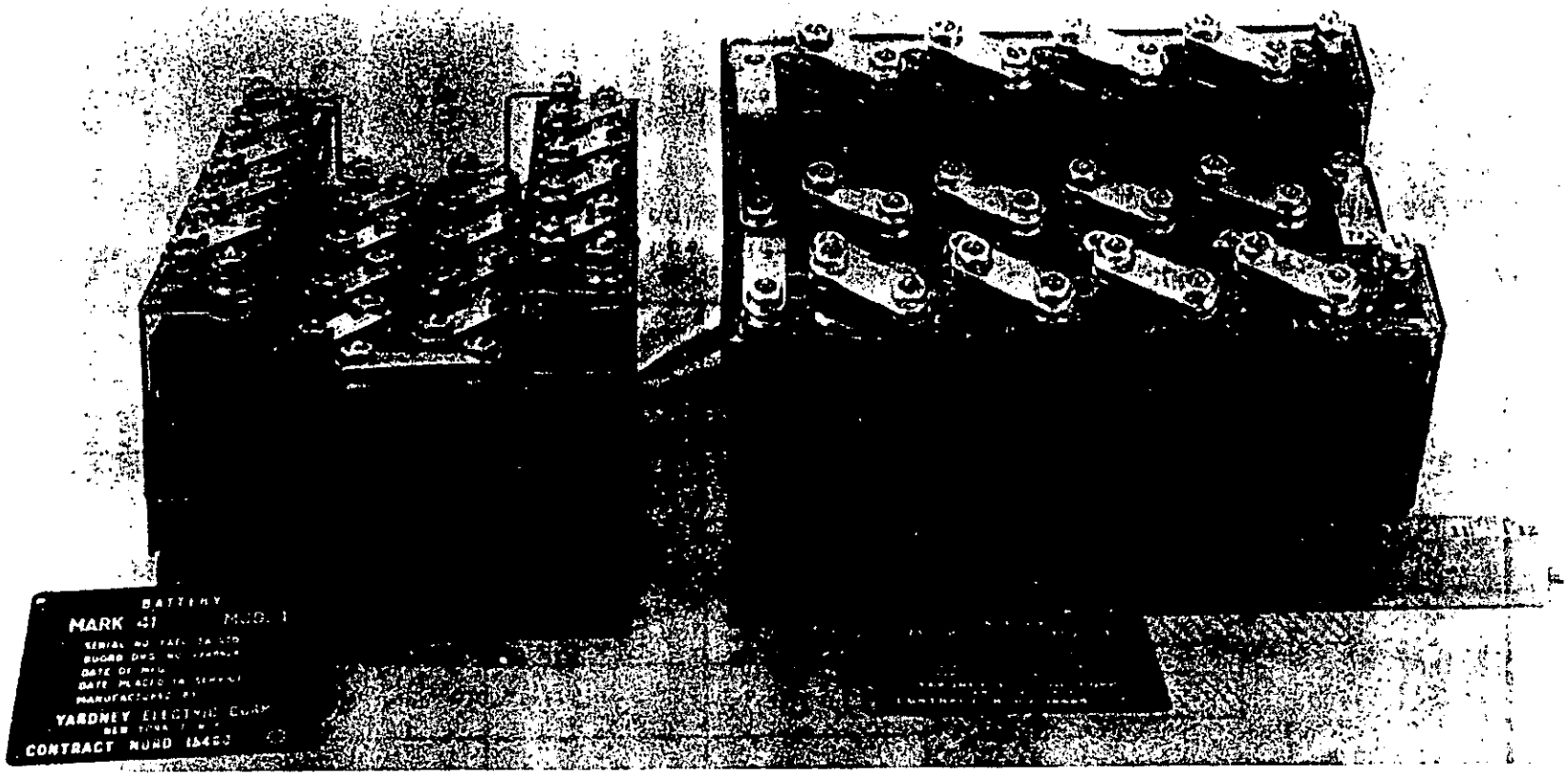
System	Mark - Mod	Density Lbs./cu.in.	Watt-Hours Per Pound
PbO_2-Pb Secondary	2 - 0	0.0745	
	32 - 3	0.0746	
AgO-Zn Secondary	47 - 0	0.0567	
	42 - 0	0.0420	
	39 - 0	0.0685	
	41 - 1	0.0600	
AgO-Zn Primary	EX-2	0.0445	
AgCl-Mg Primary	34 - 0	0.0749	



NOTE: The lighter shading shows the added capacity obtained when the AgO-Zn secondary is completely discharged (War shot or destructive discharge).

Figure 1

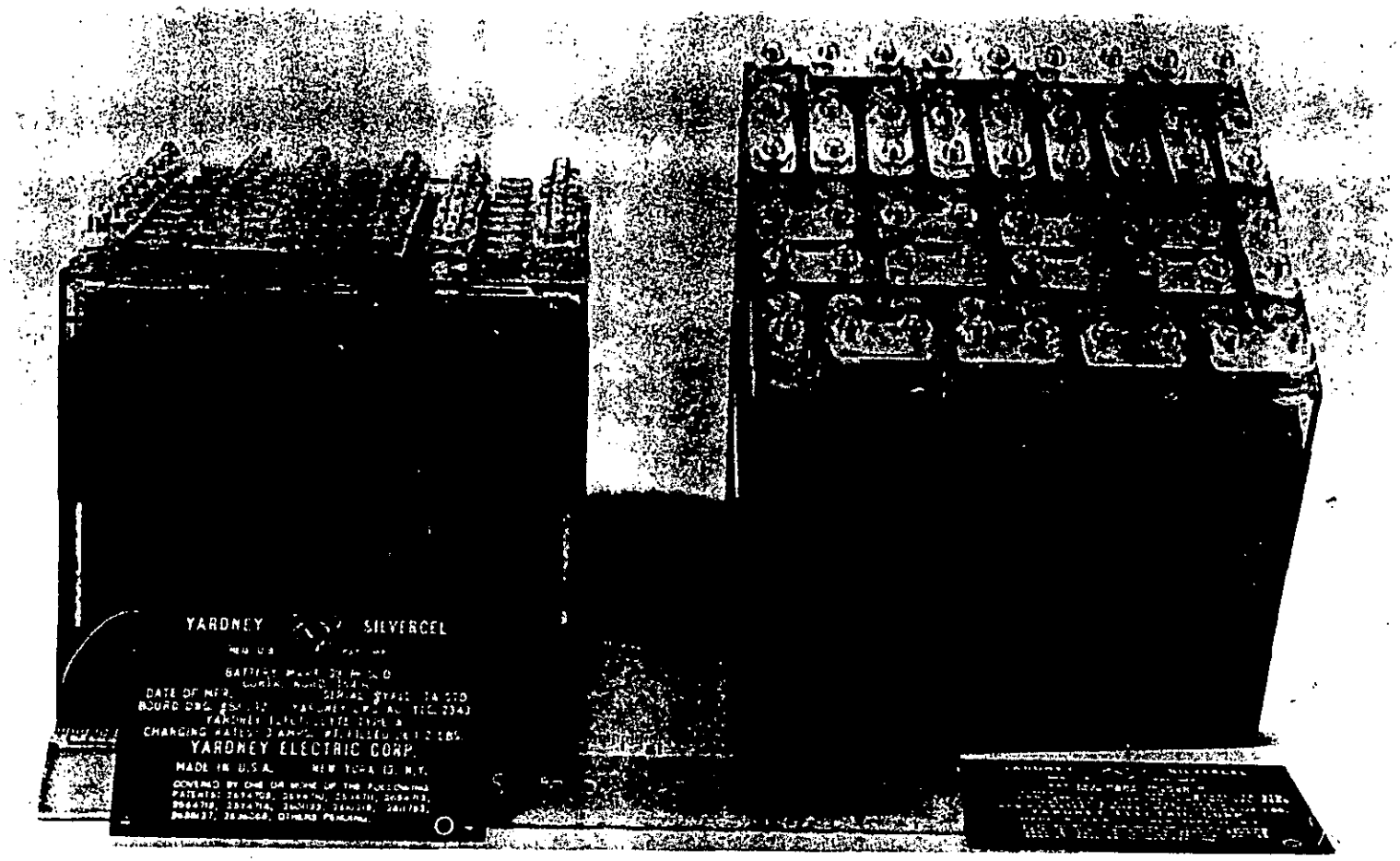
CES 206/16



Battery Mark 41 Mod 1 (20 Cells)

Wet Weight:	18.0 pounds
Dimensions:	10-5/16" L, 6-7/8" W, 5-11/16" H
Rating:	135 Amperes
	25.0 Volts (average)
	6.0 Minutes (exercise use)
	8.0 Minutes (war shot use)

Figure 2



Battery Mark 39 Mod 0 (27 Cells)

Filled Weight:	26.5 pounds
Dimensions:	7-5/16" L, 6-15/16" W, 8-9/16" H
Rating:	120 amperes
	35.0 volts (average)
	6.0 minutes (exercise use)
	11.5 minutes (war shot use)

Figure 3

Battery Mark 42 Mod 0 (33 Cells)

Filled Weight:	63 pounds
Dimensions:	13-3/4" L, 10-7/8" W, 10-3/16" H
Rating:	125 amperes
	44.5 volts (average)
	9.0 minutes (exercise use)
	21.0 minutes (war shot use)

Figure 4

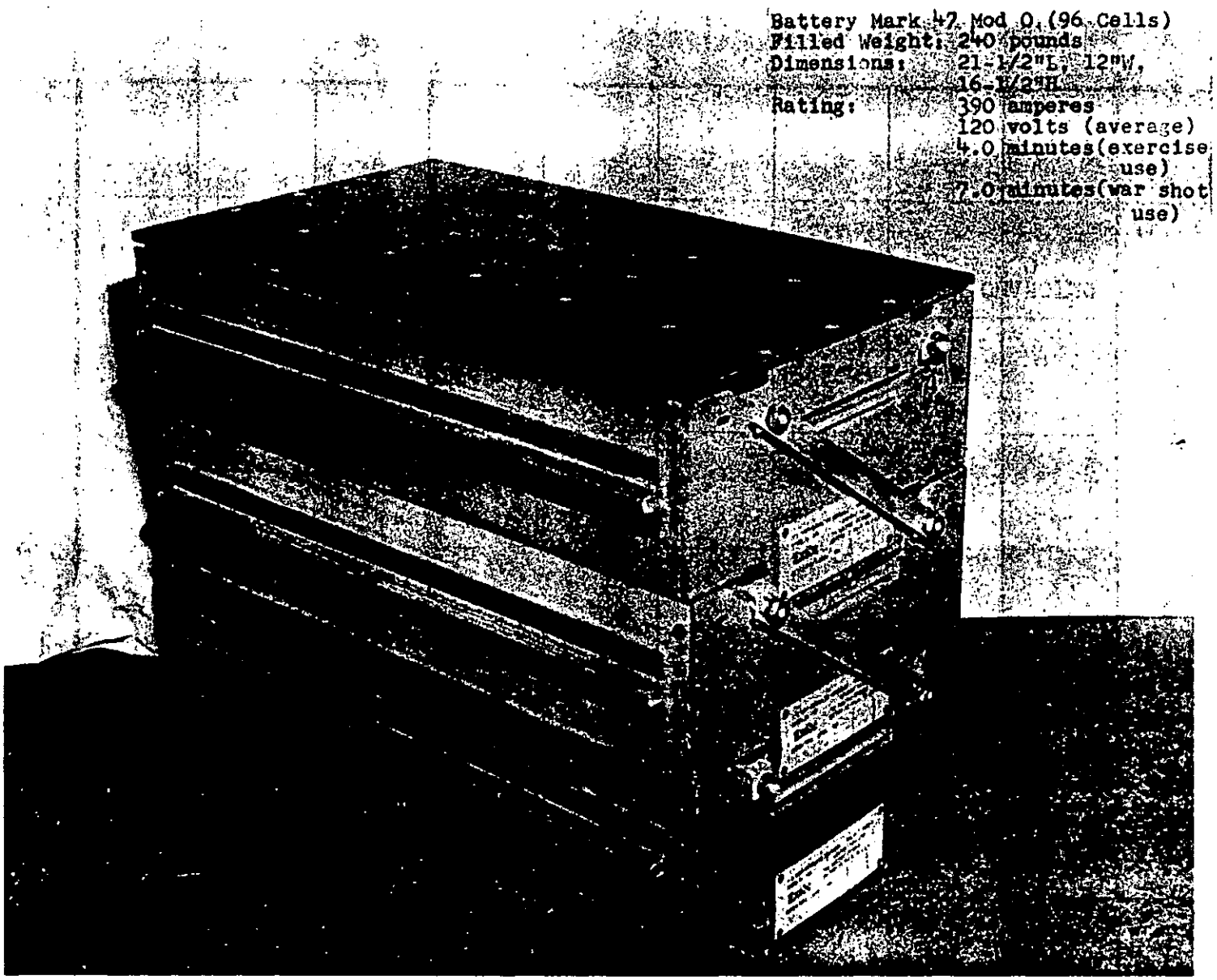


Figure 5

CES 206/16

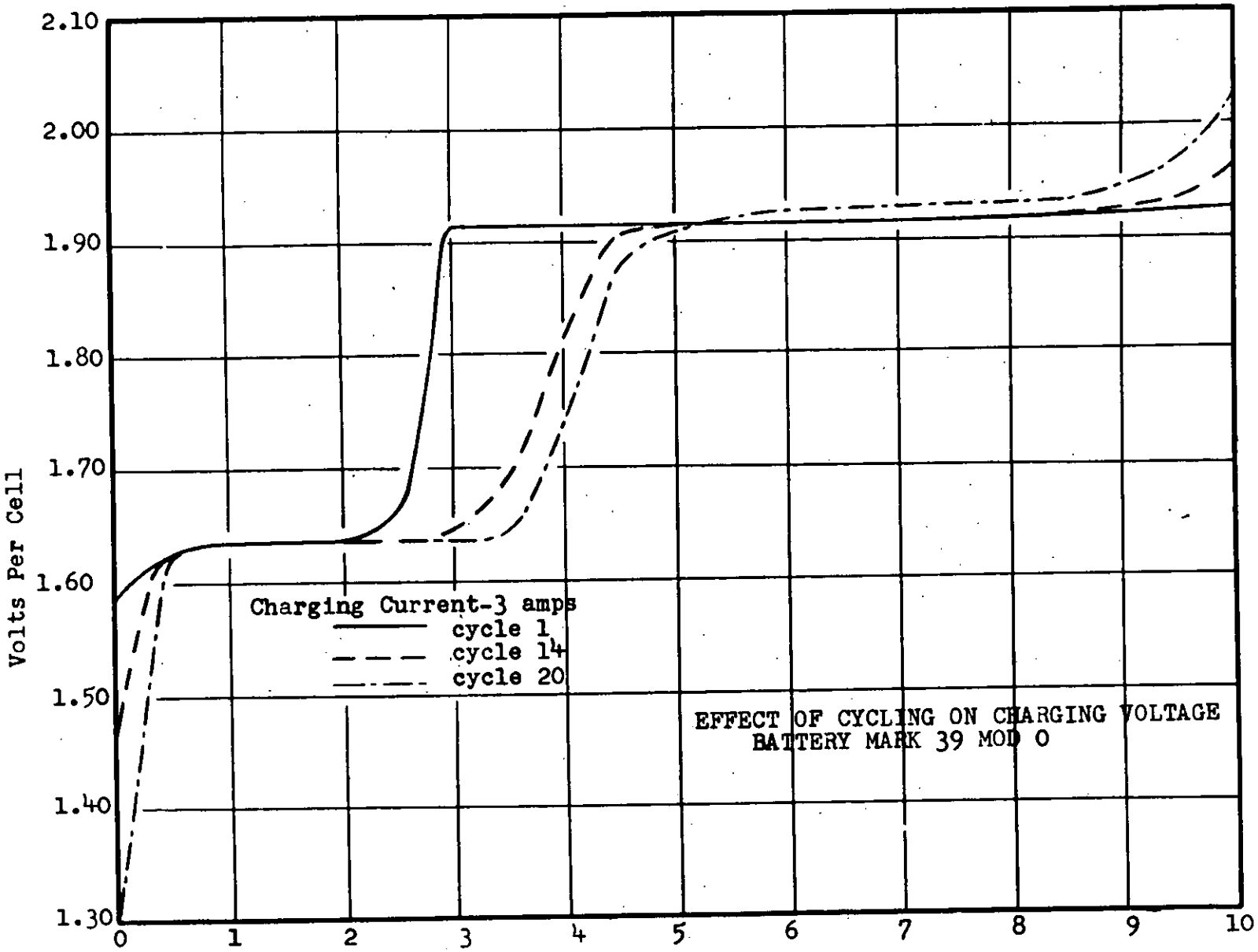


Figure 6

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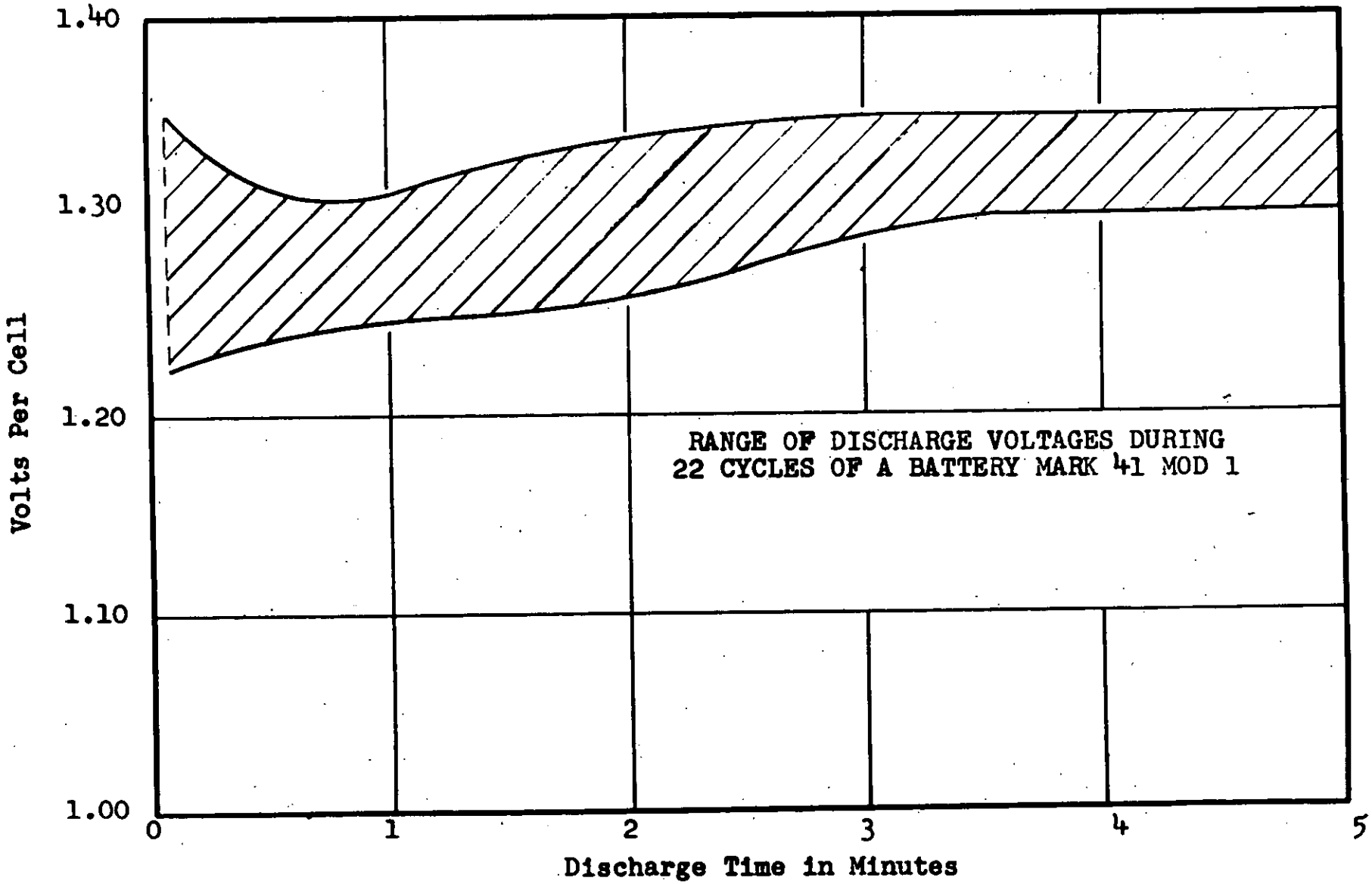


Figure 7

CES 206/16

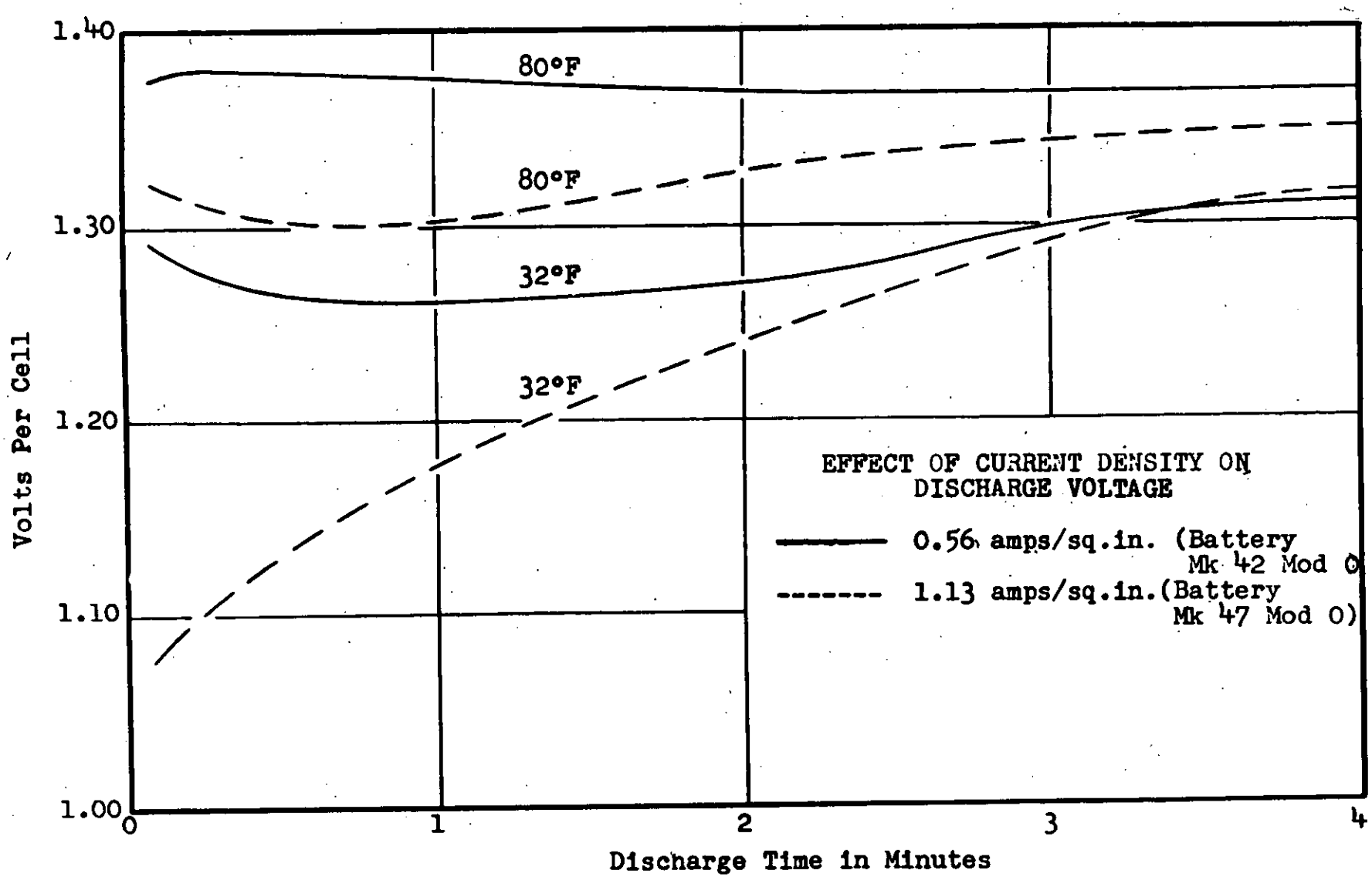


Figure 8

CES 206/16

BATTERY MARK 42 MOD 0 AFTER BEING SUBJECTED
TO A SHOCK OF 186 g's FOR 0.040 SECOND

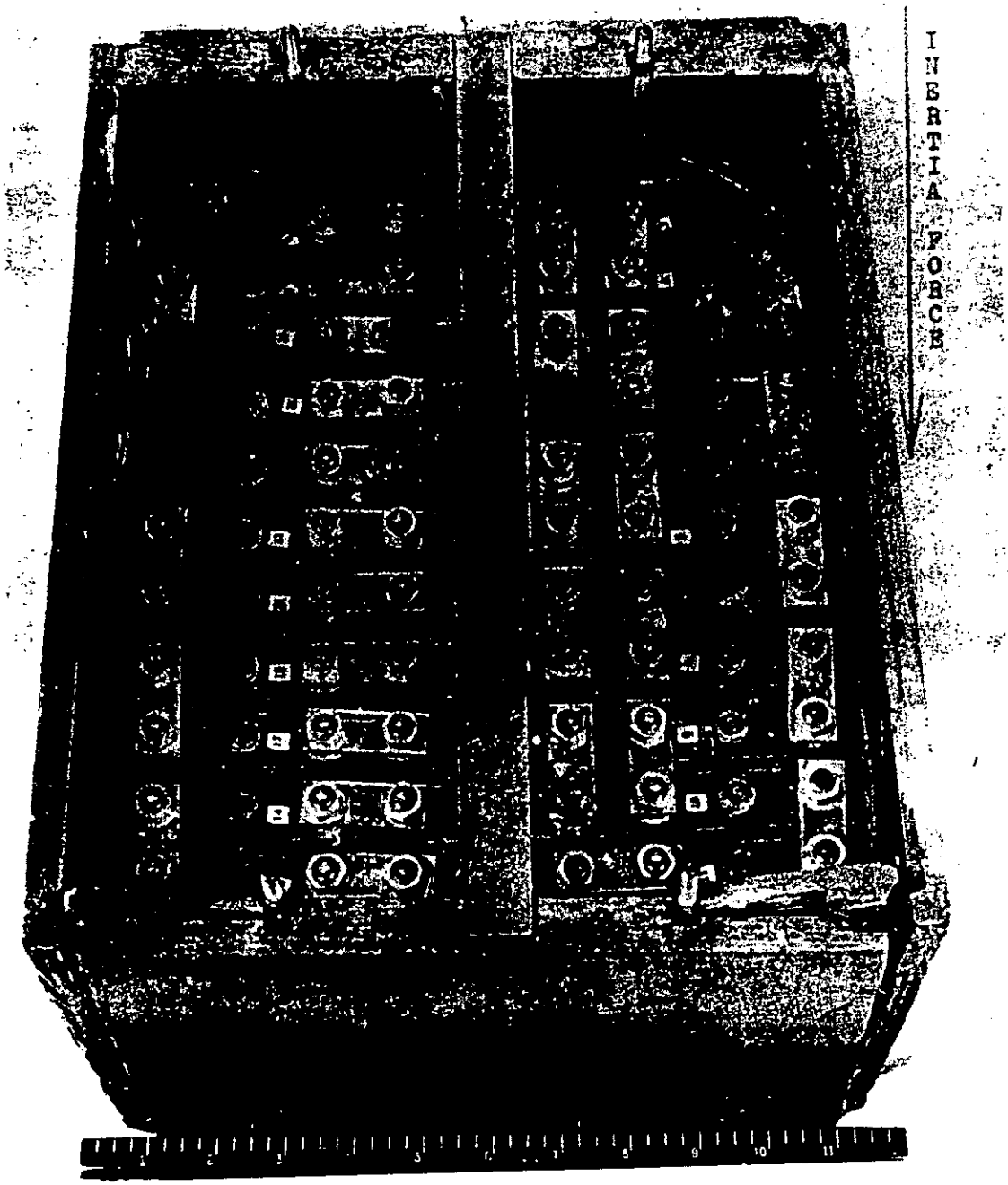
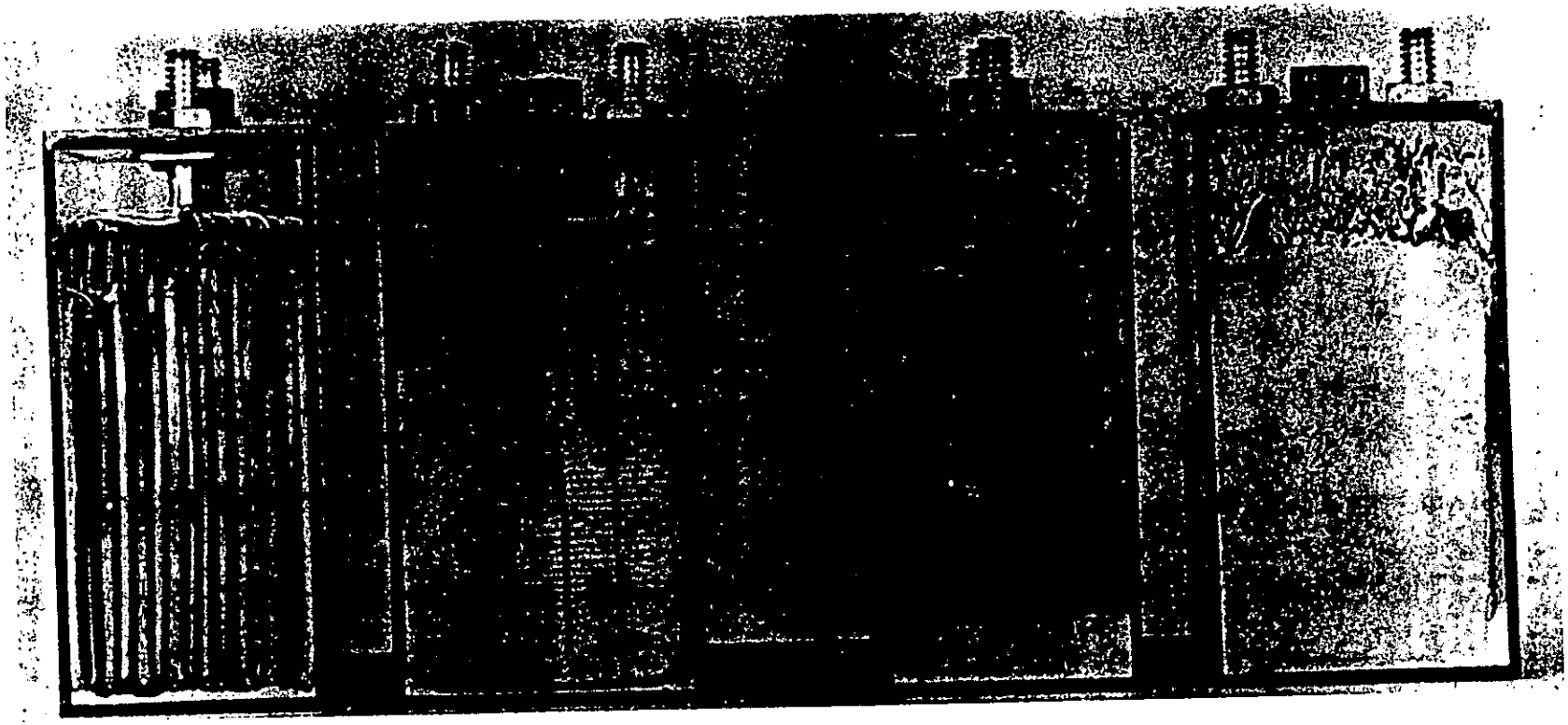


Figure 9

EFFECT OF VIBRATION ON INADEQUATELY SUPPORTED
CELLS OF A SILVER OXIDE-ZINC SECONDARY BATTERY



Cells Not Vibrated

Vibrated Cells

NOTE: The white material on the bottom and sides of the cell cases is negative plate active material.

FIGURE 10

CES 206/16

PRESENTED AT THE JOINT BATTERY CONFERENCE MEETING - 12 SEPTEMBER 1956
Sponsored by the Coordinating Committee on Equipment & Supplies
Office of the Assistant Secretary of Defense (R&D)
Washington, D. C.

THE NICKEL-CADMIUM-ALKALINE SECONDARY BATTERY

Harold Lichtenstein

Battery Section
Material Laboratory
New York Naval Shipyard

Batteries with nickel oxide in the positive plates and cadmium materials in negative plates have been in use since 1910. The flat pocket type of construction is used for both positive and negative plates. This flat pocket fabrication allows extremely thin plates to be made and permits the plates to be brought close together. The pockets or compartments are fabricated from sheet steel which is pierced by many small holes or from perforated steel ribbon both of which are nickel-plated. The pockets are approximately one-half inch high and usually vary in length and thickness. Plates are assembled from pocket elements, in almost any desired size, by being pressed into grids called frames, which are also made of nickel-plated steel. In the nickel cadmium battery, the positive and negative plates are identical in mechanical construction and appearance.

The active material in the pockets of the positive plates is either a highly purified nickel oxide, which is converted to the green nickelic hydroxide ($Ni(OH)_3$) on charge or the pockets may be filled initially with $Ni(OH)_3$. This compound is a very poor electrical conductor and therefore 25% by weight of high purity specially treated graphite is added to obtain the required conductivity. The active material in the pockets of the negative plates is cadmium oxide, CdO. On charge this is reduced to finely divided metallic cadmium and in order to overcome its tendency to coagulate, about 30 per cent by weight of Fe_2O_3, ferric trioxide, is incorporated with the cadmium oxide.

The active materials are insoluable in KOH and do not react with it when the battery is on open circuit. The generally accepted chemical reaction is $Cd + 2Ni(OH)_3 \cdot 2\frac{1}{2}H_2O$ - - - $CdO + 2Ni(OH)_2 \cdot 3H_2O$. The graphite in the positive, and the ferric trioxide in the negative plates take no

part in the reactions. Since the KOH merely acts as a conductor the specific gravity does not change appreciably through a complete cycle of charge and discharge.

The electrolyte used in the various types of nickel cadmium alkaline cells is substantially the same. It is high purity potassium hydroxide in distilled water and may have, in addition small amounts of other alkaline chemicals. The normal specific gravity is 1.190 but, if the cells are to operate in a cold climate, the specific gravity may be increased to 1.230-1.300. The higher gravity shortens the life of the battery when used at normal temperatures.

Towards the end of 1942 the Material Laboratory of the New York Naval Shipyard, began to evaluate the characteristics of the Nickel Cadmium Battery. These investigations to date include nickel cadmium batteries of the pocket type and the sintered plate type.

The Nife nickel cadmium alkaline storage batteries were among the first evaluated. These were all five cell, six volt pocket type batteries. The basic ampere hour ratings of the three groups were as listed:

a. 125 ampere hours at the 5-hour rate

b. 175 ampere hours at the 2-hour rate

c. 175 ampere hours at the 10-hour rate

The 125 ampere hour battery was designated by the manufacturer as the L12H type. The general details were as follows:

Weight per 5 cell tray	92 lbs.
Dimensions per 5 cell tray	15 x 18 x 6.5 inches
Plates per cell	21

Dimensions of plates

positive, 11, each	7.0 x 4.5x0.110 inches
negative, 10, each	7.0 x 4.5 x 0.080 inches

Ratings

1-hour	112.5 amps to 0.88 volts per cell
3-hour	41.5 amps to 1.05 volts per cell
5-hour	25.0 amps to 1.09 volts per cell
8-hour	15.6 amps to 1.09 volts per cell
10-hour	12.5 amps to 1.10 volts per cell

The component battery parts were as follows:

a. Battery Trays - The cells were mounted in hard wood crates by being suspended from the sides of these crates on ebonite insulators which fitted over welded steel suspension bosses, and into blind holes provided for the purpose. (Figure 1)

b. Cell Jars - The cell jars were of welded sheet steel construction. (Figure 2)

c. Intercell connectors - The intercell connectors consisted of copper rod pressed into a steel lug after which the whole was nickel-plated. The bolt holes in the lugs were tapered to fit tightly on the matching taper of the terminals. (Figures 1, 2, and 3)

d. Top assembly - The top assembly of the Nife cell consisted of a pressed steel cover in which were arranged the two terminals, with insulating packings, and a filler cup equipped with a hinged vent cap. The top assembly is shown in figures 2 and 3, installed and isolated, respectively.

e. Negative plates - The negative plates, as shown in figure 4, each consisted of twenty steel pockets mounted in a steel frame entirely

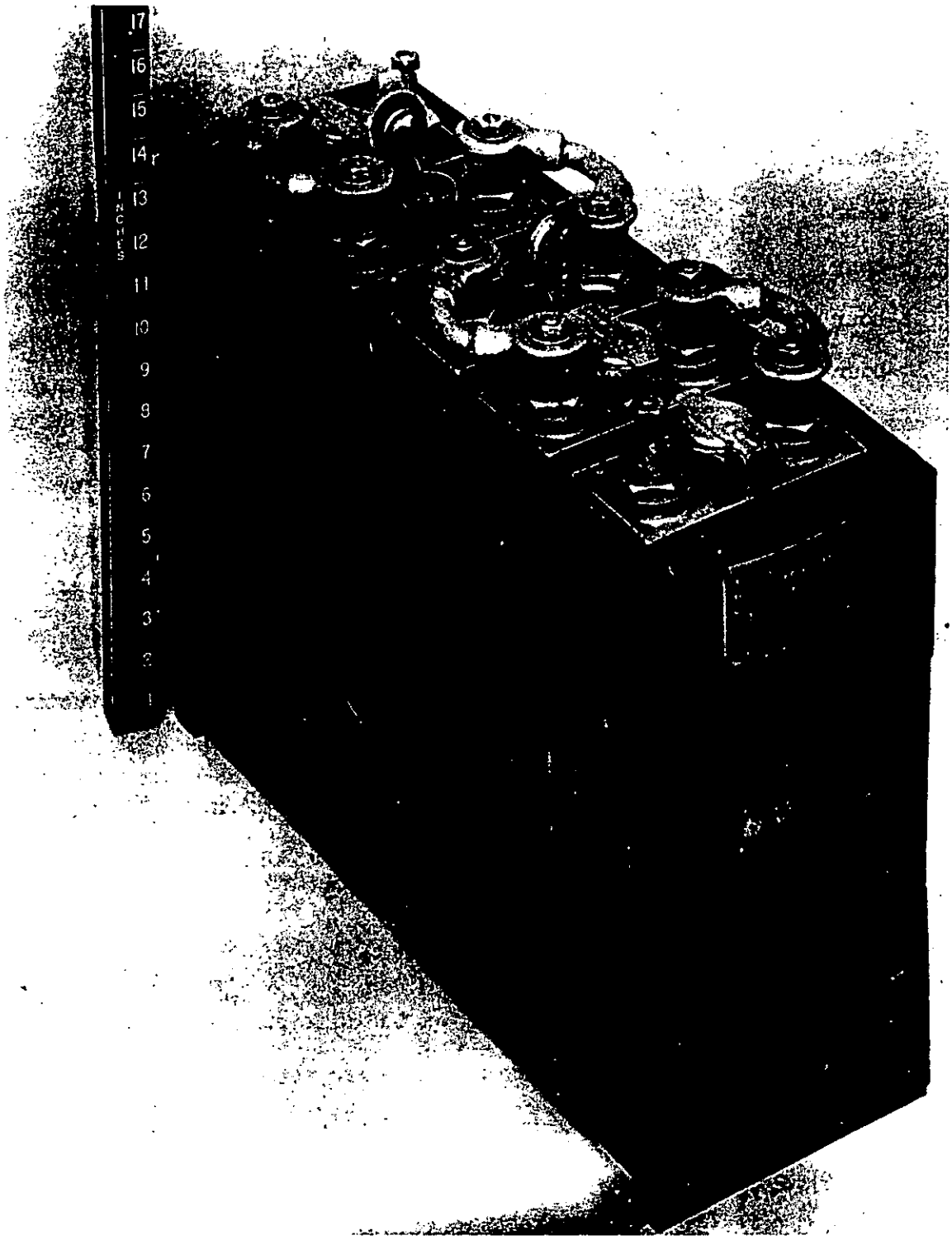


FIGURE 1- NIFE ALKALINE BATTERY

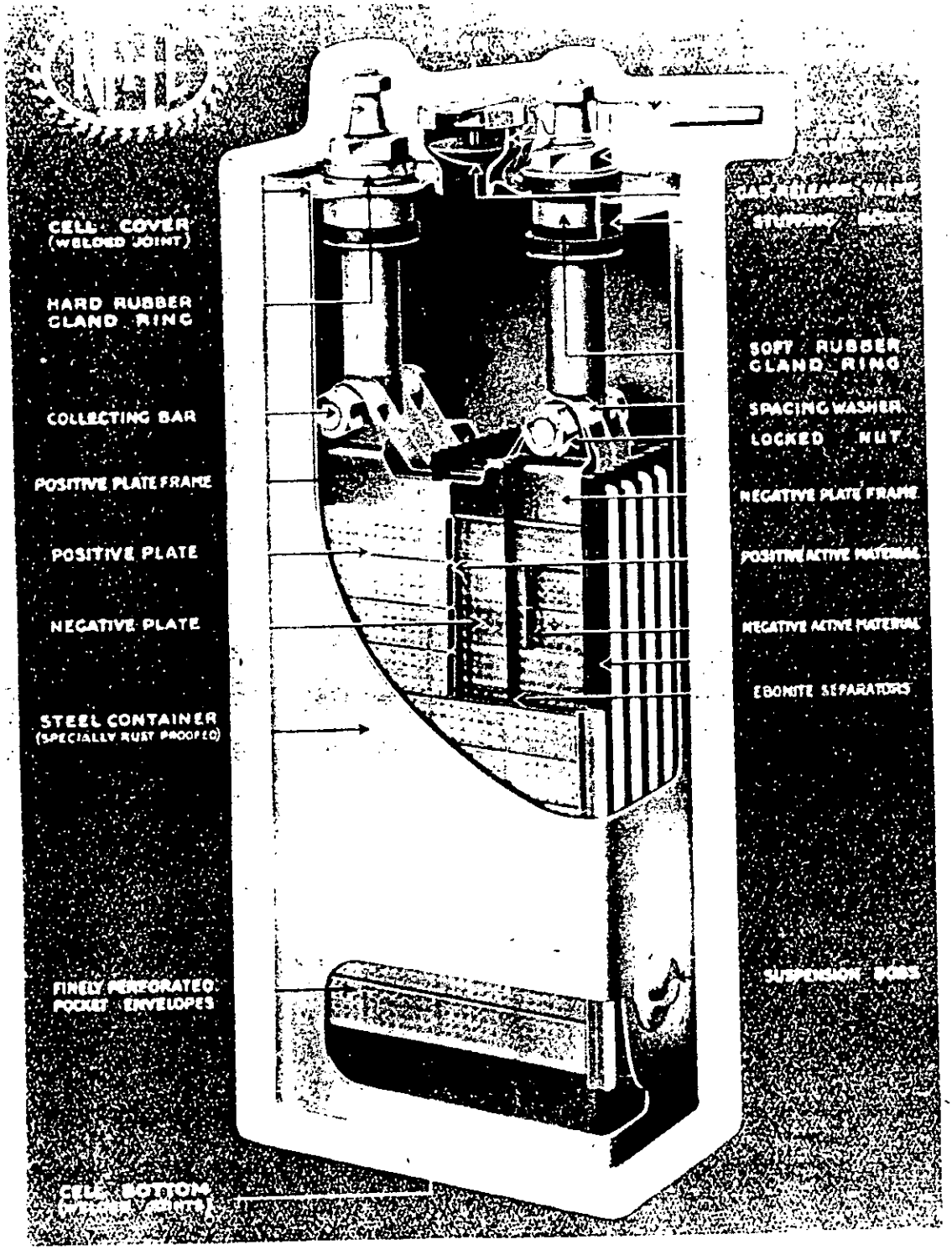
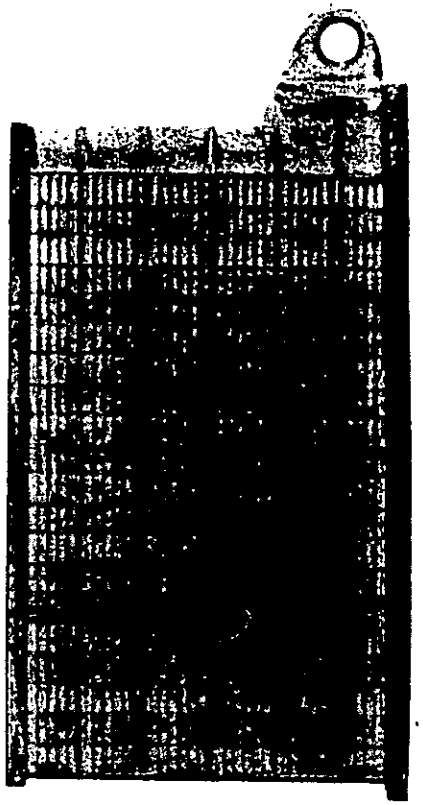
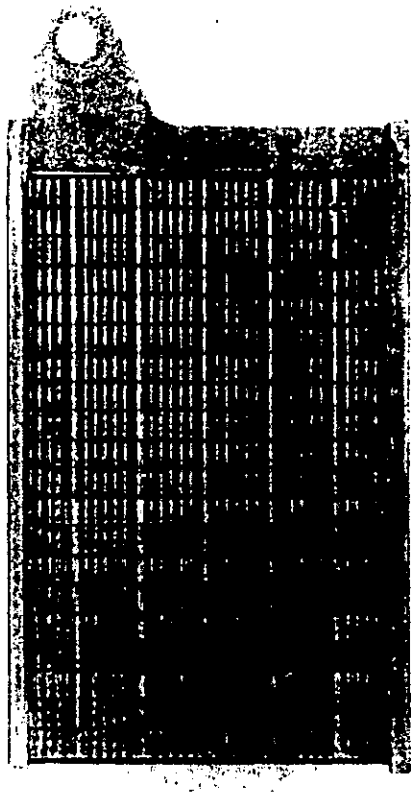


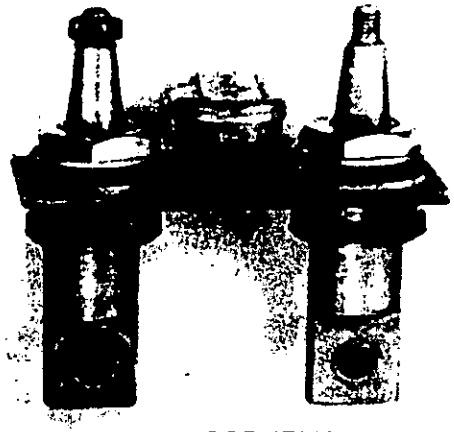
FIGURE 2- NIFE ALKALINE CELL



NEGATIVE PLATE

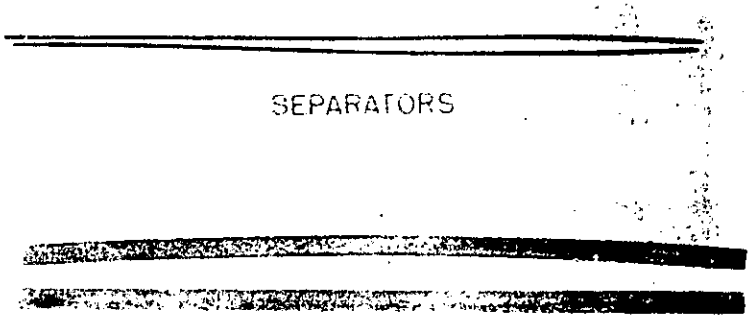


POSITIVE PLATE



TOP ASSEMBLY

INTERCELL CONNECTOR



SEPARATORS

FIGURE 3

NIFE CELL

COMPONENTS

CES 206/16

plates would, upon charge, be oxidized, go into solution, and then attack the cellophane resulting in pinhole formation. The creation of another plant solely for the sintering of nickel plaques, however, did not wholly eliminate this problem. It was found that additional copper traces were introduced from the copper electrodes employed in the welding of plate tabs and terminals. An ineffectual attempt to correct this difficulty was made by using silver electrodes. Unfortunately, silver also attacked the cellophane and shorting subsequently occurred. The development of techniques whereby nickel electrodes could be used for the welding operations eventually solved the problem of pinhole formation in the cellophane.

Since the thin sintered plate rechargeable battery is exceptionally good at low temperatures, it is necessary that the separator be temperature stable at temperatures of -40°F and below. This unfortunately is not the case with cellophane in potassium hydroxide electrolyte. The cellophane has been known to break up after a single exposure at -40°F. This is due to a dimensional instability in which the membrane expands in one direction and shrinks in the other, setting up strains which may result in disintegration of the cellophane.

In addition to the low temperature instability of cellophane, the nylon-cellophane combination has other possible disadvantages. Its electrical resistance, while not high, nevertheless results in some depression of discharge voltage particularly at high rates and low temperatures. In addition, present production standards in the manufacture of nylon parachute cloth are not sufficiently high for battery use. Considerable variations in characteristics occur from lot to lot.

These factors indicate a need for an improved type separator for the nickel-cadmium battery. Various new materials are being studied. These include non-woven alpha cellulose including a regenerated cellulose; treated non-woven fabric, principally alpha cellulose types; microporous rubber and synthetics, such as Sympor; and non-woven synthetic fiber fabrics. One of these materials, Pellon, a rubberized nylon-cellulose fabric, is presently showing considerable promise as a substitute for the nylon-cellophane combination separator.

The preceding comments refer to the conventional free electrolyte form of nickel-cadmium battery. In the case of sealed cells, the separator problems are somewhat different. Since the cell operation is dependent upon the exchange of oxygen between the positive and negative plates on charge, an open separator type is required to permit an unhindered flow of oxygen. A thin open weave nylon cloth is generally used for this purpose. Some manufacturers include a non-woven absorbent paper separator such as Viskon.

In conclusion, it is noted that extensive problems exist in connection with separators for rechargeable zinc-silver oxide and nickel-cadmium batteries. These problems are generally more serious for the zinc-silver oxide batteries due to chemical characteristics of the electrodes. Cellophane or modifications of cellophane appear to be the basic material common to both systems. The disadvantage of cellophane, however, in alkaline electrolyte, indicates a definite need for the development of inert, low resistance semi-permeable separator materials for use in these batteries. The investigation of such materials is continuing, and it is hoped that suitable materials will be forthcoming in the not too distant future.

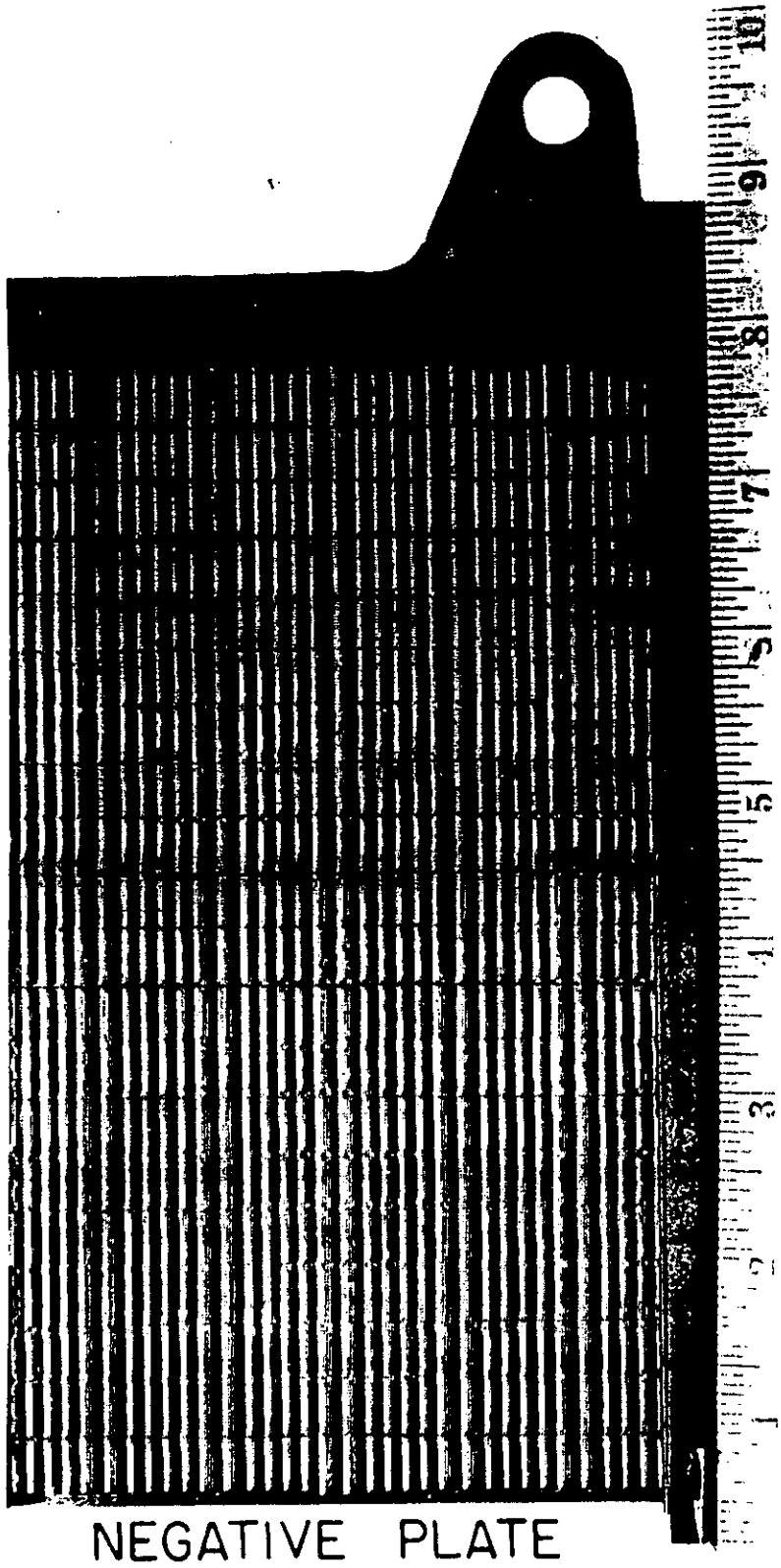


FIGURE 4- NIFE ALKALINE BATTERY

cadmium plated. These pockets, which were perforated with a large number of minute holes and transversely corrugated, contained the negative active material. Chemical analysis showed the composition of the active material at end of test was as follows:

Cadmium	60.70%
Iron	22.34%
Water of hydration and oxygen from oxides	16.96%

f. Positive Plates - The positive plates, figure 5, each consisted of twenty steel pockets mounted in a steel frame, all nickel-plated. These pockets, which were perforated with a large number of minute holes and transversely corrugated, contained the positive active material. Chemical analysis showed the composition of the positive active material at end of test was as follows:

Nickel	40.64%
Iron	1.36%
Graphite	18.00%
Water of hydration and oxygen from oxides	39.99%

g. The separators consisted of 0.060 inch diameter ebonite rods about 8.5 inches long. A set of five such rods were inserted between each pair of adjacent plates of opposite polarity. These separators are shown in figure 3 and their positions on the plates are indicated by the longitudinal lines on the plates in figure 3.

h. End Separators - The end separators consisted of 8.5 inch long strips of ebonite, 0.020 inch thick and 9/16 inch wide, bent lengthwise to form a U-shaped cross-section. Two end separators were used for each

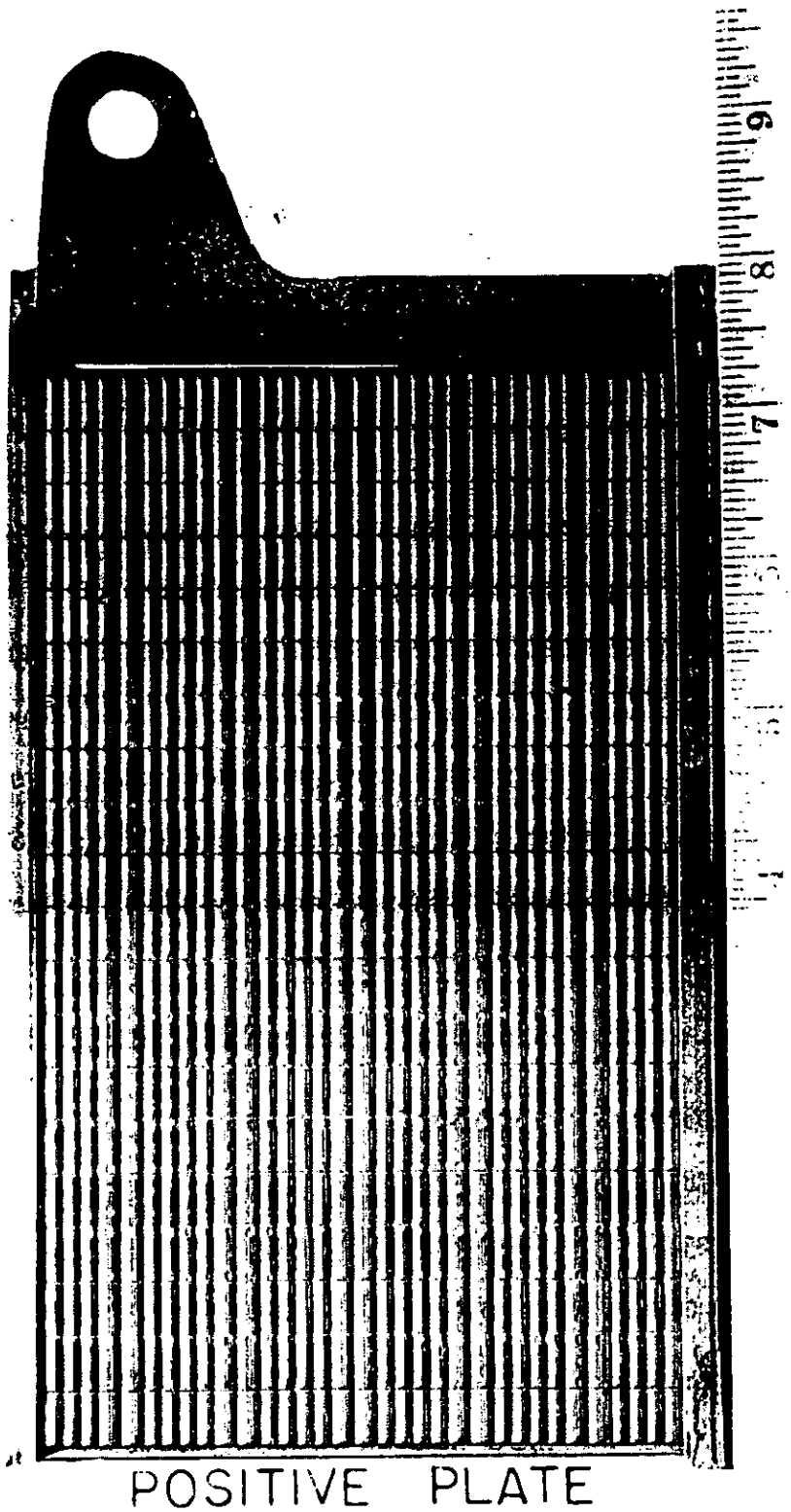


FIGURE 5- NIFE ALKALINE BATTERY

negative plate in the element.

i. Element Assembly - The assembly of element at end of test is shown in figure 6.

j. The electrolyte at end of test had a specific gravity of 1.193 at 80°F and a composition as follows:

Potassium Hydroxide	21.00%
Carbonates as Carbon Dioxide	1.71%

The discharge curve at the 5-hour rate of 25 amperes to cut-off of 5.45 volts and the charge at 30 amperes to 8.40 volts, as shown for cycle 10, (Figure 7), is characteristic for these batteries of 80 F. The charge rate was determined so that the ampere-hour input would be equal to the ampere-hour capacity withdrawn on the preceding discharge plus 50 percent overcharge.

The curves shown in figures 8 through 12 are voltage vs time curves for various discharge rates at temperatures from 80°F to -16°F. The effect of temperature on the discharge capacity was as follows:

	% of Rated Capacity				
Initial Temp.	1-hr. rate	3-hr. rate	5-hr. rate	8-hr. rate	10-hr. rate
80°F	108.5	95.8	94.9	98.9	93.5
40°F	78.0	87.3	91.0	97.0	94.9
0°F	23.5	40.8	85.0	71.0	80.3
-16°F	0.0	0.0	0.0	3.0	11.4

The curves in figure 13 show the relationship between cycle and ampere-hour capacity at 80°F for the 1-hour and 5-hour rate discharges. The discharge capacity fell off very rapidly during the first 158 cycles of life evaluation. This decline, in discharge capacity, was considerably lessened after cycle 159. It should be noted that there was no appreciable increase in capacity after electrolyte renewal at cycle 158. The change in

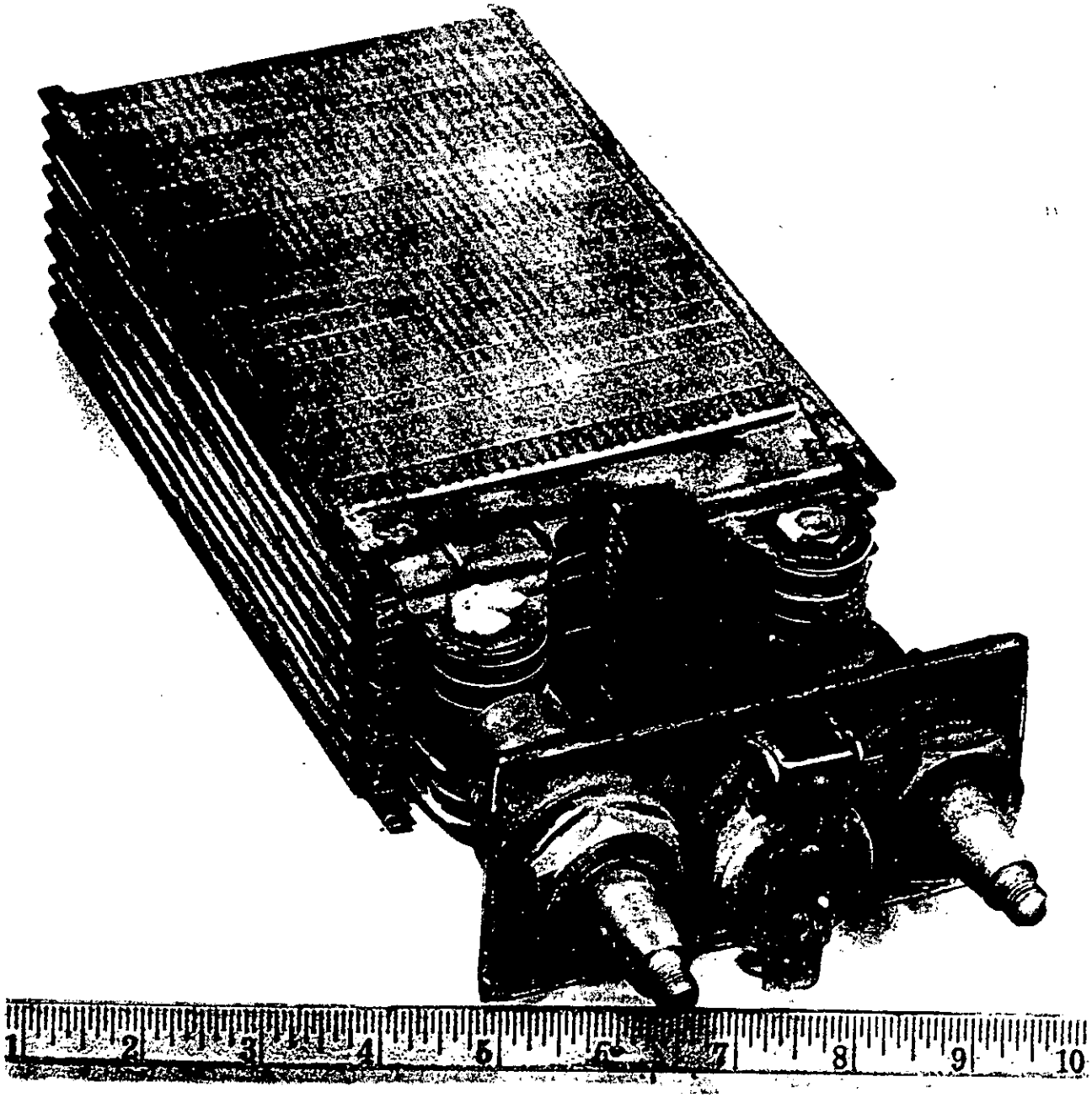


FIGURE 6- ELEMENT NIFE BATTERY

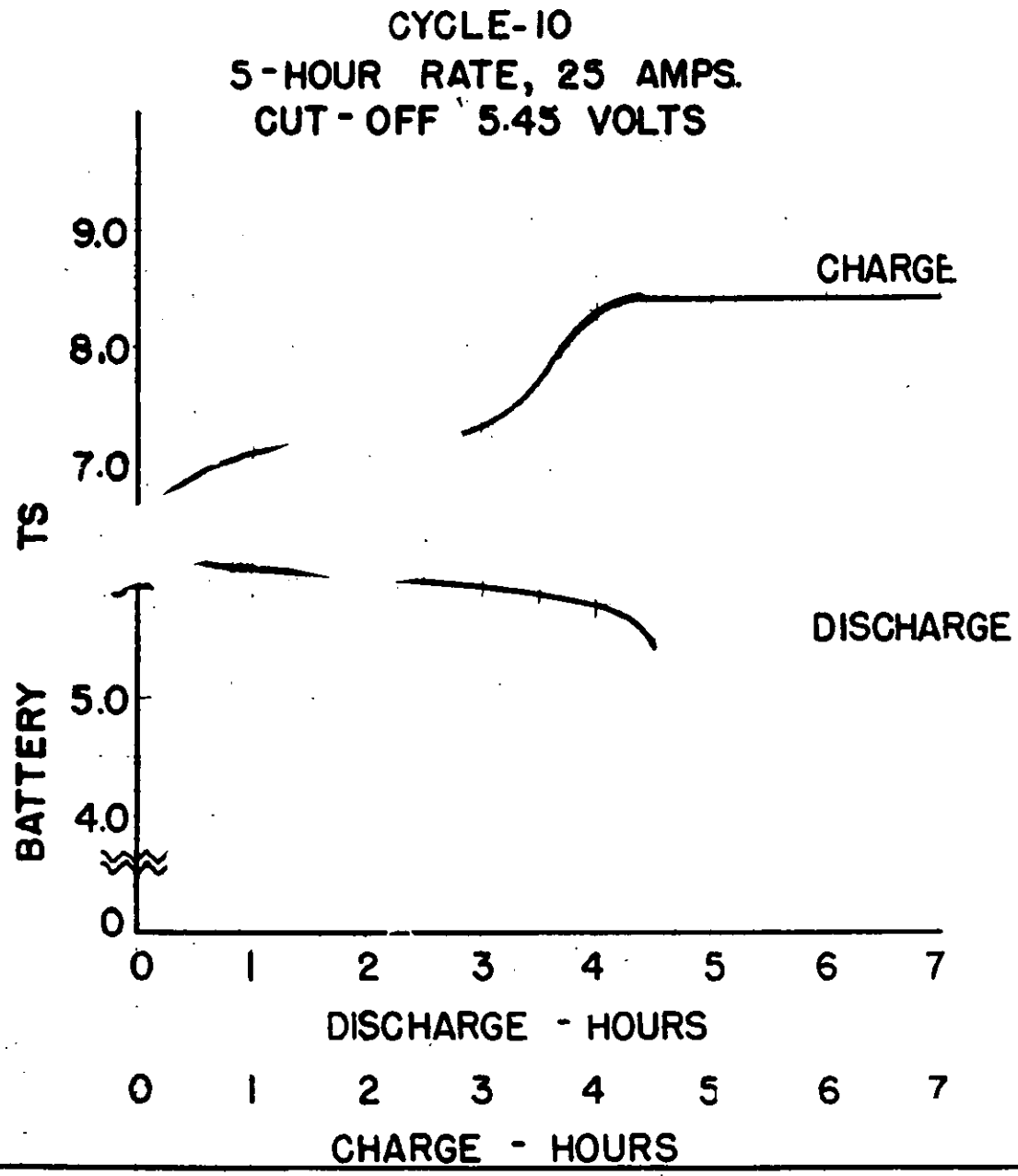
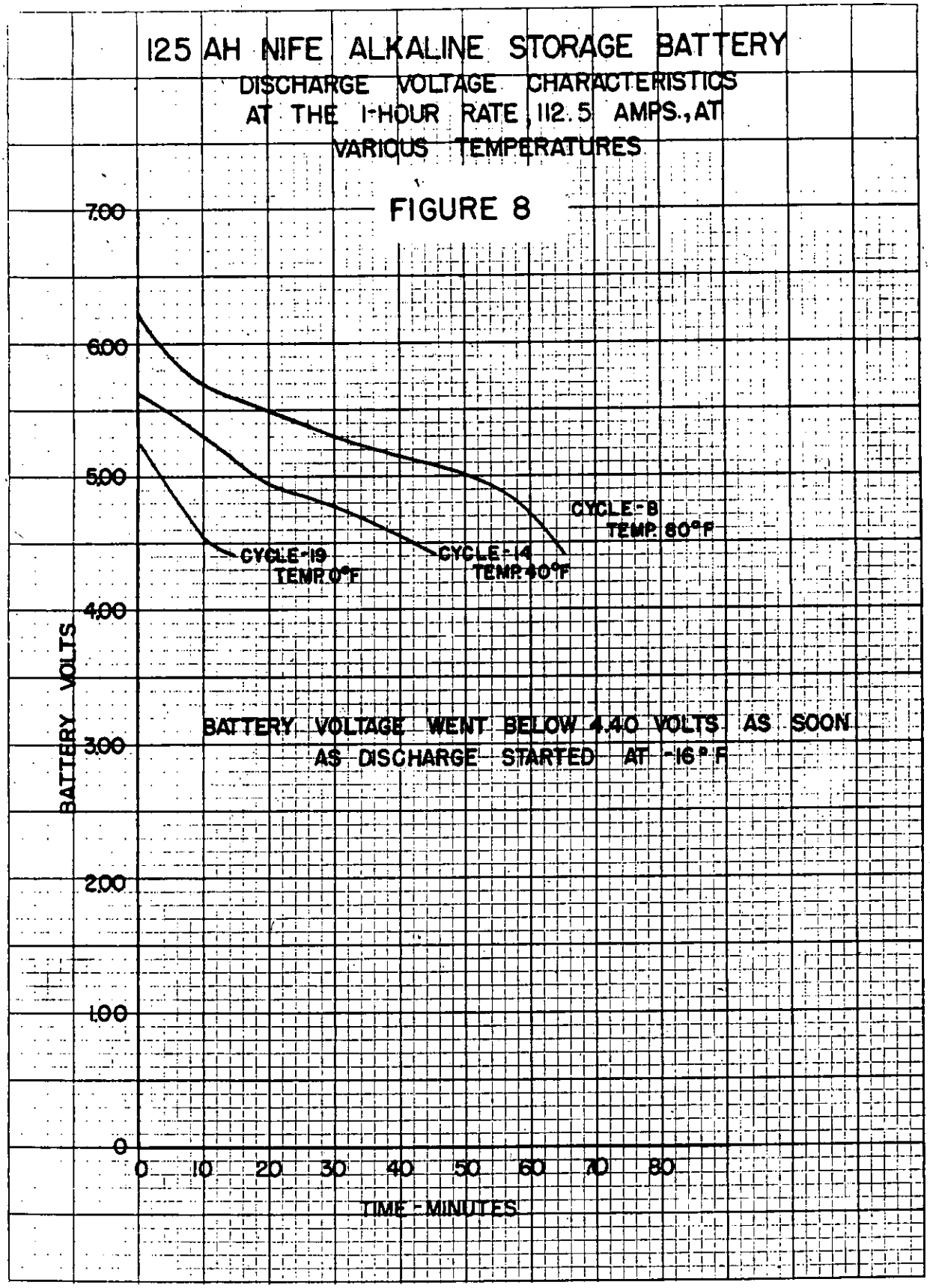
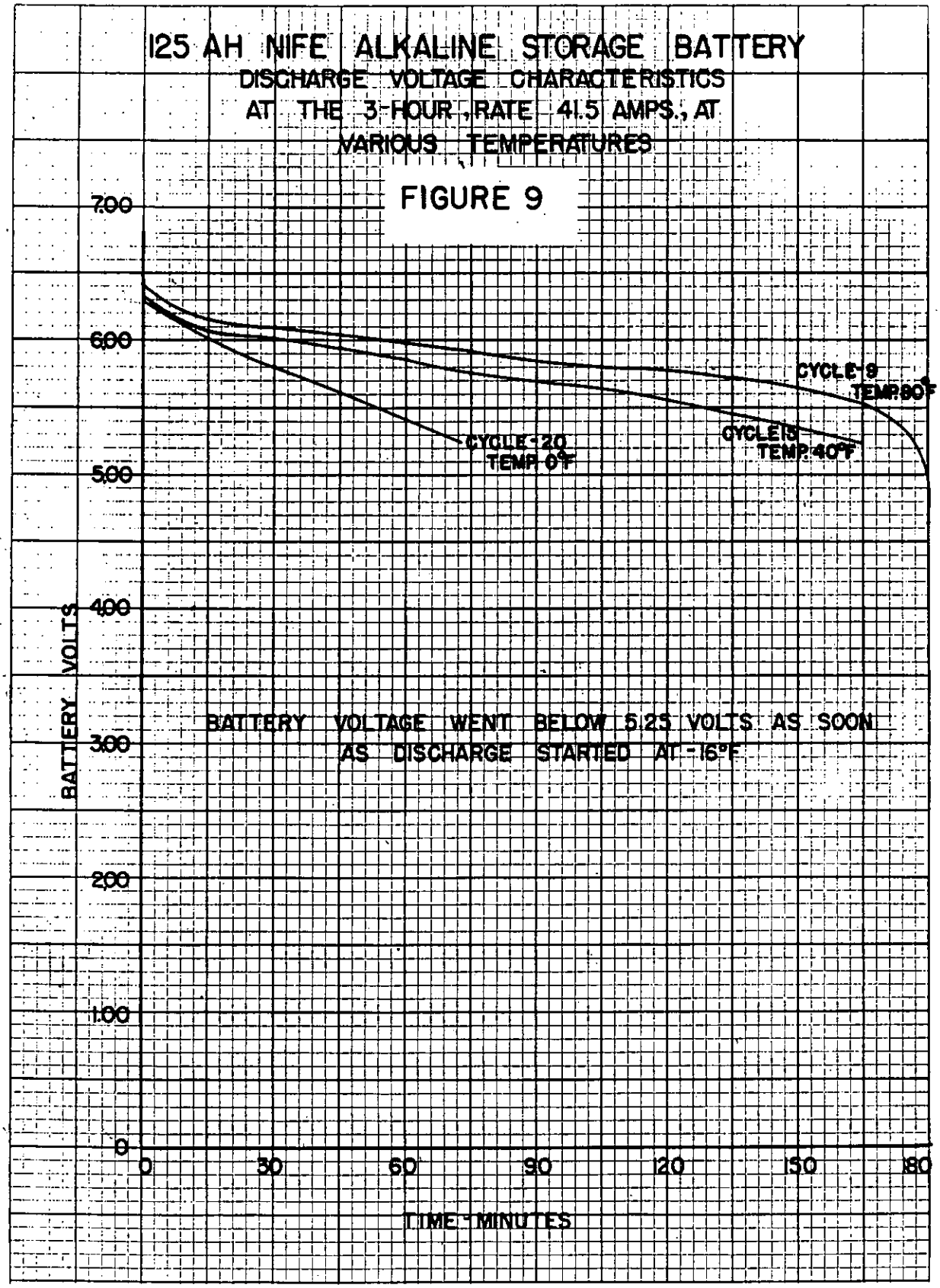
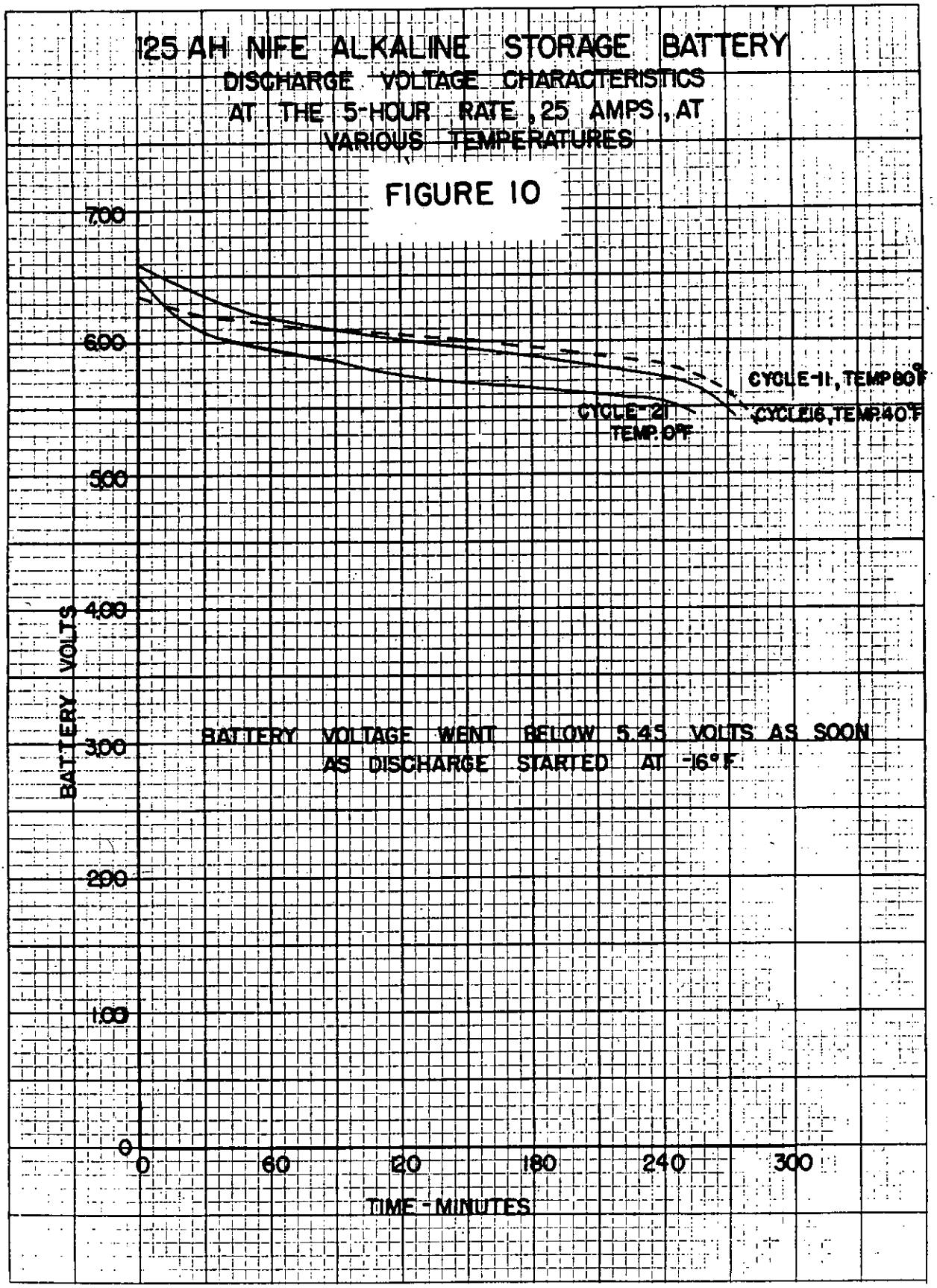
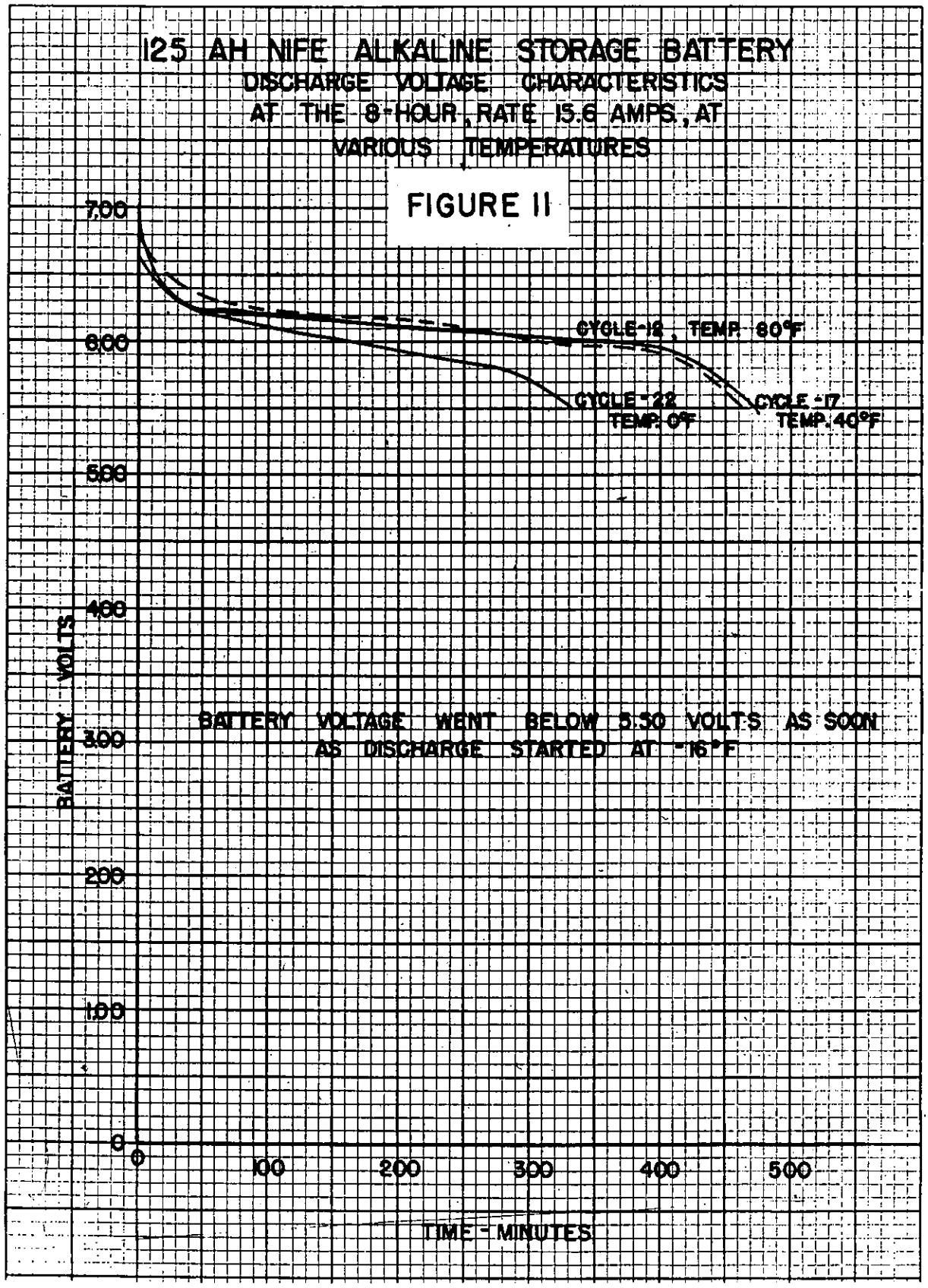


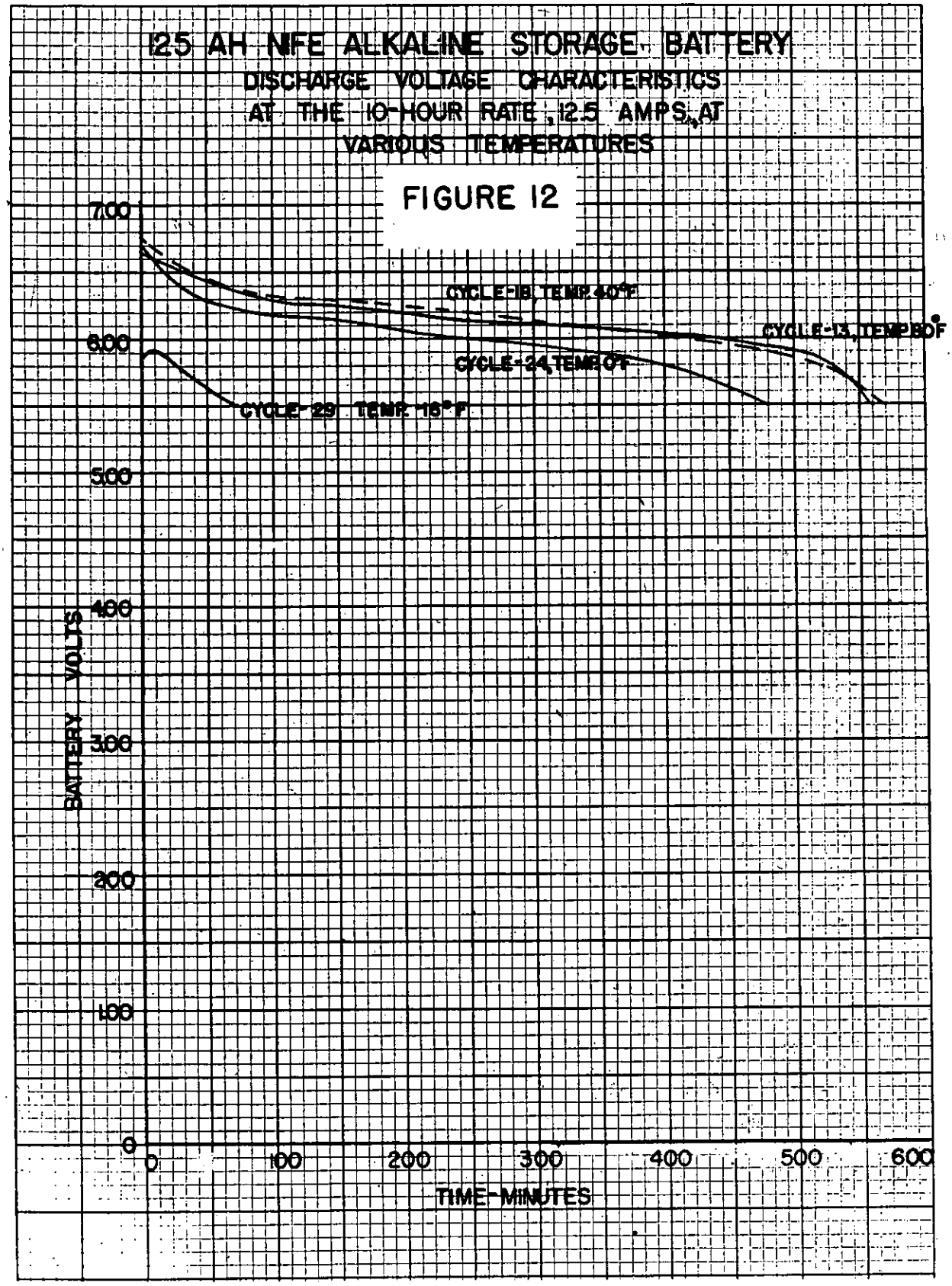
FIGURE 7
125-A.H. NIFE ALKALINE STORAGE BATTERY
DISCHARGE AND SUBSEQUENT CHARGE
VOLTAGE CHARACTERISTICS

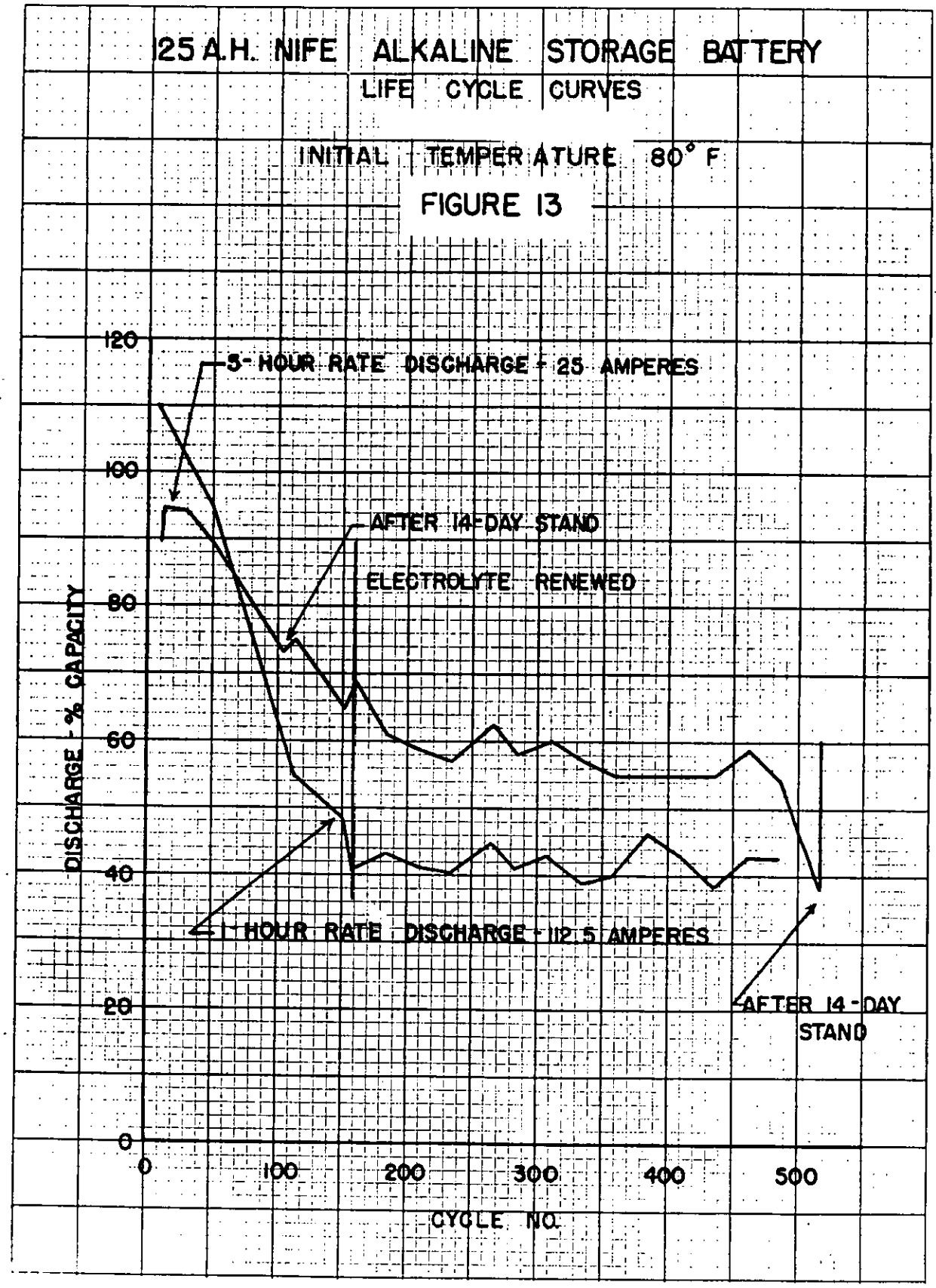

125 AH NIFE ALKALINE STORAGE BATTERY
DISCHARGE VOLTAGE CHARACTERISTICS
AT THE 1-HOUR RATE, 112.5 AMPS., AT
VARIOUS TEMPERATURES
FIGURE 8
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0
BATTERY VOLTS
CYCLE-8
TEMP. 80°F
CYCLE-14
TEMP. 40°F
CYCLE-19
TEMP. 0°F
BATTERY VOLTAGE WENT BELOW 4.40 VOLTS AS SOON
AS DISCHARGE STARTED AT -16°F
0
10
20
30
40
50
60
70
80
TIME - MINUTES


125 AH NIFE ALKALINE STORAGE BATTERY
DISCHARGE VOLTAGE CHARACTERISTICS
AT THE 3-HOUR, RATE 41.5 AMPS., AT
VARIOUS TEMPERATURES
FIGURE 9
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0
BATTERY VOLTS
CYCLE-9
TEMP.80°F
CYCLE-15
TEMP.40°F
CYCLE-20
TEMP 0°F
BATTERY VOLTAGE WENT BELOW 5.25 VOLTS AS SOON
AS DISCHARGE STARTED AT -16°F
0
30
60
90
120
150
180
TIME-MINUTES


125 AH NIFE ALKALINE STORAGE BATTERY
DISCHARGE VOLTAGE CHARACTERISTICS
AT THE 5-HOUR RATE, 25 AMPS, AT
VARIOUS TEMPERATURES
FIGURE 10
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0
BATTERY VOLTS
CYCLE-11, TEMP 80°F
CYCLE-21
TEMP. 0°F
CYCLE 16, TEMP 40°F
BATTERY VOLTAGE WENT BELOW 5.45 VOLTS AS SOON
AS DISCHARGE STARTED AT -16°F
0
60
120
180
240
300
TIME - MINUTES


125 AH NIFE ALKALINE STORAGE BATTERY
DISCHARGE VOLTAGE CHARACTERISTICS
AT THE 8-HOUR RATE 15.6 AMPS, AT
VARIOUS TEMPERATURES
FIGURE 11
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0
BATTERY - VOLTS
CYCLE-12, TEMP. 80°F
CYCLE-22
TEMP. 0°F
CYCLE-17
TEMP. 40°F
BATTERY VOLTAGE WENT BELOW 5.30 VOLTS AS SOON
AS DISCHARGE STARTED AT -16°F
0
100
200
300
400
500
TIME - MINUTES

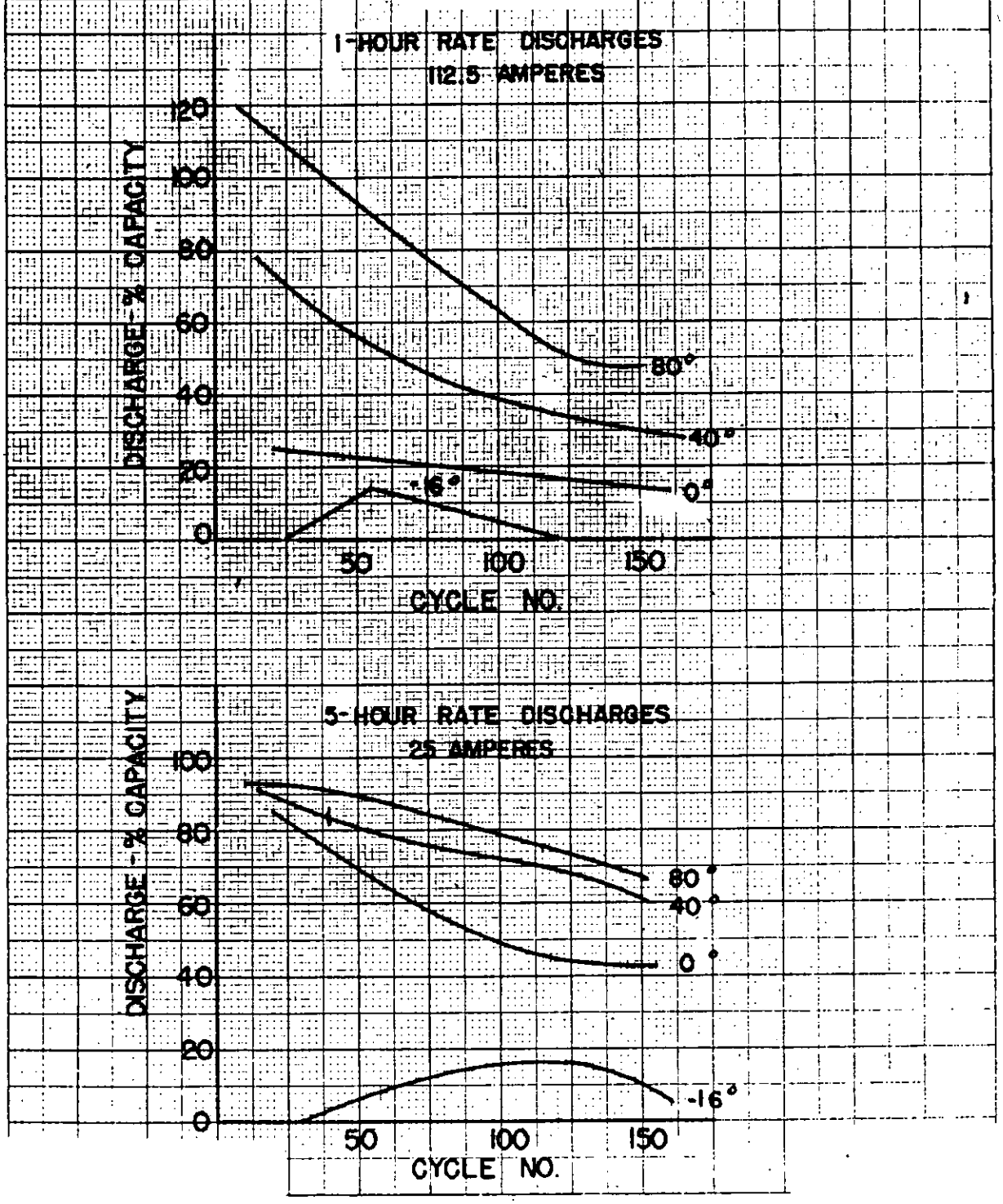

125 AH NIFE ALKALINE STORAGE BATTERY
DISCHARGE VOLTAGE CHARACTERISTICS
AT THE 10-HOUR RATE, 12.5 AMPS, AT
VARIOUS TEMPERATURES
FIGURE 12
CYCLE-18, TEMP. 40°F
CYCLE-13, TEMP. 80°F
CYCLE-24, TEMP. 0°F
CYCLE-29 TEMP. -15°F
BATTERY VOLTS
700
600
500
400
300
200
100
0
0
100
200
300
400
500
600
TIME-MINUTES


25 A.H. NIFE ALKALINE STORAGE BATTERY
LIFE CYCLE CURVES
INITIAL TEMPERATURE 80° F
FIGURE 13
3-HOUR RATE DISCHARGE - 25 AMPERES
AFTER 14-DAY STAND
ELECTROLYTE RENEWED
1-HOUR RATE DISCHARGE - 112.5 AMPERES
AFTER 14-DAY STAND
DISCHARGE - % CAPACITY
120
100
80
60
40
20
0
0
100
200
300
400
500
CYCLE NO.

125-A.H. NIFE ALKALINE STORAGE BATTERY

CAPACITY CHARACTERISTIC CURVES AT VARIOUS INITIAL TEMPERATURES

FIGURE 14



specific gravity of electrolyte ranged from 1.180 to 1.183 during the 14 day stand period. The water consumption during the various stages of this investigation was as follows:

Cycles 1-50	129 cc/cycle
Cycles 51-100	80 cc/cycle
Cycles 475-485	55 cc/cycle

The discharges of cycles 475 to 485 were 30% of rated capacity.

The curves in figure 14 show the relationship between cycle and the ampere hour capacity obtained at the various temperatures. The capacities were measured as a percentage of the ampere-hour capacity obtained at the 1-hour and 5-hour at 80°F.

The second group of Nife nickel cadmium alkaline storage batteries evaluated were also five cell, six volt pocket type batteries. This evaluation was started during the latter part of 1948. The KD-175AH battery was rated at the 2-hour rate of 87.5 amperes and the TA-175AH battery was rated at the 10-hour rate of 17.5 amperes. The general details of the batteries were as follows:

	TA-175AH	KD-175AH
Length	22 7/8 inches	32¼ inches
Width	6 9/16 inches	6 9/16 inches
Height	15 1/16 inches	14 15/16 inches
Weight	98 lbs.	157 lbs.

All other constructional details were similar to the 125 AH batteries previously described.

The KD- 175 AH battery was cycled in accordance with the method specified for engine cranking batteries using 155 amperes for the 1-hour discharge to end voltage of 1.09 volts per cell, and 650 amperes for the discharge at zero degrees F to 3.00 volts. The TA-175AH battery was

cycled at the 2-hour rate of 70 amperes to 4.75 volts.

The Navy requirement for the 6 volt lead acid engine cranking battery is that after storage at zero degrees F for 24 hours the battery must be capable of delivering 650 amperes for a minimum of 3.3 minutes to end voltage of 3.00 volts. The results for the discharge of the KD-175AH battery are listed below:

DISCHARGE DATA KD-175AH

Cycle	Rate amps	Temperature Initial °F	Temperature End °F	o.c. Voltage volts	5 sec Voltage volts	Time sec	End Voltage volts
3	650	0	4	7.00	2.80	5	2.80
51	650	0	6	6.94	3.44	31	3.00
52	650	0	5	6.57	2.68	5	2.68
101	650	-20	-14	6.94	0.00	0	—
103	650	0	7	7.10	2.30	5	2.30

At cycle 101 the electrolyte became slushy-frozen. Prior to the discharge at cycle 103 the electrolyte specific gravity was adjusted to 1.210.

The TA-175AH battery failed to deliver 80% of the 10-hour rate capacity at cycles 150, 160 and 170. According to the Military Specification this indicates failure.

In the last twenty years, the sintered plate battery has been developed. The early work on this construction was limited to thick sintered plates. During World War II a German concern did considerable work on thin sintered plates of high porosity in order to obtain a battery having improved high rate performance for starting applications. Extensive use of this battery was limited because of a shortage of nickel as well as the early failure of the negative plate on cycle service.

Since World War II considerable interest has existed, both here and

abroad, in thin plate sintered nickel-cadmium battery in an at' to develop better high rate and low temperature characteristics. Basically the sintered plate battery uses nickel oxide as the positive active material, but it differs from standard nickel-cadmium batteries in the method of support. The grids for the sintered plate battery are usually made of a coarsely woven wire cloth about 20 mesh and may or may not have a frame around the wire. The grids are usually of nickel or nickel-plated steel. Plates are made from nickel powder which is molded into shape over the wire grid and then heated at an elevated temperature in a non-oxidizing atmosphere. This results in a plate which has a porosity of about 80%. Active material impregnation into the pores is accomplished by electrolysis in solutions of nickel salts for the positive plates and cadmium salts for the negative plates. The plates are arranged in groups connected by welded group straps and are separated by layers of thin synthetic fabric. Positive and negative plate groups are intermeshed and these units are placed in individual cell containers usually made of high impact alkalie resistant plastic. Batteries made up of a number of cells are assembled in alkalie resistant steel cases.

Late in 1954 the Material Laboratory undertook to make an exhaustive evaluation on sintered plate nickel cadmium batteries manufactured by the Battery Division of the Sonotone Corporation. The batteries were five cell, six volt batteries rated at 100AH. The evaluation procedure as given below, including modifications requested by the manufacturer for his battery, was used to determine the cycling characteristics both with high rate charges and with lower rate charges such as are normally used in life tests of the Navy engine cranking batteries. In this manner the two evaluations, the high rate charge and the low rate charge, would accumulate cycles at the same rate.

Procedure	100AH Sintered Plate Battery	100AH Sintered Plate Battery	130AH Standard Lead Battery
Routine Charge	42.5 Amps-3 hrs.	18.2 Amps-7 hrs.	18.2 Amps-7 hrs.
Open Circuit Stand	2 hrs.	0 hrs.	0 hrs.
Routine Discharge	90 Amps-1 hr.	90 Amps-1 hr.	100 Amps-1 hr.
Open Circuit Stand	2 hr.	0 hrs.	0 hrs.
Routine Overcharge	140%	140%	120%
10-hr. rate Discharge	10 Amps	10 Amps	17 Amps
1-hr. rate Discharge	90 Amps	90 Amps	100 Amps
Engine Starting Rate at 0°F (Required 3.3 min)	650 Amps	650 Amps	650 Amps

For the first 48 routine cycles, the batteries that were operated at the high rate charge had an end of charge voltage that averaged 1.63 volts per cell, and a 15 second discharge voltage that averaged 1.25 volts per cell. The end of discharge voltage at cycle 1 was 1.16 volts per cell. The end of discharge voltage at cycle 48 ranged from 0.97 volts to 1.14 volts. Voltages at end of charge and the 15 second discharge voltage were slightly higher for the batteries that were operated at the low rate charge. However, end of discharge voltage at cycle 48 ranged from 0.70 to 1.11 volts.

The data obtained on the capacity discharge cycles for the sintered plate batteries are given below:

DATA ON ROUTINE CYCLES * BATTERY NO.2

DISCHARGE							NEXT CHARGE				
			TEMP		VOLTS				END	TEMP	
CYCLE	RATE AMPS	TIME HRS	START °F	END °F	15 SEC.	END	RATE AMPS	TIME HRS	VOLTS	START °F	END °F
0							45	3.5	1.64 1.62 1.62 1.62 1.62	83	98
1	90	1.0	85	110	1.24 1.24 1.24 1.24 1.24	1.16 1.16 1.16 1.16 1.16	42.5	3.0	1.65 1.62 1.63 1.61 1.61	102	93
20	90	1.0	97	118	1.26 1.26 1.26 1.26 1.27	1.06 1.15 1.16 1.16 1.17	42.5	3.0	1.64 1.66 1.67 1.67 1.67	100	106
48	90	1.0	95	117	1.26 1.27 1.27 1.27 1.27	0.97 1.06 1.07 1.07 1.14	42.5	3.0	1.65 1.64 1.63 1.66 1.80	104	106

CES 206/16

DATA ON ROUTINE CYCLES - BATTERY NO.3

DISCHARGE							NEXT CHARGE				
			TEMP		VOLTS				END	TEMP	
CYCLE	RATE AMPS	TIME HRS.	START °F	END °F	15 SEC.	END	RATE AMPS	TIME HRS	VOLTS	START °F	END °F
									1.69		
									1.69		
0							45	3.5	1.65	84	99
									1.69		
									1.69		
					1.32	1.19			1.66		
					1.32	1.19			1.68		
1	90	1.0	92	110	1.32	1.16	18.2	7.0	1.64	77	88
					1.32	1.19			1.68		
					1.32	1.19			1.68		
					1.35	1.10			1.74		
					1.34	1.00			1.65		
20	90	0.6	106	109	1.34	1.00	18.2	7.0	1.59	118	104
					1.32	0.80			1.60		
					1.33	1.10			1.70		
					1.34	1.11			1.76		
					1.35	1.11			1.74		
48	90	0.7	100	117	1.34	0.91	18.2	7.0	1.60	120	102
					1.33	0.70			1.60		
					1.34	1.11			1.76		

Cycle	Rate amps	Cycled at High Rate Charge	Cycled at Low Rate Charge
49	90	1.0 hrs.	0.7 hrs.
50	10	11.4 hrs.	7.8 hrs.
51	650	3.38 min.	1.55 min.
52*	10	11.4 hrs.	7.4 hrs.
53	90	1.1 hrs.	0.8 hrs.
54	10	12.0 hrs.	7.9 hrs.
55	650	4.13 min.	3.72 min.
56*	10	11.5 hrs.	8.5 hrs.

(*after 14 day stand on open circuit)

As predicted by the manufacturer, the batteries charged in 7 hours were much inferior to those charged in 3 hours. The difference in performance was due to the result of charge rates and is corroborated by results of older investigations on pocket-type nickel cadmium cells in which the charge rate was progressively reduced with proportional increase in charge time. It was found that the capacity after a charge diminished as the rate of charge diminished. Apparently, the relatively large plate area of the sintered plate cell accentuates the effect. This effect does not mean that the cell cannot be maintained fully charged by a trickle charge. It does mean that the cell cannot be charged from the fully discharged condition at a low rate without sacrificing capacity on the next discharge.

Figure 15 shows the sintered plate battery as received while Figure 16 is a representative view of all the batteries after 51 cycles of operation. The material is a heavy carbonate encrustation.

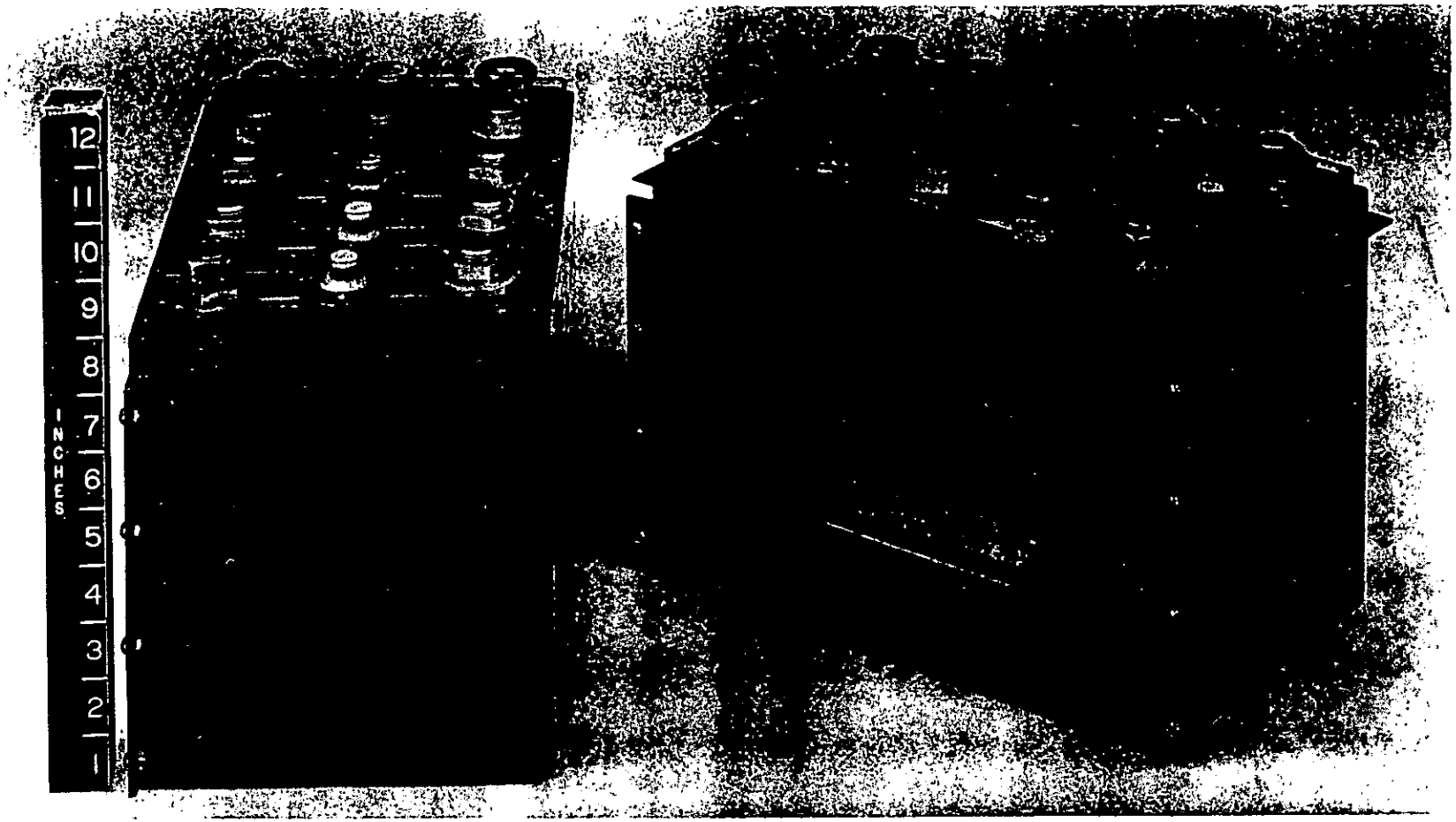


Figure - 15 **TOP VIEW OF NO. 1 AND NO. 2 SONOTONE BATTERIES, UPON RECEIPT**

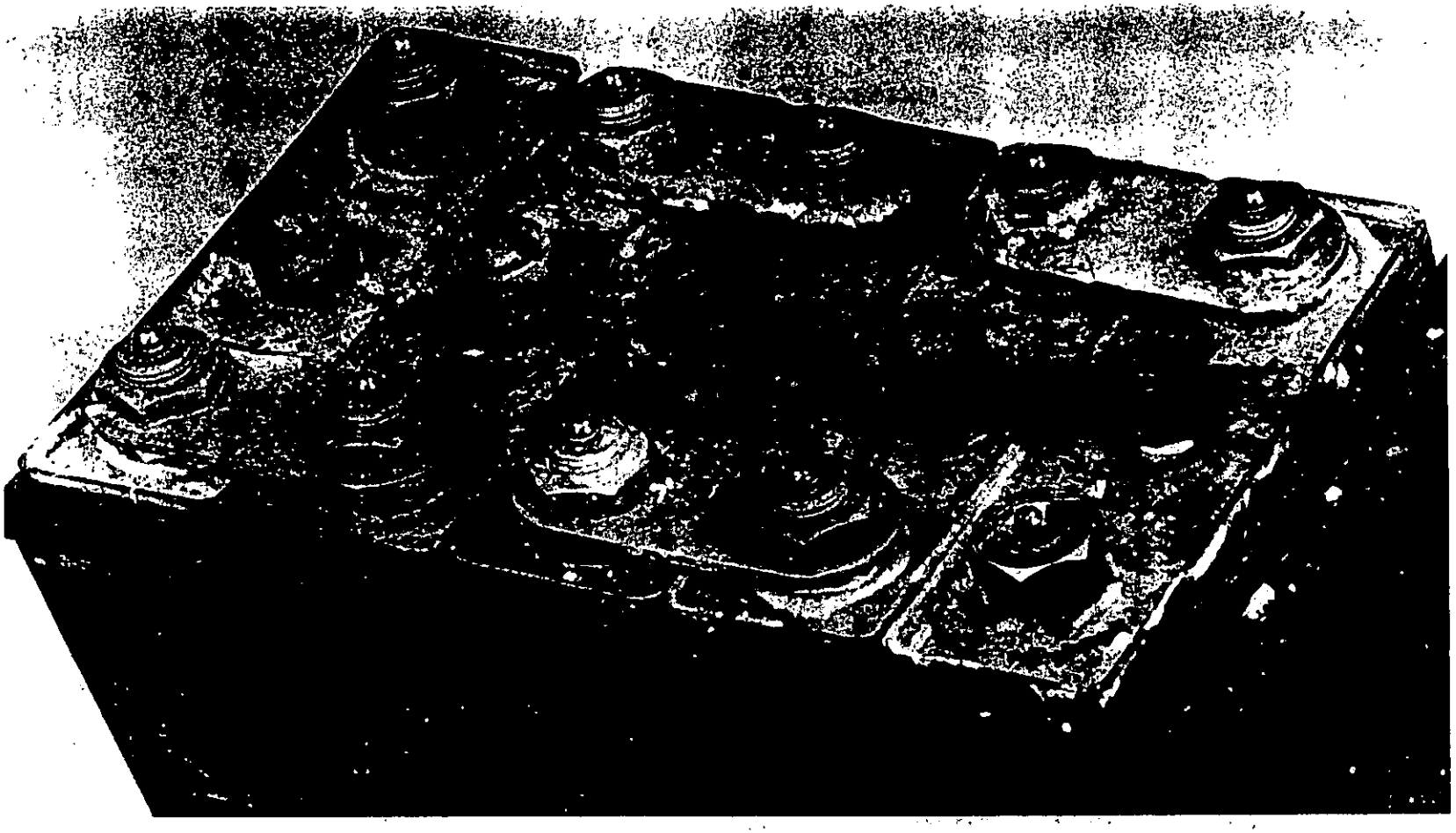


Figure - 16 TOP VIEW CLOSE UP OF NO. 2 SONOTONE BATTERY AFTER 51 CYCLES OF OPERATION

CES 206/16

During the charge of Cycle 64 one of the batteries operating on the low rate charge developed an internal short circuit. Figures 17, 18, 19, 20 show various view of the damage. Examination of cell 2 showed that on a few of the plates the separator material did not fully insulate the adjacent positive and negative plates. This was attributed to faulty assembly. Evaluation of the batteries cycling on the high rate of charge was continued. At cycles 101 and at 117 the engine cranking test was conducted giving an average of 2.38 minutes for cycle 101 and 1.83 minutes for cycle 117. At cycle 151 an average of 2.47 minutes was obtained for the engine cranking rate. Cycles 153 and 201 were run after a 160% recharge after the previous discharge as against the preceding 140% recharges. At cycles 153 and 201, the high rate of charge batteries operated for 4.19 and 2.37 minutes, respectively.

The total amount of distilled water consumed during cycling is given below:

Cycles	Battery No. 1 and No. 2 (high rate charge)	Battery No. 3 and No. 4 (low rate charge)
1-52	7527 cc	11135
53-108	6404 cc	(Battery No. 3 failed at cycle 64)
154-201	5799 cc	

Evaluation was terminated after cycle 201. The Material Laboratory is now awaiting circuit availability to evaluate four replacement sintered plate batteries.

During October 1954, the Material Laboratory commenced some preliminary investigations on the SAFT sealed sintered plate nickel cadmium system. The active materials of the SAFT system are similar to those of the non-sealed sintered plate system described previously. The SAFT

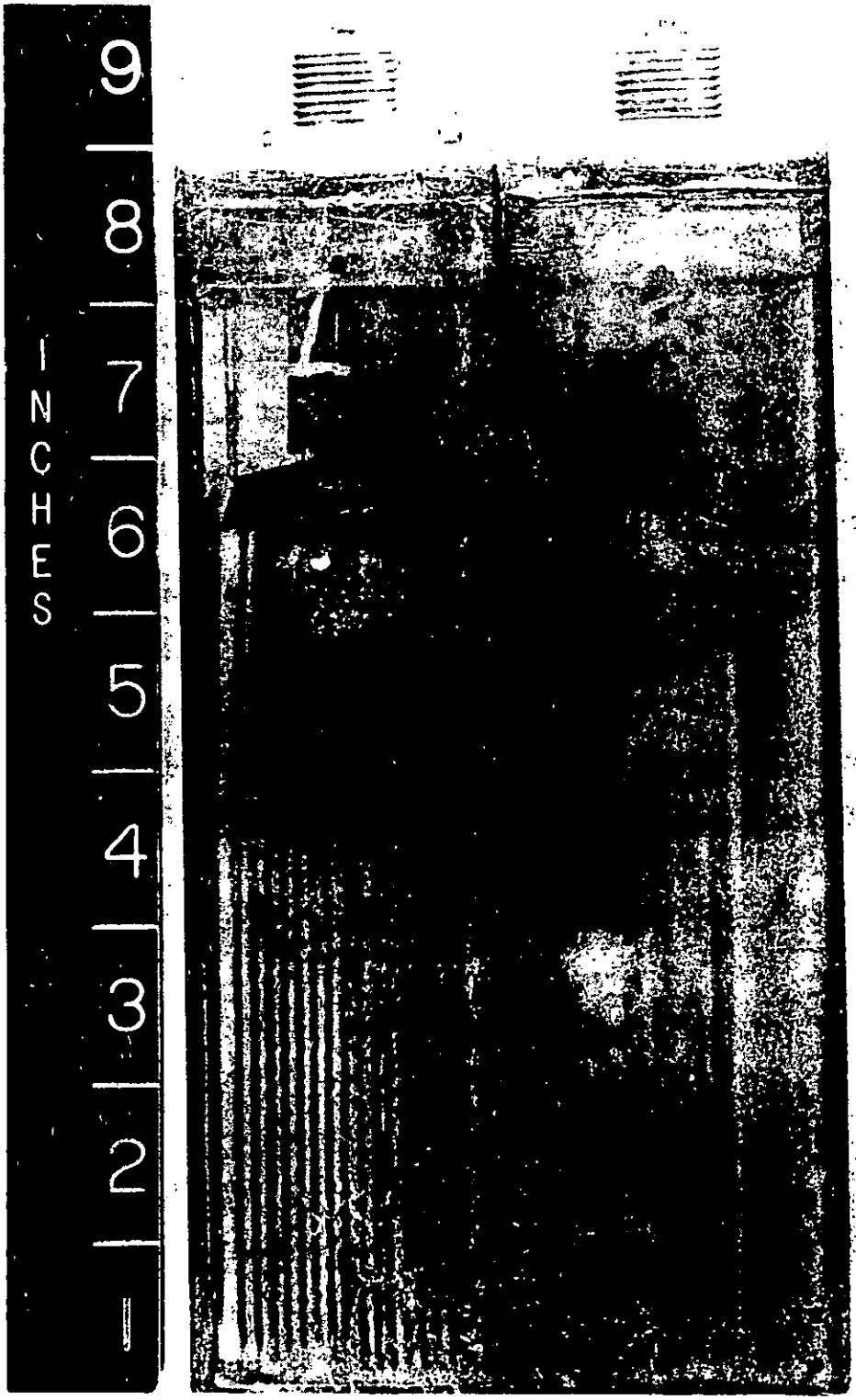


Figure - 17 END VIEW CELLS 1 AND 2 OF BATTERY 3

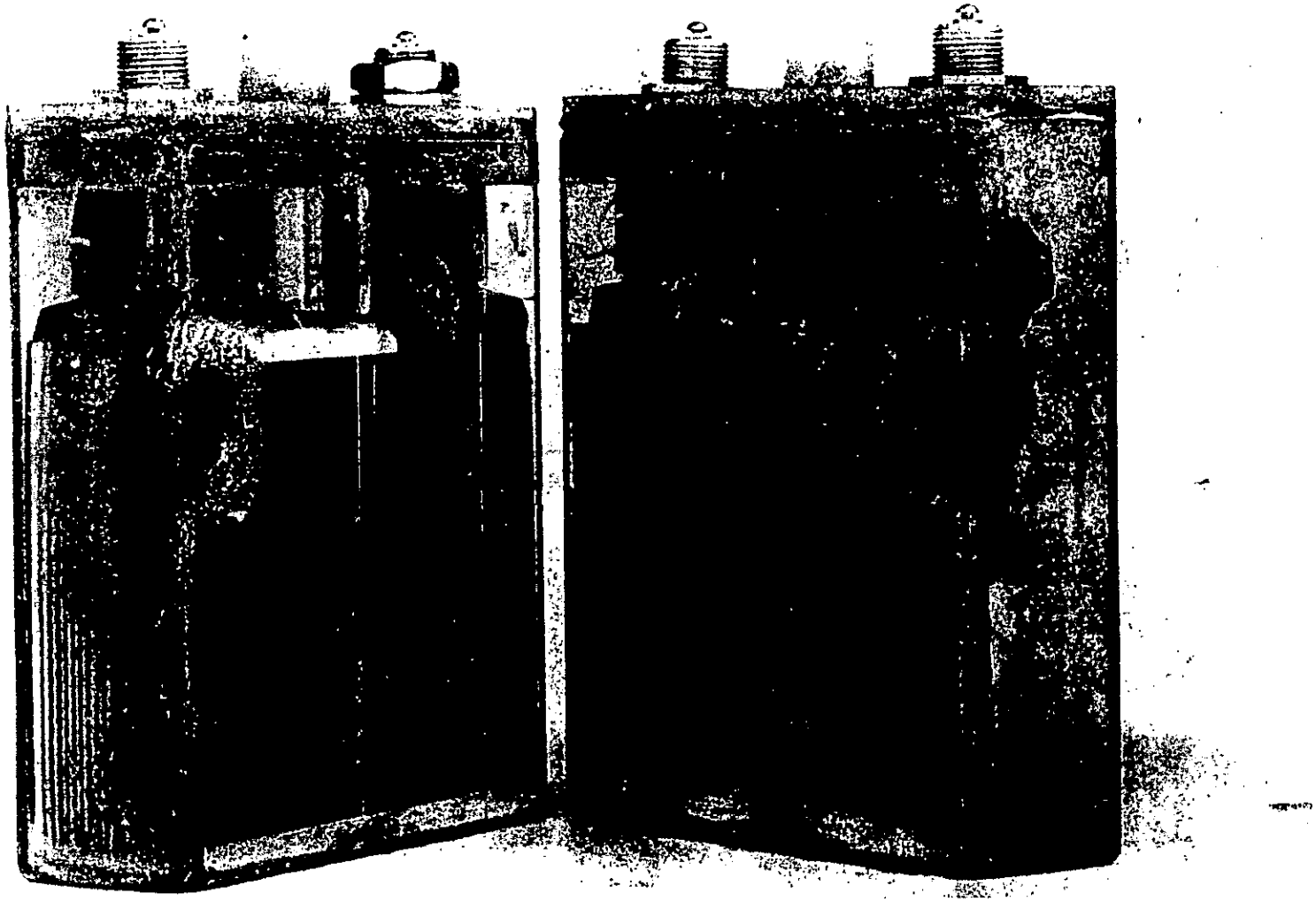


Figure - 18 END VIEW OF CELLS 1 AND 2, SEPARATED

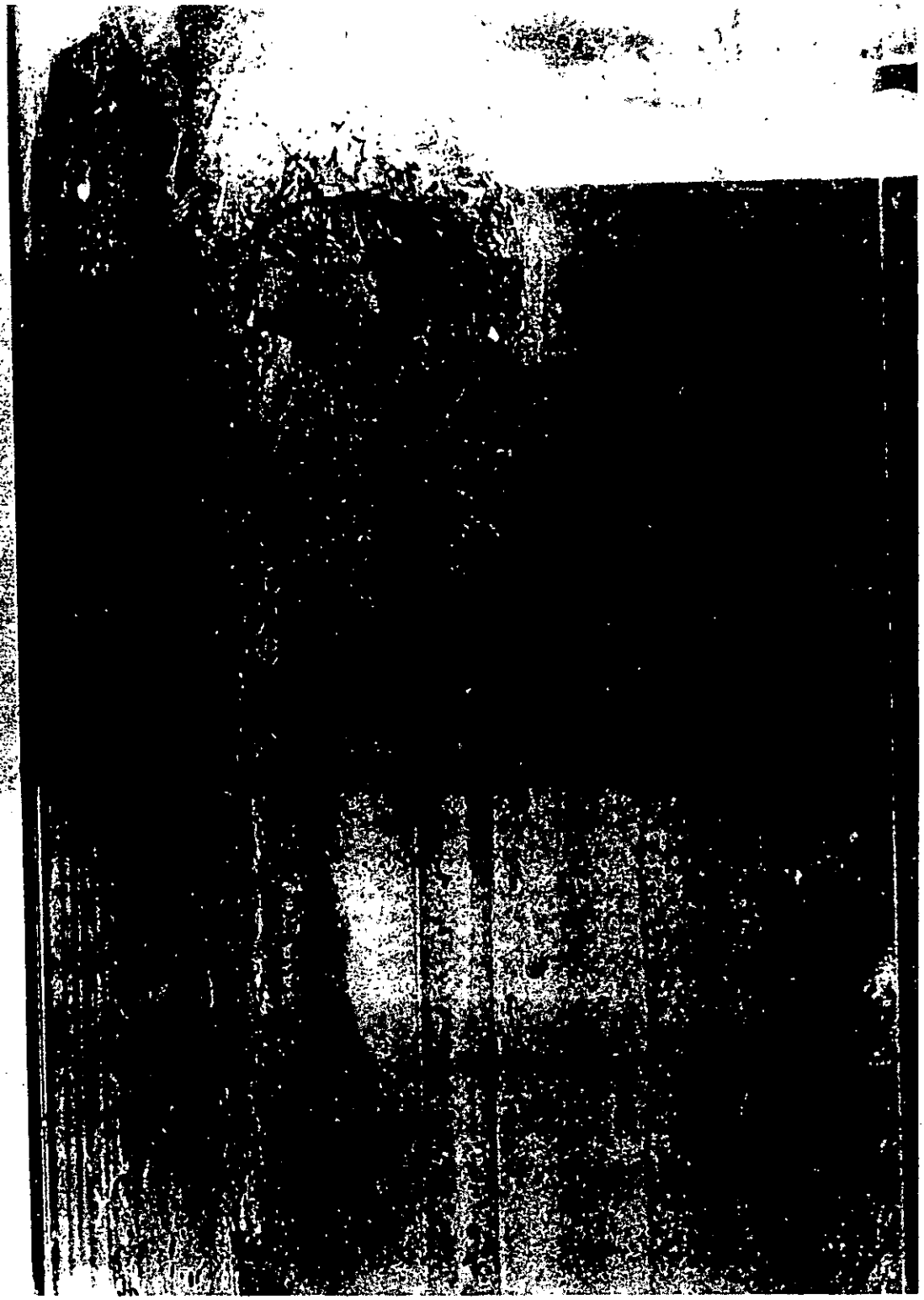


Figure - 19 CLOSE-UP OF CELL 1

Figure - 20 CLOSE-UP OF CELL 2

DATA ON CAPACITY DISCHARGE

BATTERY NO. 1

CYCLE	RATE AMPS	TIME MIN	TEMP START °F	TEMP END °F	VOLTS 15 SEC	VOLTS END
101	650	2.18	0	-	4.20	3.00
117	650	2.08	0	-	4.19	3.00
151	650	2.87	0	-	4.40	3.00
153*	650	4.50	0	-	4.30	3.00
201*	650	2.75	0	-	4.25	3.00

BATTERY NO. 2

CYCLE	RATE AMPS	TIME MIN	TEMP START °F	TEMP END °F	VOLTS 15 SEC	VOLTS END
101	650	2.58	0	-	4.20	3.00
117	650	1.58	0	-	4.00	3.00
151	650	2.07	0	-	4.14	3.00
153*	650	3.88	0	-	4.20	3.00
201*	650	2.00	0	-	4.00	3.00

* Discharge after 160% recharge after a 10-hour rate discharge.

CUBIC CENTIMETERS OF DISTILLED WATER PER CELL CONSUMED DURING CYCLING

BATTERY NO. 1

CYCLES	CELL NO. 1	2	3	4	5
1- 52	747	715	700	732	749
53-108	660	695	593	573	597
109-153	350	356	291	308	316
154-201	595	615	480	520	530

BATTERY NO.2

CELL NO. 1	2	3	4	5
772	729	806	775	802
660	635	626	659	706
376	371	331	331	382
634	585	623	600	617

BATTERY NO.3

CYCLES	CELL NO. 1	2	3	4	5
1-52	1177	1151	1178	1156	1127

BATTERY NO. 4

CELL NO. 1	2	3	4	5
1077	1127	1085	1006	1051

cells differ in construction and assembly. The plates are comprised of perforated nickel-plated steel strips on which have been sintered a porous body of nickel. Active material impregnation into the pores is accomplished by electrolysis in solutions of nickel salts for the positive plates and cadmium salts for the negative plates. Insulation between positive and negative plates is achieved by a continuous length of fabric separator passed successively between the plates. The positive and negative plates, after being compressed are fitted without any clearance, into the nickel-plated steel case. The cell is hermetically sealed with a welded cover and equipped with a resealing valve.

The first SAFT cell evaluated at the Material Laboratory was a VO-160 cell. This cell shown in figure 21 was rated by the manufacturer at 160 amperes for one hour. The cell was received from the manufacturer with a pressure gage attached. The operating procedure for this cell was as follows:

1 - Discharge: 10-hour rate at 20 amps to 0.9V

2 - Charge : 40 amps - 4.2 hrs.

10 amps - 8.2 hrs.

If while on charge at 40 amperes the voltage reached 1.45 volts or the pressure 5 pounds, the charge rate was reduced to 10 amperes. If while on charge at 10 amperes the voltage reached 1.45 volts or the pressure reached 20 pounds, the charge was terminated.

During the first five cycles the VO-160 cell was capable of delivering more than 240 ampere-hours at 20 amperes (10-hour rate). It was also noted that the cell could be cycled without building up excessive internal pressure. Pressures at beginning of the five charges, ranged from zero to four pounds and at end of the five charges from 10 to 20

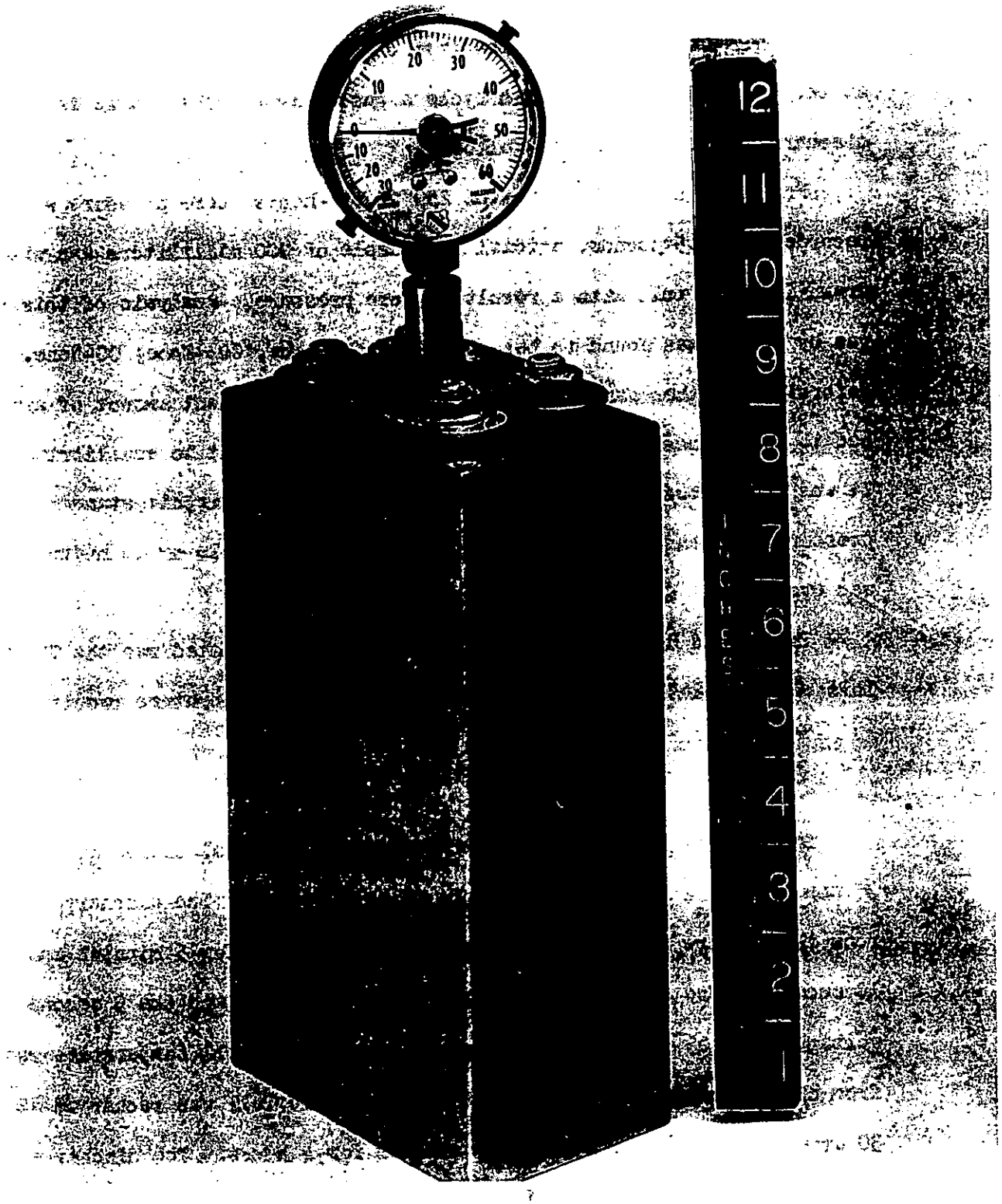


Figure - 21 SAFT NICKEL CADMIUM CELL TYPE VO-160
WITH REINFORCED JACKET REMOVED

pounds. Pressures at the beginning of the five discharges ranged from 7 to 19 pounds and at end of the five discharges from 1.5 to 4 pounds. At the conclusion of the fifth cycle a gas analysis of a charge and discharge cycle was made as follows:

Following a normal charge of 250 ampere-hours where pressure was recorded at 14.5 pounds, a total gas sample of 200 milliliters was withdrawn from the cell with a resultant zero pressure. Analysis of this gas by volume was found to be: O_2-35.7%, H_2-None, CO_2-None, CO-None. Before any further gas tests could be made an equivalent amount of air had to be put back into the cell in order to return it to equilibrium. It was also noted that during discharge and on open circuit stand no pressure was generated, which is indicative that little or no hydrogen was evolved.

The second SAFT sealed nickel cadmium cell evaluated was the VO-80. This cell was designed to meet the high rate low temperature requirements of engine starting batteries for the Military Specification MIL-B-15072A.

The program for this cell was as follows: Initial charge at 30 amperes for 2 hours and at 7 amperes for 7 hours. The discharge at room temperature at 650 amperes to 0.6 volts lasted for 5 minutes and 10 seconds. The open circuit voltage was 1.36 volts and the 5 second voltage was 1.05 volts. During this discharge the cell temperature ranged from 82°F at the start to 120°F at cut off. The cell was recharged at 30 amperes for 1.4 hours and at 7 amperes for 4 hours. The discharge of the VO-80 cell at 650 amperes from an ambient temperature of 0°F, after 24 hours stand on open circuit while being cooled at 0°F, operated for 2 minutes and 15 seconds to 0.6 volts. The open circuit voltage was

1.32 volts and the 5 second voltage was 0.80 volts. The results indicate the inability at this time of the VO-80 cell to meet the cold test required for Navy standard engine starting batteries. At present, awaiting circuit availability is a SAFT 5 VO-160 sealed battery.

To date this is the extent of the Material Laboratory investigation in the field of nickel cadmium batteries. The Navy is in no way opposed to the investigation of nickel cadmium batteries. However, when the cost of these batteries is taken into account, and their use of critical materials, there must be shown very significant advantages to justify their use. SAFT prices, based on duty free certificates, for their hermetically sealed batteries are:

Battery	Price in quantities (10-99)
5 VO-80 (6 volts)	$261.77
10 VO-80 (12 volts)	505.69
5 VO-125	279.75
10 VO-125	546.75
5 VO-160	445.34

Sonotone prices for large quantities, to commercial specifications are:

Battery	Prices in quantities (10-99)
6V-100AH	$215.00
12V-100AH	410.00
6V-150AH	300.00
12V-150AH	575.00

For comparison, the standard Navy lead-acid 6 volt, 175AH battery can be purchased for about $35.00. It is realized that the true price ratio would not be as great if production were equal. The Navy is also aware of the danger that laboratory tests may be improperly designed as a

basis of evaluation for service use. This danger is small for a well known product but is real for a new product. Consequently, the Navy will continue to investigate all developments in the nickel cadmium field in the attempt to obtain a satisfactory unit that will comply with Navy requirements.

PRESENTED AT THE JOINT BATTERY CONFERENCE MEETING - 12 SEPTEMBER 1956
Sponsored by the Coordinating Committee on Equipment & Supplies
Office of the Assistant Secretary of Defense (R&D)
Washington, D. C.

New Developments in Storage Battery Separators

by Albert Glowasky

Battery Section
Material Laboratory
New York Naval Shipyard

The study of newly developed separators in fully assembled storage battery cells under cycling conditions is recognized as an important phase in battery research and development. The separator constitutes one of the most important parts of a storage battery and consequently is a determining factor in establishing battery voltage, capacity and life characteristics. The primary function of this separator is to provide an insulating barrier in order to prevent treeing or metallic conduction between plates of opposite polarity, while permitting free electrolyte diffusion at a very low electrical resistance.

Many types of separators have been used in storage batteries for military applications. Some of those used are wood, microporous rubber and plastics, fibrous materials impregnated with insoluable resins, regenerated cellulose films with a resin and layers of diatomaceous earth with glass mats used either as retainers or separators.

Up to a few years ago, wood separators were the most commonly used in storage batteries. However, where long life requirements demanded durability, wood separators were no longer satisfactory as:

a. acceptable separator lumber with uniform qualities was gradually being exhausted and was in poor supply, also,

b. the effect of 1.250 to 1.300 specific gravity sulfuric acid electrolyte in charring and weakening the wood fiber for long life has been definitely established.

At the present time, the microporous rubber separator has somewhat supplanted the wood separator, especially for military applications, and has become established as a standard. The main reason for this is that this separator does not readily become soft with use and lose its insulating value and physical strength as does the wood separator. This being true, the separator life is longer, and failures due to soft and weak separators are greatly reduced. This separator has also demonstrated that it usually will outlast the life of the battery plates with little or no adverse effect on them.

It is in time of national emergency when the supply of natural rubber becomes critical, with the demand for microporous rubber separators be met and the resultant higher cost, that new research and development programs have been encouraged and many industrial firms are presently carrying out this work. Detailed information is not available in the technical literature and the lack of published information does not permit a valid comparison at this time. It is toward this end that the Material Laboratory has been investigating various newly developed separator materials for utilization in storage batteries for military applications.

These investigations were conducted with standard Navy portable storage batteries of the type shown in figure 1, utilizing the various

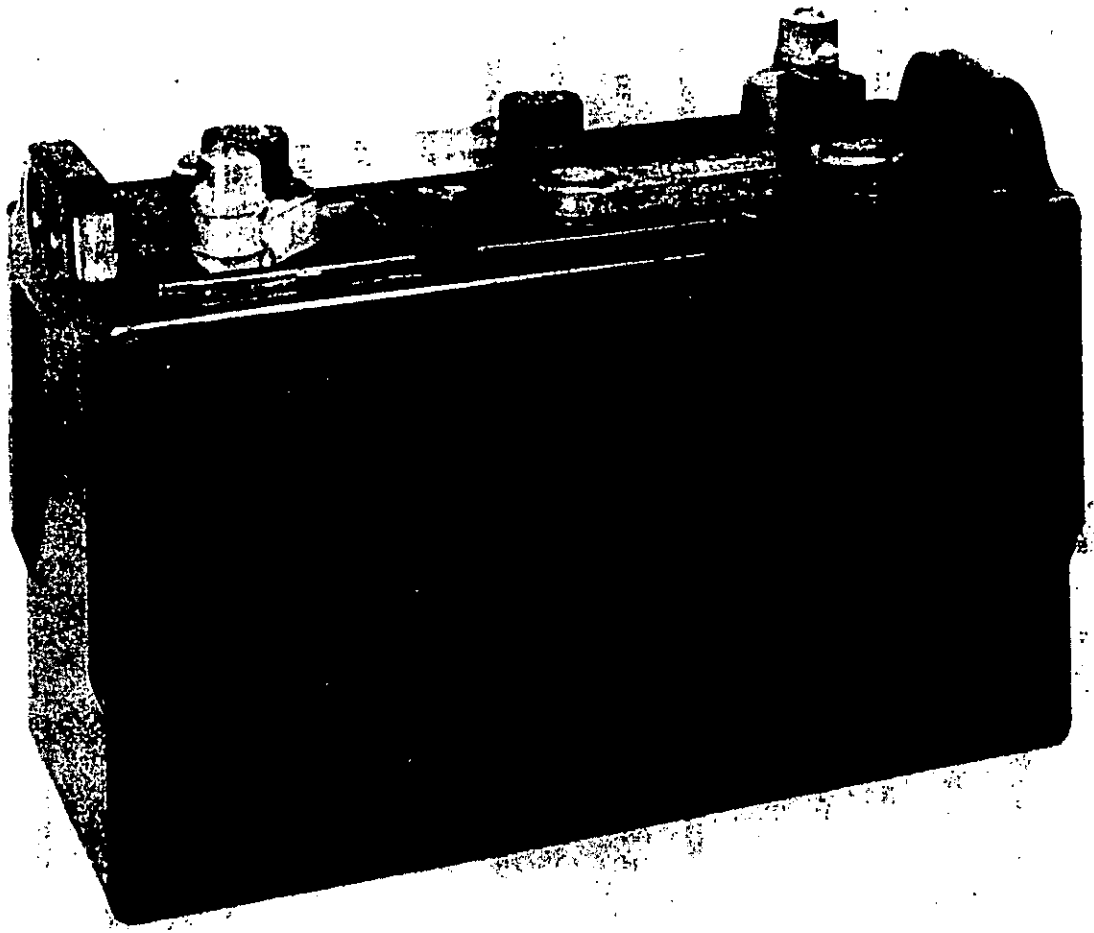


FIGURE I
NAVY CLASS 6V-SBMD-130 A.H.
NAVY CLASS 6V- SBM -100 A.H.
PORTABLE STORAGE BATTERIES

CES 206/16

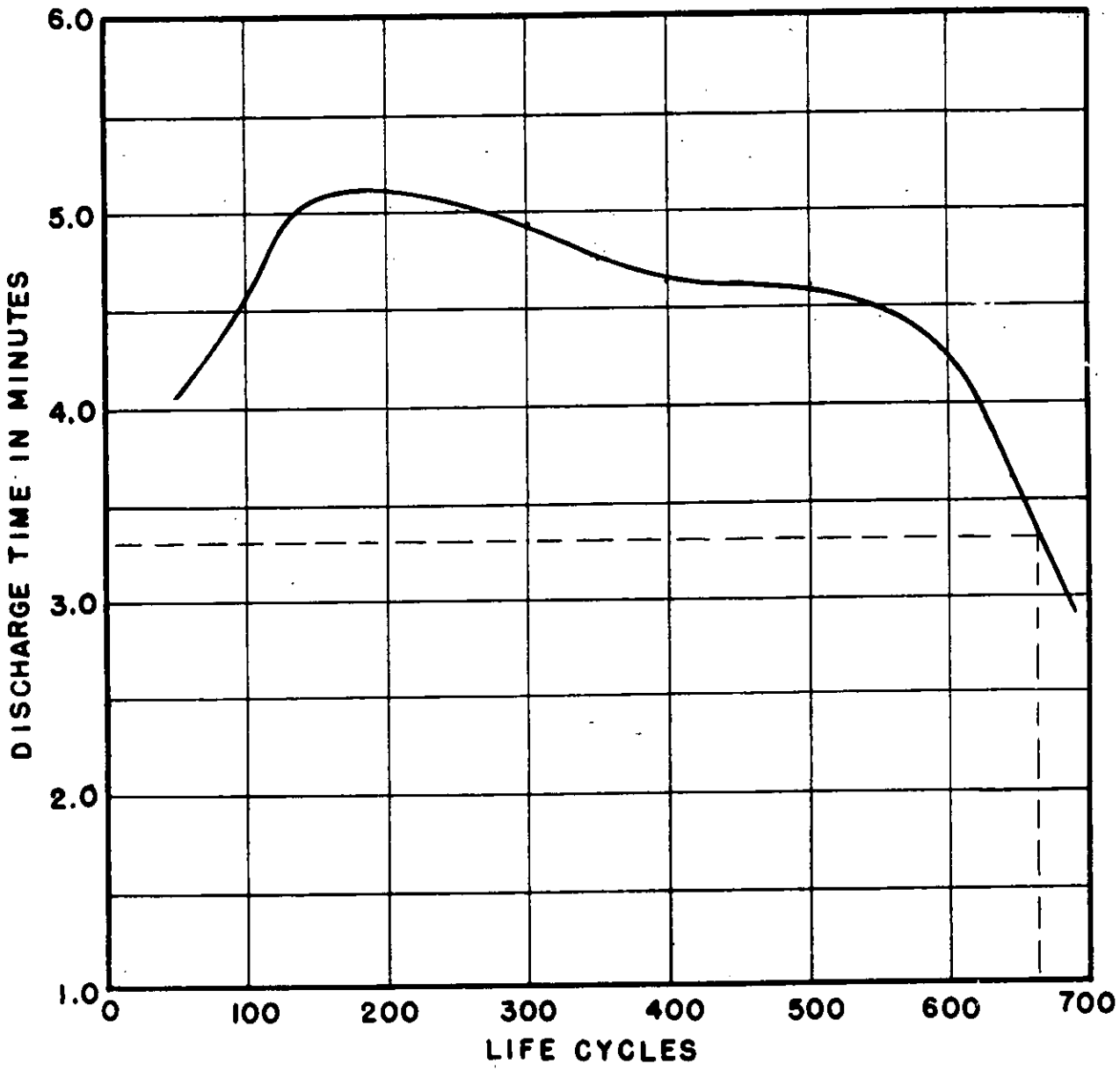
types of separator materials in evaluating cycle life characteristics as follows:

a. The Willard Storage Battery Company of California submitted samples of Navy type engine starting lead acid 27 plate portable storage batteries, class 6V-SBMD-130A.H., which were manufactured in 1951 under contract N383-155s-45383 and supplied with standard microporous rubber separators. These batteries are normally evaluated for a minimum of 150 life cycles and usually up to a full allowance of 250 life cycles. However, in this particular case this evaluation was continued until the batteries failed to deliver the cranking rate of 650 amperes from a temperature of zero degrees F for 3.3 minutes to 3.0 volts per battery. Batteries in this group actually averaged 654 life cycles, as shown in figure 2, when failing to meet the above condition. Upon inspection of the elements, particular attention was paid to the microporous rubber separators. These separators still appeared to be in excellent condition. They were flexible and without any indication of etching or charring by the sulfuric acid electrolyte or plates after 654 life cycles. These separators indicated that they could have been cycled many more times if the plates in these batteries were designed to deliver the additional electrical energy.

b. The Owens-Corning Fiberglass Corporation submitted in 1951 samples of their combination glass fiber and

FIGURE 2

CYCLE LIFE CHARACTERISTICS OF
NAVY CLASS 6V-SBMD-130 A.H. PORTABLE STORAGE BATTERIES
WITH MICROPOROUS RUBBER SEPARATORS

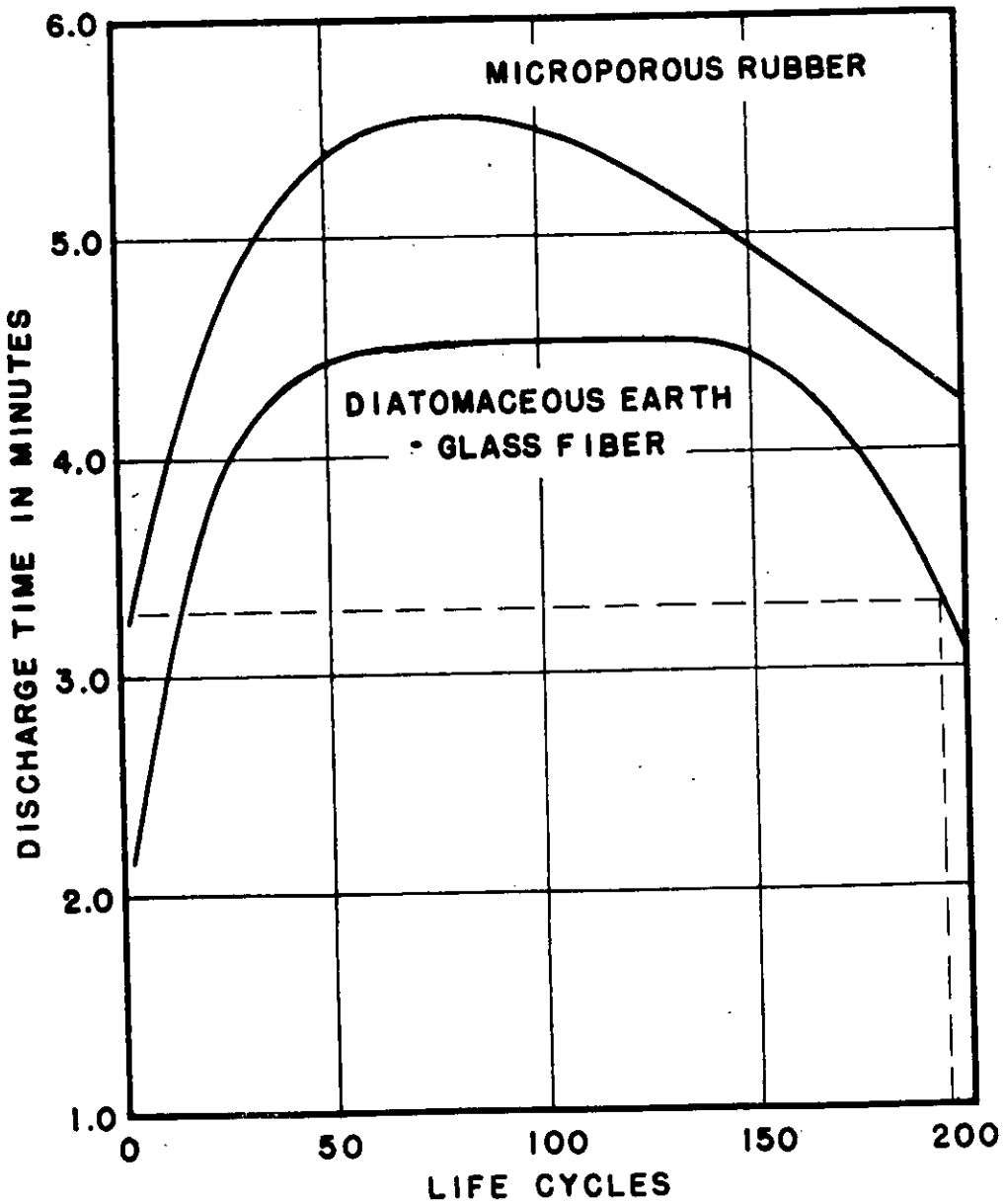


CES 206/16

diatomaceous earth storage battery separators which they claimed should be satisfactory for use in Navy class 6V-SBMD-130A.H. storage batteries. In order that these separators might be evaluated properly, a control had to be established. The Material Laboratory was furnished with six Navy class 6V-SBMD-130A.H. storage batteries manufactured by The Electric Storage Battery Company under the same contract. Three of these batteries were furnished with the standard microporous rubber separators and the other three with Owens-Corning improved glass fiber and diatomaceous earth separators. These batteries were then evaluated for cycle life characteristics for Navy class 6V-SBMD-130A.H. engine starting storage batteries. Results obtained as shown in figure 3, indicated that the batteries with the glass fiber diatomaceous earth separators showed satisfactory performance up to 150 life cycles, but at cycle 200 the three batteries could only deliver the cranking rate of 650 amperes from zero degrees F for 3.08, 3.12 and 3.12 minutes respectively to 3.0 volts, whereas 3.3 minutes is the required minimum. It is to be noted however that the three control batteries with the microporous rubber separators were still delivering 4.20, 4.18 and 4.17 minutes respectively at the 650 ampere cranking rate at cycle 200. Upon completion of cycle 200, examination of the cells showed the microporous rubber separators to be in very

FIGURE 3

CYCLE LIFE CHARACTERISTICS OF
NAVY CLASS 6V-SBMD-130 A.H. PORTABLE STORAGE BATTERIES
WITH DIATOMACEOUS EARTH-GLASS FIBER
AND MICROPOROUS RUBBER SEPARATORS

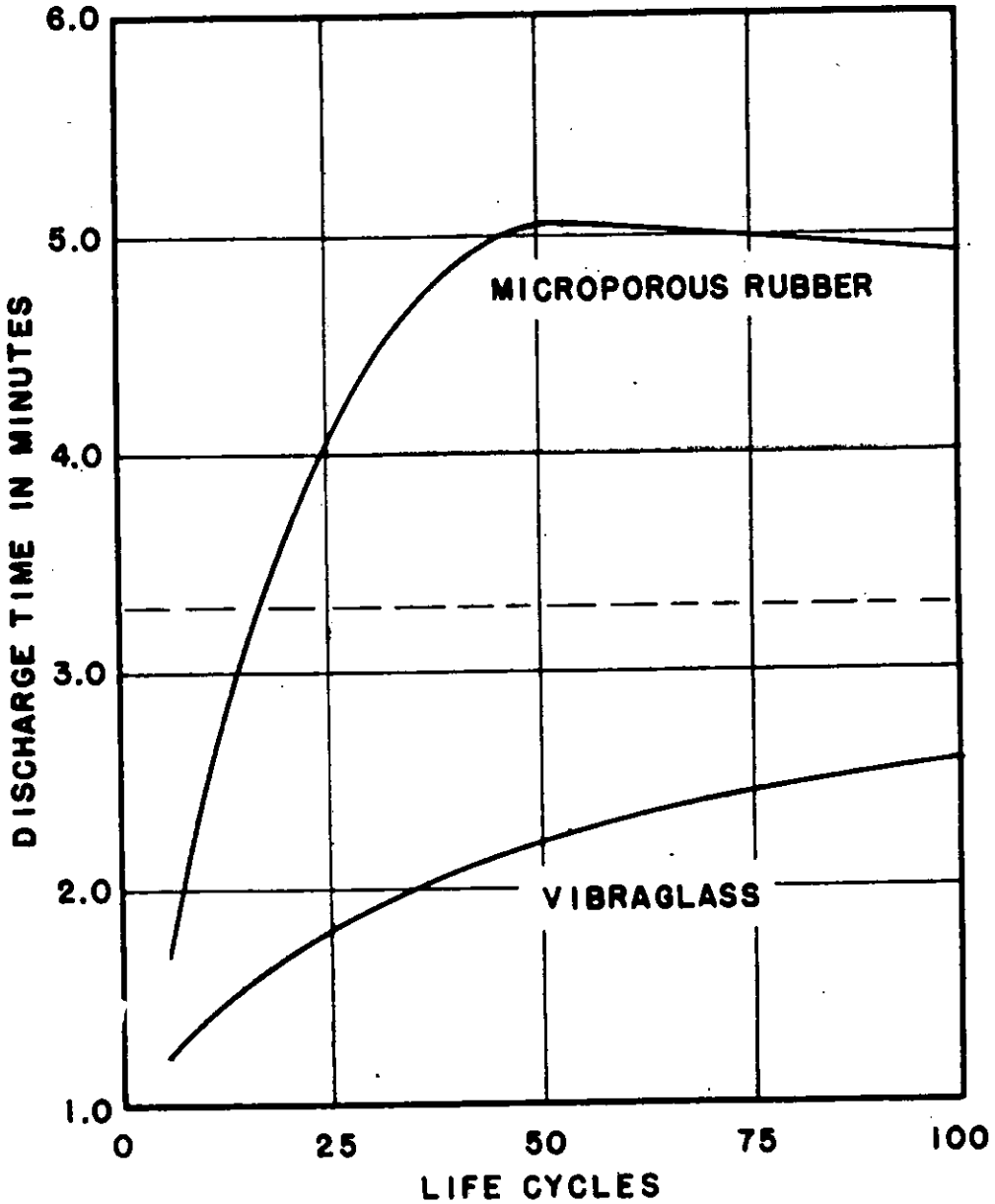


CES 206/16

good condition. On the other hand the glass fiber diatomaceous earth separators, while intact, adhered to the negative plate material quite strongly and had to be pulled away. This condition restricted electrolyte circulation and brought about premature sulphation of the negative plates. It was also believed that the Owens-Corning separator had moderately higher resistance than the microporous rubber separators.

c. The Vibradamp Corporation of Los Angeles, California developed a storage battery separator known as Vibraglass. This separator was made of fiberglass with an insoluble binder. Sufficient samples were submitted in 1951 to the Material Laboratory for evaluation. Four Navy class 6V-SBMD-130A.H. portable storage batteries of the same manufacture and same age were utilized for this project. The microporous rubber separators were removed from two of the batteries and replaced with the Vibraglass separators. The other two batteries retained the original. The four batteries were then cycled for life characteristics. After cycling for 100 life cycles, it was observed that at the cranking high rate of discharge of 650 amperes from an initial temperature of zero degrees F to 3.0 volts per battery, the batteries with the microporous rubber separators performed for an average of 4.91 minutes, while the batteries with the Vibraglass separators performed only for an average of 2.54 minutes as against the required minimum of 3.3 minutes as shown in figure 4.

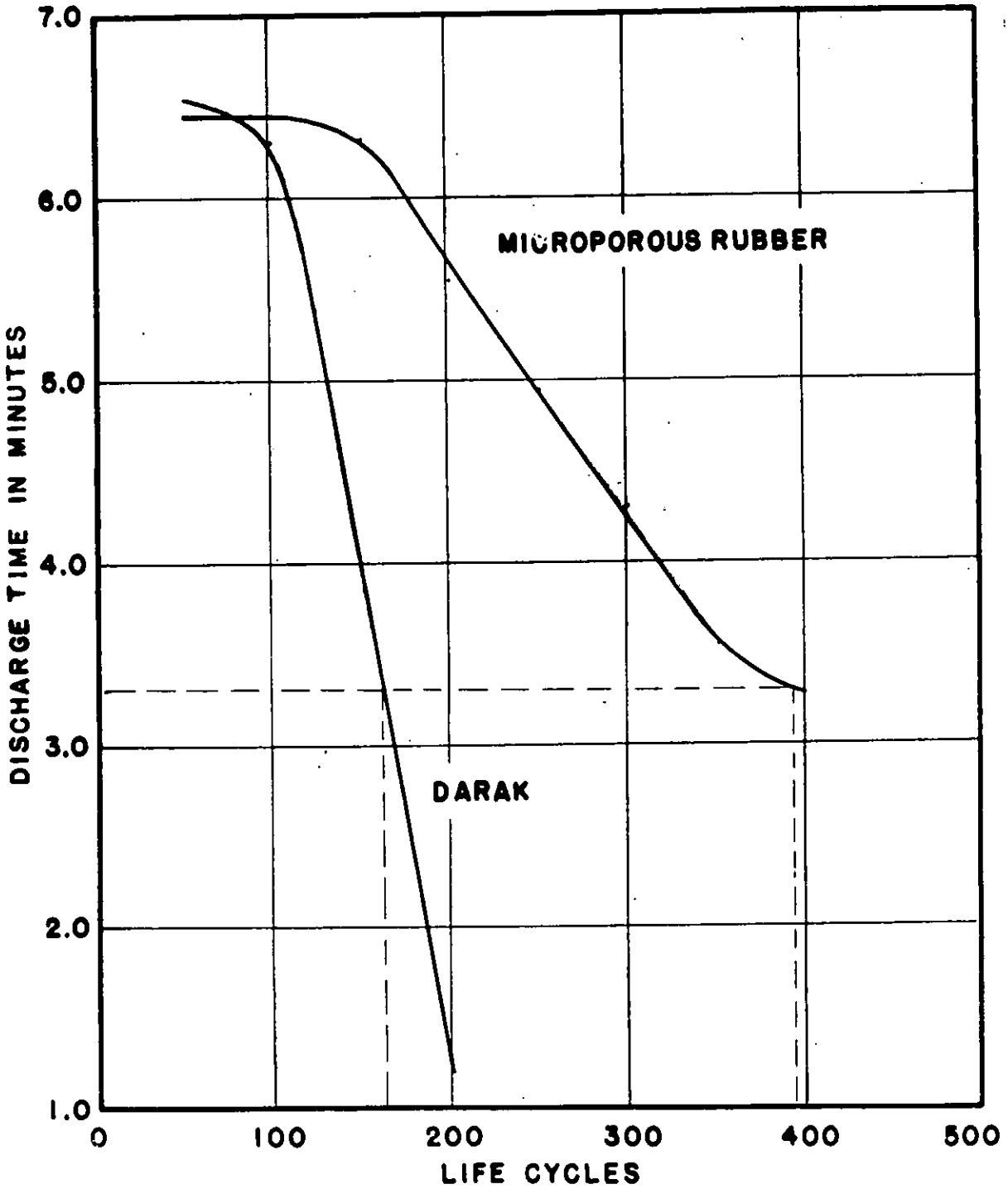
FIGURE 4
CYCLE LIFE CHARACTERISTICS OF
NAVY CLASS 6V-SBMD-130 A.H. PORTABLE STORAGE BATTERIES
WITH VIBRAGLASS AND MICROPOROUS RUBBER SEPARATORS



This was apparently due to the resistance of these separators being moderately higher than that of the microporous rubber separators. In view of this poor performance demonstrated by the Vibraglass separators, cycling was discontinued and the cells were opened for inspection. Examination of the elements showed that the Vibraglass separators had adhered to the negative plates like wet blotting paper and the active material of the negative plate appeared to be in an overexpanded and sulphated condition.

d. The Dewey and Almy Chemical Company of Cambridge, Massachusetts, developed the Darak battery separator and requested approval for these separators for use in the 27 plate Navy portable storage batteries. These separators were of two-ply flat-back construction and were made of cellulose fibers felted into a porous sheet and impregnated with a synthetic acid resistant resin. The two plies were spot bonded together with polystyrene resin. Two Navy class 6V-SBMD-130A.H. portable storage batteries manufactured by the Reading Batteries, Inc., in 1954 were assembled with these separators. For purposes of control and comparison, the evaluation was conducted simultaneously with two identical Reading batteries assembled with microporous rubber separators. The four batteries were then cycled for cycle life characteristics - that is, until each separator group showed that it

FIGURE 5
CYCLE LIFE CHARACTERISTICS OF
NAVY CLASS 6V-SBMD-130 A.H. PORTABLE STORAGE BATTERIES
WITH DARAK AND MICROPOROUS RUBBER SEPARATORS

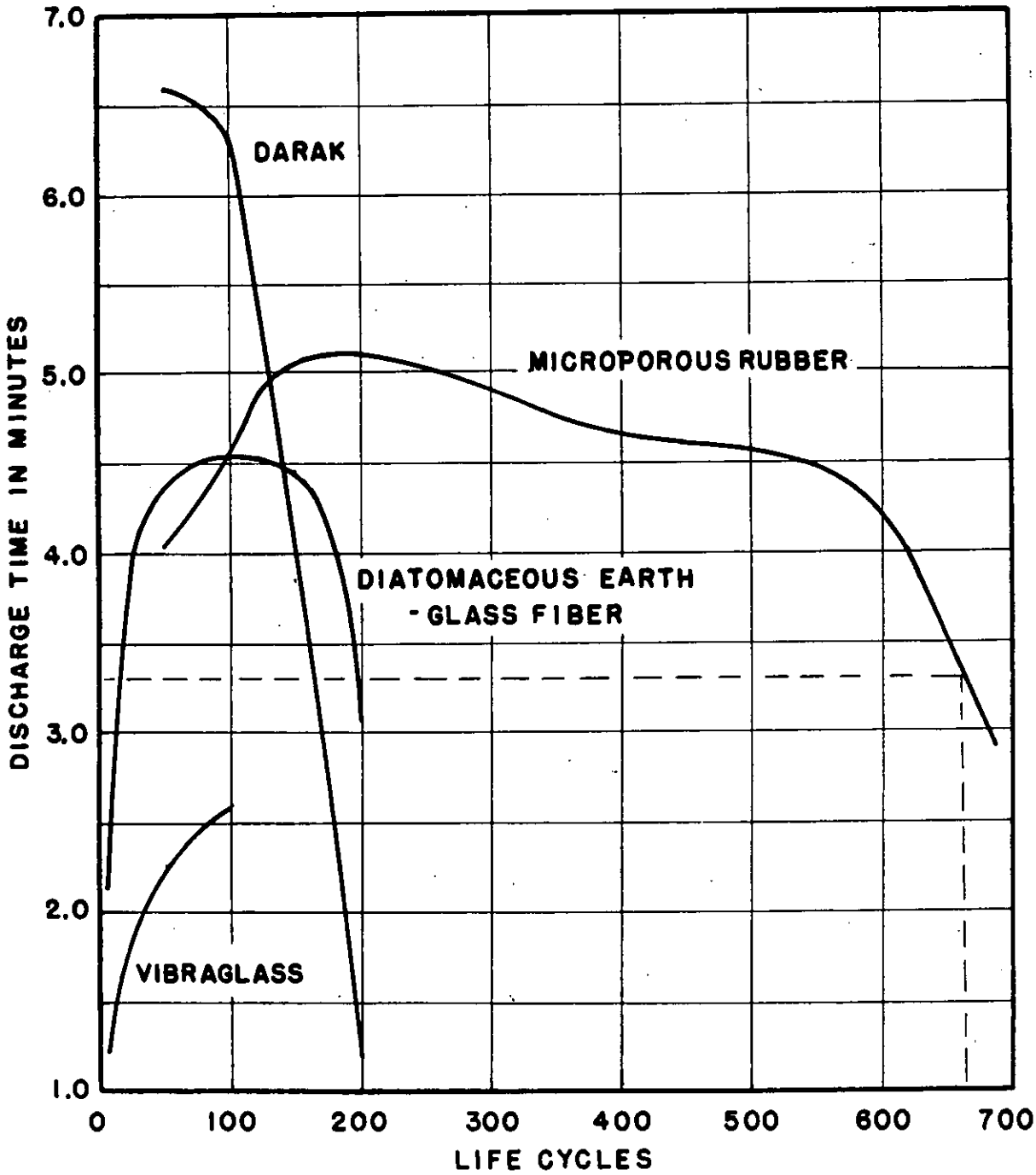


could not be discharged at the 650 ampere rate from zero degrees F for 3.3 minutes to 3.0 Volts per battery. The results obtained as shown in figure 5 indicate that the batteries with the microporous rubber separators again showed to advantage. They averaged 396 life cycles while the batteries with the Darak separators averaged only 161 life cycles. Inspection of the elements with the Darak separators showed that all the separators had adhered to the negative plates and had to be pulled away. Upon closer examination, it was observed that each of the separators had at least 6 pin holes in it and was severely etched. These pinholes were sufficient to establish conduction between plates for short circuits to develop which resulted in battery failure.

It has therefore become evident that a substitute for the microporous rubber separator for Navy class 6V-SBMD-130A.H. portable storage batteries which will demonstrate good zero degree F performance and provide a minimum of 250 life cycles has yet to be developed, as can be observed from the composite curves shown in figure 6.

In another application of battery separators, for Navy portable storage batteries, the Chicago Development Company in 1950 under contract NObs-46315, developed a veneer type sulphur separator applicable for use in the 17 plate type Navy class 6V-SBM-100A.H. portable storage batteries. The electrical resistance of these separators ranged from 0.085 to 0.098 ohms per square inch of surface area, which is nearly double that of microporous rubber material. Three Navy class 6V-SBM-100A.H. storage batteries with veneer type sulphur separators

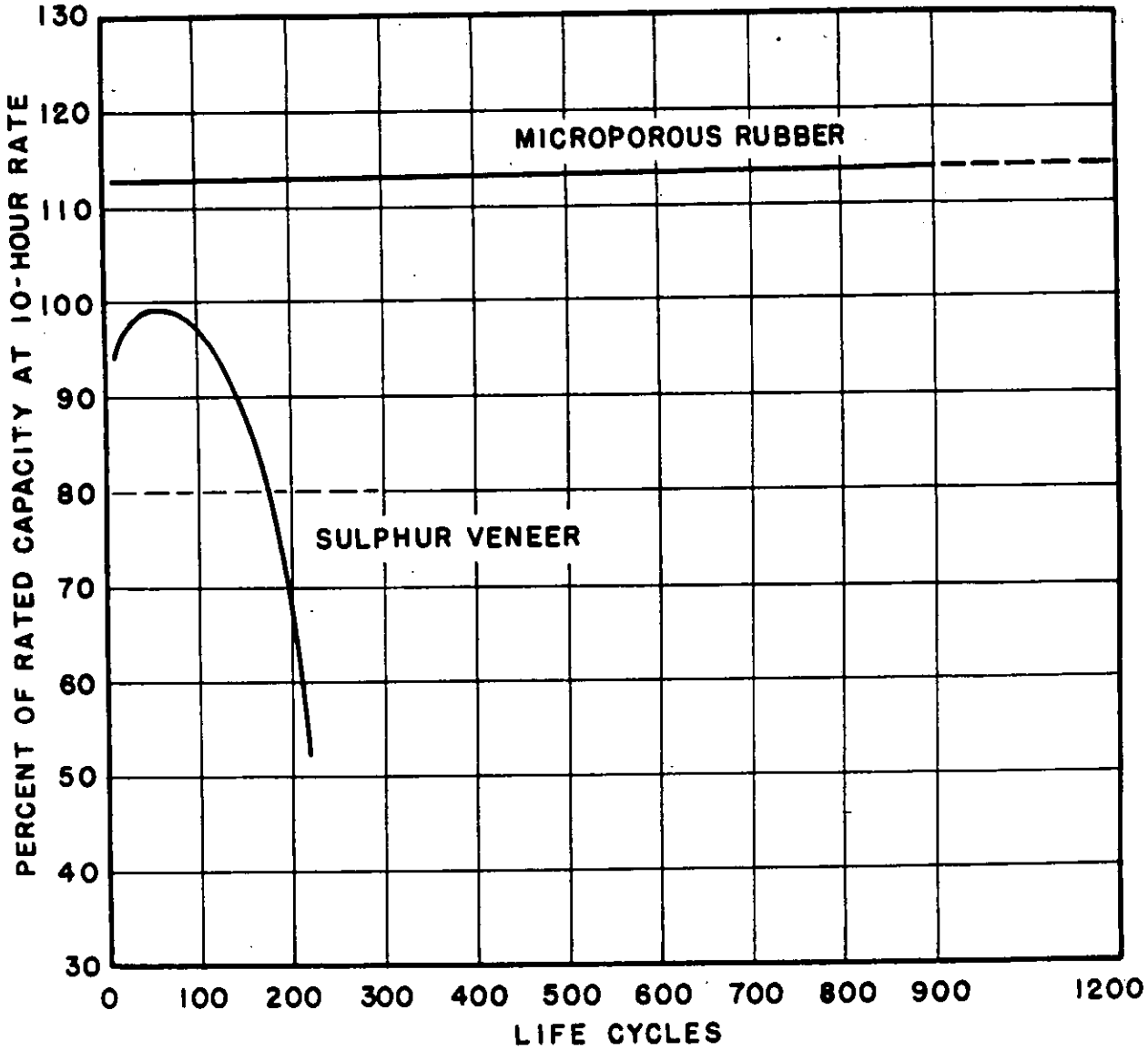
FIGURE 6
CYCLE LIFE CHARACTERISTICS OF
NAVY CLASS 6V-SBMD-130 A.H. PORTABLE STORAGE BATTERIES
WITH VARIOUS TYPES BATTERY SEPARATORS



were furnished for evaluation. Batteries of this type are normally evaluated for a minimum of 600 life cycles and usually up to a full allowance of 1200 cycles or until the battery fails to deliver at least 80 percent of rated capacity at the 10-hour rate. Evaluation of these batteries indicated that they averaged only 180 life cycles prior to reaching the 80 percent condition. Cycling was therefore terminated. Inspection of the elements showed that primary failure of the batteries was due to deterioration and disintegration of the sulphur separators. Similar Navy class 6V-SBM-100A.H. storage batteries which were manufactured under contract N140-155s-46509B and supplied with standard microporous rubber separators were evaluated for the full 1200 life cycles and the 10-hour rate capacity still averaged about 115 percent of capacity, as can be observed in figure 7. Examination of these cells after 1200 life cycles showed the microporous rubber separators still to be in good condition. These sulphur veneer separators cannot therefore be considered as alternates to microporous rubber separators for portable battery service.

The ultimate usefulness of the storage battery separator for military application is in the submarine main storage battery cell, which is shown in figure 8, whose purpose is to provide the electrical power necessary for main propulsion of our modern submarines which are ever requiring higher submerged speeds and greater submerged endurance. For this severe service, the standard microporous rubber separator has so far shown itself to be the only separator which has outlasted the useful life of the cell without contributing to its failure. Storage battery cells designed for submarine main propulsion service are

FIGURE 7
CYCLE LIFE CHARACTERISTICS OF
NAVY CLASS 6V-SBM-100 A.H. PORTABLE STORAGE BATTERIES
WITH SULPHUR VENEER AND MICROPOROUS RUBBER SEPARATORS



CES 206/16

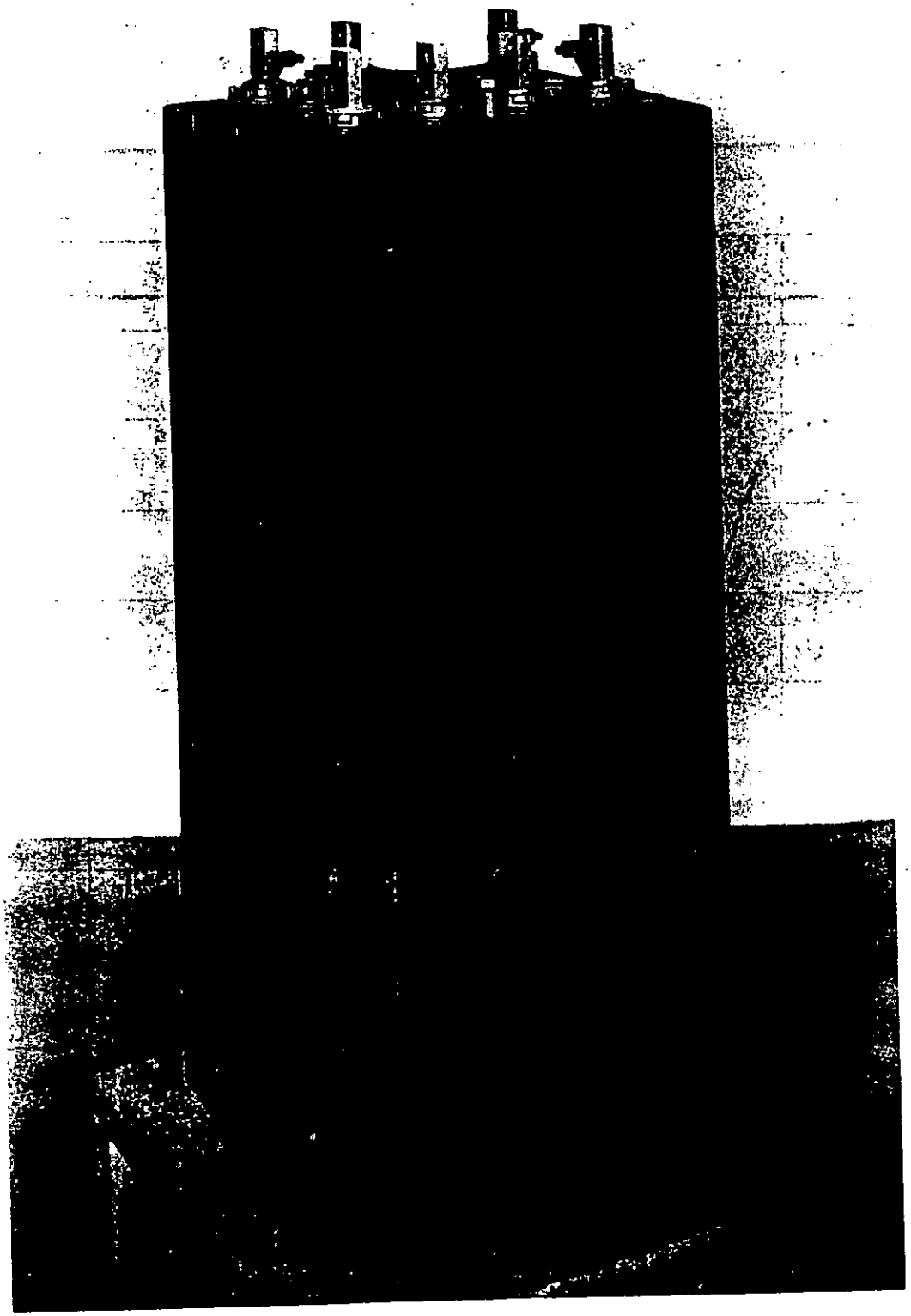


FIGURE 8
GUPPY CLASS SUBMARINE MAIN STORAGE BATTERY CELL

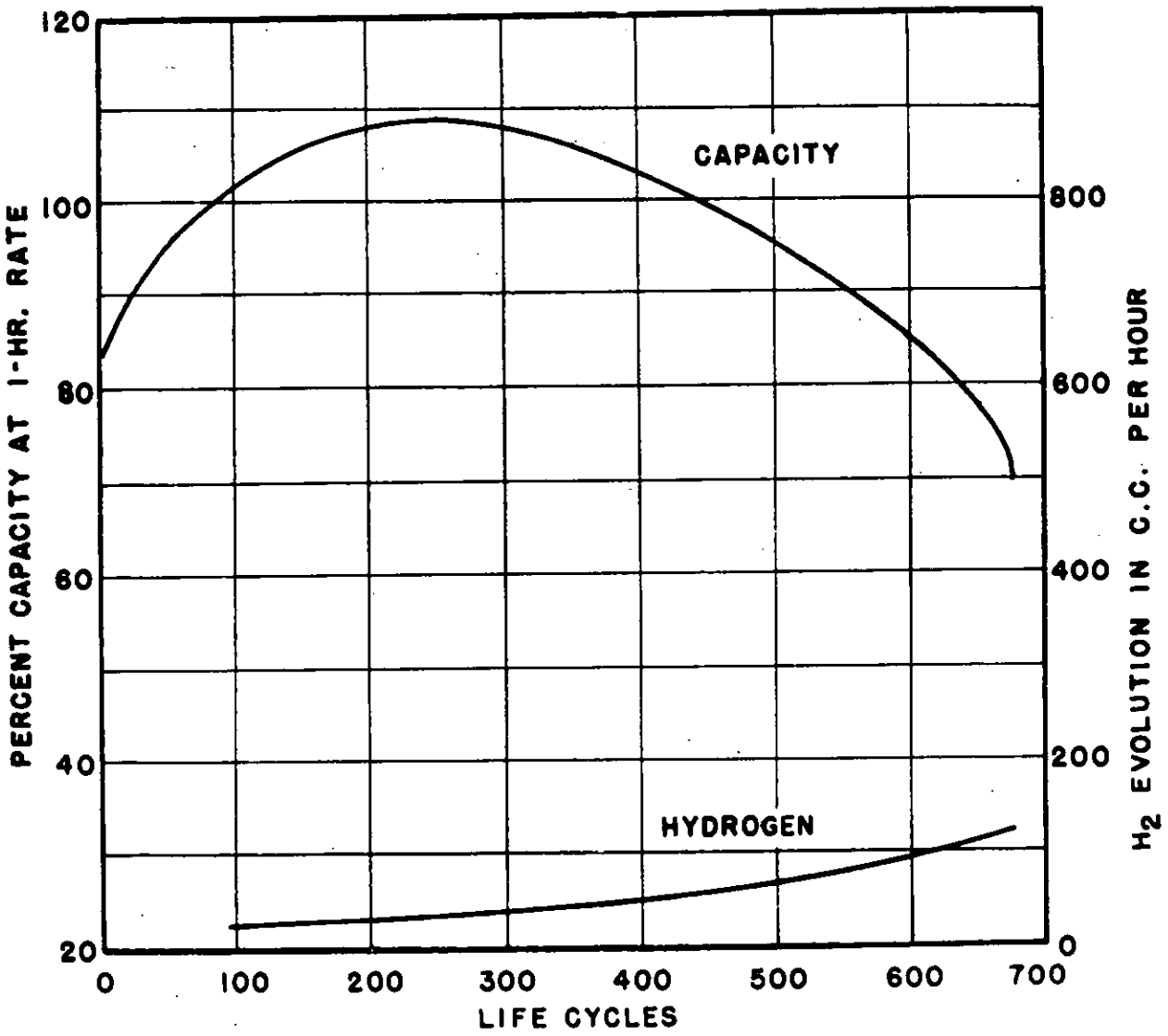
required not only to deliver maximum power output for a specified size and weight of cell for maximum cycle life but also have during it cycle life a minimum level of hydrogen evolution which normally results from local action during stand periods on open circuits.

It is toward this end that several storage battery and separator manufacturers have bent their research and development efforts in order to produce an acceptable substitute for microporous rubber separators for submarine service. As a result of this work, the Material Laboratory has undertaken to investigate these new separator materials in full size GUPPY 67 plate type submarine main storage battery cells under simulated submarine cycle life characteristics as follows:

a. The Gould-National Batteries, Inc. in 1951 submitted three Gould type TPX-C-67 GUPPY class submarine main storage battery cells under contract NObs-50339 which were furnished with standard microporous rubber separators. These cells were evaluated under simulated submarine cycle life conditions. The results of this evaluation as shown in figure 9 indicate that the cells were capable of being cycled for 680 laboratory cycles prior to the end of their useful life, which is at 80 percent of rated capacity at the 1-hour or 4340 ampere rate. It is to be noted that the average hydrogen evolution during the same period in c.c./hr./cell/1000A.H. of 10-hour rating, varied from 25 c.c. to 110 c.c., which is considered normal for an antimonial lead cell of this type. Upon examination of the element, it was found that

FIGURE 9

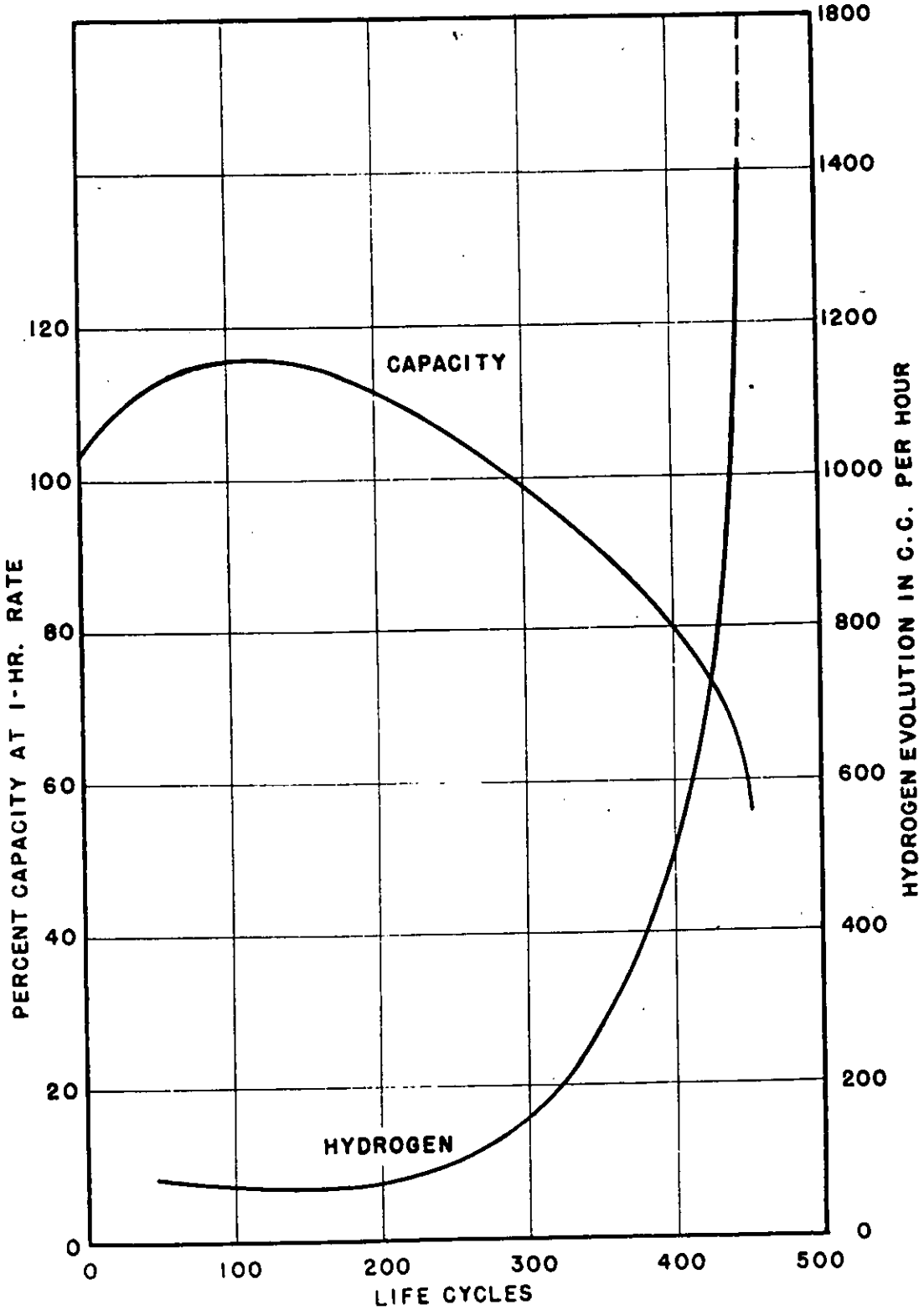
CYCLE LIFE AND HYDROGEN EVOLUTION CHARACTERISTICS OF GOULD TYPE TPX-C-67 GUPPY SUBMARINE MAIN STORAGE BATTERY CELLS WITH MICROPOROUS RUBBER SEPARATORS



cell failure was due to corroded positive grids, while the microporous rubber separators were found to be in very good condition and showed excellent resistance to etching and corrosion. This separator is therefore considered to be very suitable for submarine service.

b. The Electric Storage Battery Co., in 1953 submitted three Exide type MAW-67C GUPPY class 67 plate submarine main storage battery cells under contract NObs-55161, which were furnished with their plastic "Pormax" type microporous separators of polyvinylchloride. Evaluation of these cells under simulated submarine service cycle life conditions indicates, as shown in figure 10, that these cells were only capable of being cycled 400 laboratory cycles prior to reaching 80 percent capacity at the 1-hour or 4340 ampere rate. During this same period however it is to be noted that the hydrogen evolution remained normal only up to 250 life cycles after which it broke away from 100 c.c./hour to 1786 c.c./hour at cycle 450 with corresponding drop in capacity at the 1-hour rate. This unusual behavior may be attributed possibly to the fact that the separators had sufficiently yielded to become etched and corroded by the plates and electrolyte and in some measure assisted the tremendous increase in hydrogen evolution during stand periods on open circuit as a result of increased local action. At the same time this separator deterioration contributed to the premature drop

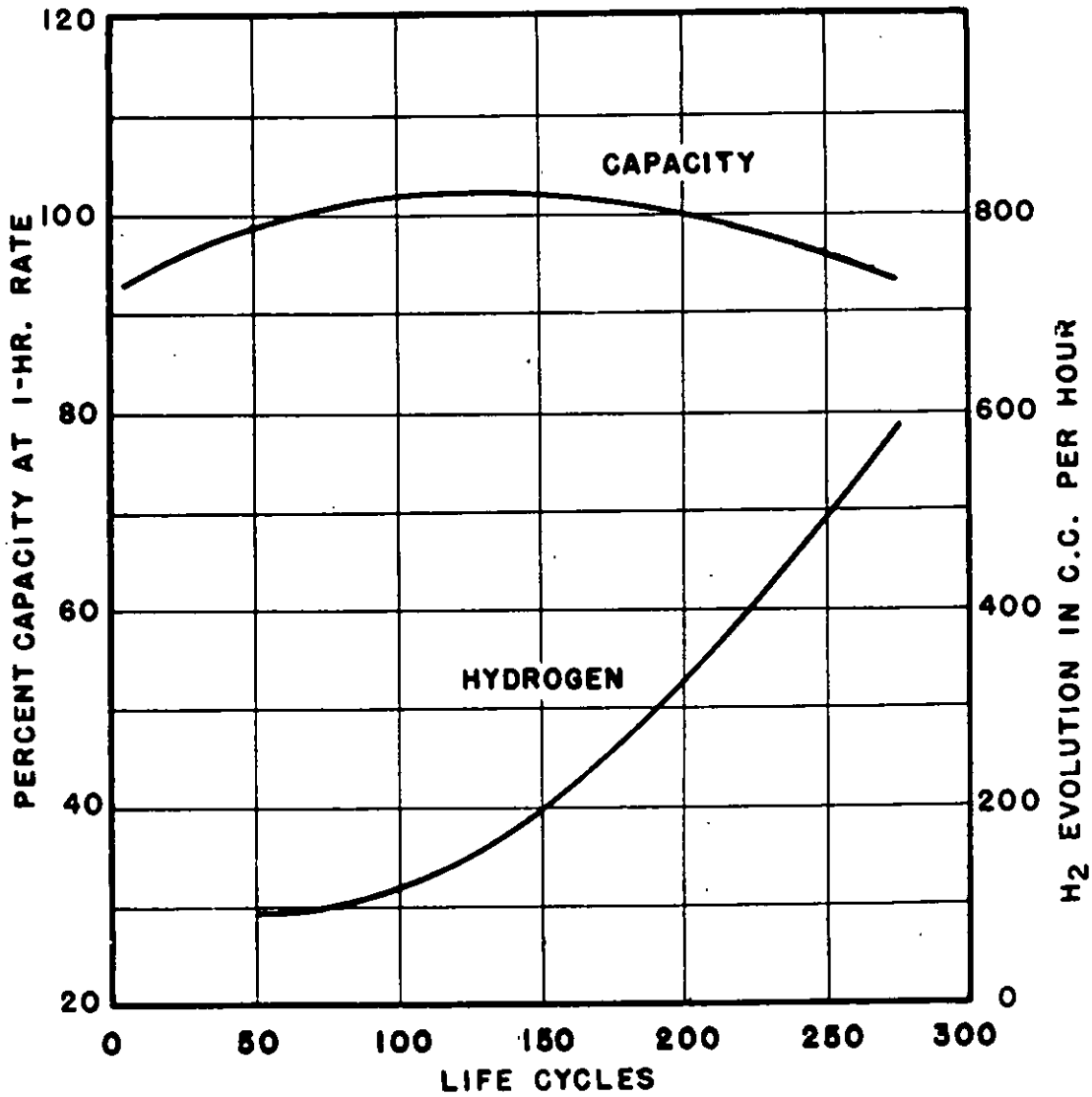
FIGURE 10
CYCLE LIFE AND HYDROGEN EVOLUTION CHARACTERISTICS OF
EXIDE TYPE MAW-67C GUPPY SUBMARINE MAIN STORAGE BATTERY CELLS
WITH PORMAX SEPARATORS



in capacity at the 1-hour rate causing it to fall away very rapidly from cycle 250 to cycle 400. Examination of the elements showed that premature failure of these cells was caused in some measure by the badly etched and corroded separators. Therefore this type of "Pormax" separator cannot be considered as satisfactory for submarine service.

c. The Gould-National Batteries, Inc. in 1952 submitted three Gould type TPX-C-67 GUPPY class 67 plate submarine main storage battery cells under contract NObs-55198, which were furnished with separators made of a combination of paper and glass impregnated with plastic, as manufactured by the Dewey and Almy Chemical Company. Under simulated submarine service cycle life evaluation, it was observed, as shown in figure 11, that a high level of hydrogen evolution of 89 c.c./hour during open circuit stand was apparent at cycle 50 and rose at an increasing rate to 585 c.c./hour at cycle 274, at which point cycling was terminated and the cells were opened for inspection. This inspection revealed the plates to be in good condition, as is indicated by the fact that the 1-hour rate capacity at cycle 276 is still reasonably high at 92.8 percent. However, it was found that the separators had been etched sufficiently through the top and bottom layers of this paper-glass-paper sandwich, but not in the same spots on each side to cause short circuits at this stage in life.

FIGURE 11
CYCLE LIFE AND HYDROGEN EVOLUTION CHARACTERISTICS OF
GOULD TYPE TPX-C-67 GUPPY SUBMARINE MAIN STORAGE BATTERY CELLS
WITH DEWEY AND ALMY CO. -DARAK- SEPARATORS

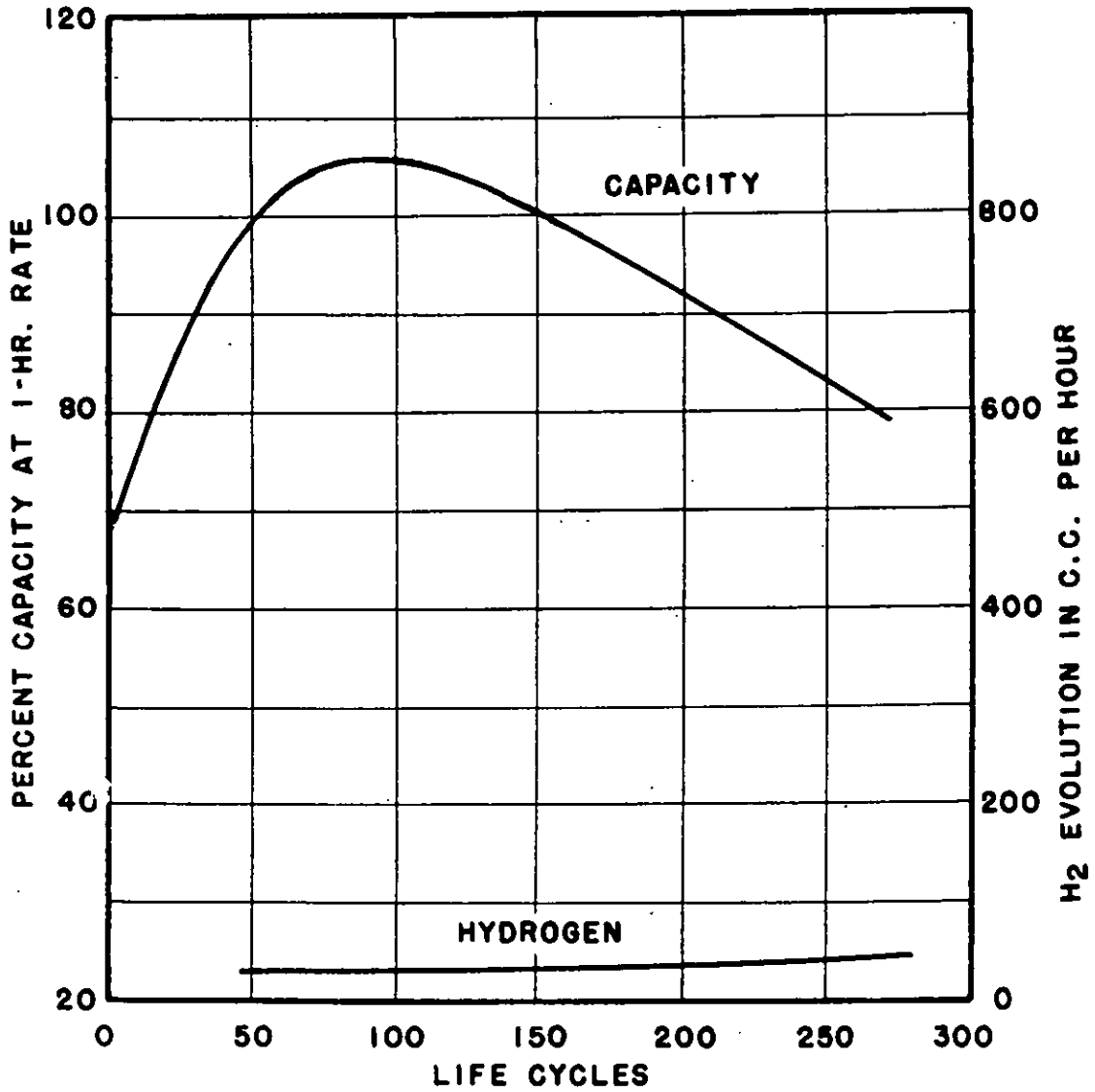


CRS 206/16

Apparently sufficient oxidation had resulted in plating on to the negative plate so that increased local action was produced resulting in an increasing high rate of hydrogen evolution. This separator failed in the same way as the "Pormax" separator and is likewise unacceptable for submarine service.

d. The Gould-National Batteries, Inc., in 1952 also submitted an additional three Gould type TPX-C-67 GUPPY class 67 plate submarine main storage battery cells under the same contract, but furnished with ribbed sheet microporous Geon separators of unplasticized polyvinyl chloride as manufactured by the Hood Rubber Company. These cells also were evaluated under a simulated submarine service cycle life with the following results. As shown in figure 12, this separator could be considered acceptable in that a low level of hydrogen evolution was maintained during life, averaging 32 c.c./hour at cycle 47 to only 45 c.c./hour at cycle 270, which indicates little or no oxidation or etching of the separator. It is to be noted, however, that during this same period, the capacity at the 1-hour rate diminished quite rapidly so that the cell failed to deliver 80 percent of capacity at cycle 265. Upon examination of the elements, it was observed that the plates and separators were in good condition but that on the positive side of each separator were large segments of negative active material. This was sufficient to cause the cells to fail prematurely. This condition had appar-

FIGURE 12
CYCLE LIFE AND HYDROGEN EVOLUTION CHARACTERISTICS OF
GOULD TYPE TPX-C-67 GUPPY SUBMARINE MAIN STORAGE BATTERY CELLS
WITH HOOD RUBBER CO. -GEON- SEPARATORS



CES 206/16

ently been brought about by the nonuniformity of the porosity of the separators in that there existed throughout each separator a sprinkling of large enough pores to permit treeing or conduction through the separators to form short circuits. These ultimately caused premature failure of these cells. These separators therefore proved to be unacceptable for submarine service.

As a result of this investigation undertaken by the Material Laboratory to evaluate various newly developed storage battery separator materials, it has been determined experimently that for portable storage batteries as well as the more critical service of submarine main storage battery cells, the microporous rubber separator has been found to be the only acceptable battery separator for high capacity and long military service life.

A great deal of research and development work has been done on separators made of materials which are currently considered the most promising substitutes for rubber. However if an acceptable battery separator for military service is to be developed as an alternate for microporous rubber, a great deal more work has yet to be accomplished. These new materials should show characteristics which will not limit cycle life, will have a comparatively low electrical resistance in order to provide maximum capacity at high discharge rates and still have high resistance to electrolyte corrosion in order to maintain a low level of hydrogen evolution during stand periods on open circuit.

The need of such an alternate will become especially urgent in view of the critical status of natural rubber for portable battery

and submarine main storage battery microporous separators during emergencies.

PRESENTED AT THE JOINT BATTERY CONFERENCE MEETING - 12 SEPTEMBER 1956
Sponsored by the Coordinating Committee on Equipment & Supplies
Office of the Assistant Secretary of Defense (R&D)

CES 206/16

THE NICKEL-CADMIUM SEALED RECHARGEABLE "DRY CELL", GOULD-NATIONAL BATTERIES, INC. HERMETAC TYPE

BY

J. B. TROUT

I. Introduction

A. The cell discussed herein is a nickel-cadmium alkaline electrolyte cell which is sealed against loss of electrolyte and may be used in any position. It is not truly hermetically sealed as will be evident in later paragraphs. This cell is a Belgian development and the American licensee is the Gould-National Batteries, Inc. Depew, New York.

B. Description of Construction (D-Size Cell)

1. The positive active material is composed of nickel oxide powder which is compressed into pellets. The pellets are stacked about eight high and are enclosed in a tube of very fine mesh nickel wire screen. Nylon cloth is then wrapped around the tube for separation.

2. The negative active material is composed of cadmium oxide powder which is compressed into strips which are the length of the positive pellet stack. The width of these strips is about one third the circumference of the nylon-wrapped positive stack. The strips are curved slightly across their width so that three of them fit closely in a circle around the positive stack.

3. The assembled positive stack, separator and negative strips are then enclosed in another tube of fine mesh nickel wire screen so that the dimensions of the resulting assembly are about 0.5 inch diameter by 2 inches long. Four of these assemblies are connected in parallel to make a D-size cell.

C. Principle of Operation Permitting "Hermetical" Seal

After a battery has been on charge until it is completely charged, continued charging results in electrolysis of water with consequent generation of hydrogen and oxygen gas. This fact has made it difficult to make a truly hermetically sealed battery. The Hermetac battery is not hermetically sealed since gas may be measured as it evolves during charge, discharge and idle stand. The gas evolution during overcharging of the Hermetac cell is minimal, however, due to purposeful use of excess negative active material. As a result of the excess negative material (cadmium), the nickel oxide positive becomes fully charged before the negative does. Oxygen is then evolved at the positive and migrates to the negative, oxidizing an equivalent amount of reduced (charged) cadmium. Thus, if the charging rate does not exceed the rate at which oxygen can diffuse from the positive to the negative, the cadmium is never charged completely enough to permit evolution of hydrogen.

D. Sizes Available

Sizes are available equivalent to ASA dry cell sizes #6, F, D and AA as well as two minature button cell sizes having volumes of 0.386 and 0.172 cubic inches. Physical characteristics of these cells are given in the table below:

Cell Size	Diameter inches	Height inches	Volume cu.in.	Weight pounds	Density #/cu.in.
F	1.22	3.74	4.34	0.441	0.102
D	1.22	2.36	2.74	0.308	0.113
AA	0.55	1.97	0.47	0.0661	0.141
18B(button)	0.71	0.983	0.386	0.0055	0.0143
12B(button)	0.472	0.983	0.172	0.00187	0.0109

E. The claims made for this cell by the licensee are as follows:
1. Does not release gas during charge.
2. Does not require watering.
3. Does not spill electrolyte.
4. Has excellent power output.
5. Has excellent stand characteristics; retains 50% of capacity during oneyears stand.
6. Has good life; 100-500 cycles, depending on type of service.
7. May be put on float charge at 1.35 volts.
8. Life on overcharge at rated charge current and voltage is over oneyear.
9. Good performance at low temperatures.

II. Tests Performed.

Twenty-eight D-size, twenty-five F-size and five 15-cell button-cell batteries were provided to the Bureau of Ships for evaluation tests. The D and F-size cells were tested by the National Bureau of Standards. The button-cell stacks are to be tested at the New York Naval Shipyard Material Laboratory.

The tests at the Bureau of Standards were designed to determine the effects of temperature, charged stand, loading and float charge on capacity and cycle life, as well as the effect of cycling on capacity. The discussion below is based on tests of the D-size cells.

III. Discussion of Characteristics.

A. Rating vs. Initial Capacities

The Hermetac D-cell is rated at 2.5 ampere-hours at the 5 hour rate. The capacity of cells tested on the 4 ohm and 2.25 ohm continuous test ranged from 2.2 to 2.75 ampere-hours during the first few cycles of life. The average of these capacities was 2.48 ampere-hours.

B. Load vs Capacity

1. Figure 1 shows the hours of continuous service to an end voltage of 0.9 volts obtained from the test samples when discharged through 2.25, 4, 16, 64 and 256 ohm loads. The formula which fits this curve is:

$$t = 2.18R$$

where, t = hours to 0.9V, continuous discharge.
R = constant resistance load in ohms.

For comparison, the curve for Leclanche D-cells made with natural ore is also shown. The two curves cross in the vicinity of 13 ohms. Below 13 ohms, the nickel-cadmium dry cell is superior to the Leclanche and above 13 ohms the reverse is true. At 13 ohms the watt-hour output of the Hermetac cell is 12% greater than the Leclanche cell.

2. Figure 2 shows the effect of load on ampere-hour capacity to 0.9 volts. It can be seen that dropping the resistance by a factor of 64 reduces the ampere-hour output by 5.8%. A similar decrease in ohmic load on Leclanche cells (from 250 ohms to 5 ohms) decreases the ampere-hour output by 80%.

3. Figure 3 shows some sample voltage versus time curves for discharges at various loads at 21°C (69.8°F).

4. Figure 4 shows the effect of discharge resistance on energy output at 21°C (69.8°F). Decreasing the resistance load by a factor of 64 times decreases the energy output per pound from 11.3 to 10.0, or 11.5%. The corresponding decrease in resistance load on D-size Leclanche cells made with natural ore decreases the watt-hour/pound output from 38 to 5.4 or 86%. However, the output of the Leclanche cell is superior to the Hermetac cell at resistance loads above about 14 ohms/cell.

C. Effect of Temperature on Characteristics

1. Figure 5 is a plot of the data obtained by discharging test cells through 4 ohms to 0.9V at various temperatures. For comparison the data of National Bureau of Standards Letter Circular LC965, table 16, also are plotted. These latter data are from F cells discharged through 83-1/3 ohms/cell, which is a considerably lighter drain than that of the tests.

Below 20 F, the curve for the Hermetac cell is very steep, lending some doubt to interpolated values; however the points are each the average of two rather close test values. In the range 0°F to 50°F, the Hermetac cell is considerably superior to the data for the F-size Leclanche cell, being able to deliver 78% of its 70°F capacity at 20°F compared to 48% for the F-cell. If the drain on the F-cell were comparable, the difference would be considerably larger.

2. The effect of temperature on the ability to accept charge was studied at 32°F, 70°F and 113°F. The data obtained were inadequate to base quantitative statements on. It may be stated qualitatively, however, that for equal charge voltages, the charge current at 113°F appears to be about double that at 70°F and three to four times that at 32°F for the first portion of the charge. The table below gives an example at the end of 6 to 6-1/3 hours of charge.

	CELL A		CELL B	
T°F	Volts	Amps	Volts	Amps
32	1.50	0.18	1.52	0.24
70	1.50	0.39	1.50	0.42
113	1.48	0.76	1.48	0.73

The cells in the above table had been subjected to a minimum of 84 cycles when the data were obtained. The maximum values recommended by the manufacturer for charge voltage and charge current are 1.50 volts and 0.50 amperes. The excessive charge rate at 113°F did not result in sufficient gas formation to explode the cells.

After subjection to charge at these temperatures, cycling was continued at 70°F. No effect was noticed on ampere-hour capacities in subsequent cycles as a result of charging at the various temperatures.

D. Charged Stand Characteristics (Shelf-life)

1. Figure 6 is a plot of the data obtained by discharging three cells after various periods of charged stand at 21°C (69.8°F). The data from the three cells are plotted separately since they appear to be affected by an additional variable, i.e., cycle age. Cell #1 exhibited very poor shelf-life relative to the other two cells, however it had been cycled at least thirty more times than either of the other two cells at the time of the 30 to 37 day stand tests. Cell #4 had poorer shelf-life than cell #11 and it also had been cycled more than cell #11. Further testing is required to determine whether cycle life significantly interacts with capacity after charged stand.

2. It appears safe to state however, that cells which have been cycled less than 110 times will retain at least 70% of their ampere-hour capacity after charged stand for 180 days at 21°C (69.8°F). (Capacity retention is based on the percent of capacity obtained on cycles immediately prior to the stand test.
An equivalent loss is experienced in one week if the storage temperature is raised to 113°F.

E. Cycle-ability and effect of cycling on capacity.

1. An obvious advantage of the Hermetac cell over the Leclanche cell is its ability to be recharged after use. This advantage applies equally to any storage battery. In order to test this ability, cells were cycled individually and as a battery. The load was 4 ohms per cell for three of the individual cells, 4 ohms per cell for the five cell battery and 2.25 ohms per cell for three other cells. The end voltage was 0.9 volts per cell. The discharge temperature was 21°C (69.8°F). The end of life was considered to be the cycle when the cells gave less than 50% of the ampere-hour capacity obtained on the discharge after the first charge. The table below gives cycle life for the cells tested under this schedule. Where end of life has not been reached, the percent initial capacity and latest cycle are recorded. Figure 7 shows a plot of capacity versus cycle-life for the five cell battery.

CELL No.	CYCLES TO 50% INIT.A-H	LATEST DATA	DISCHARGE LOAD OHMS/CELL
5-cell bat.	302	--	4
1	--	125% at cycle 154	4
4	--	70% at cycle 112	4
5	--	59% at cycle 52	4
11	--	105% at cycle 52	4
15	--	89.4% at cycle 114	4
16	--	61.5% at cycle 111	4
27	190	--	4
28	--	52% at cycle 195	4
29	171	--	4
30	141	--	2.25
31	118	--	2.25
32	--	54.4% at cycle 202	2.25

2. One interesting feature of the above table is the significant difference between the long cycle life of the 5 cell battery and the shorter cycle life of the individual cells. Part of the difference is accounted for by the performance of one of the cells which after 350 cycles in the battery and four more cycles by itself still gave 66% of the original battery capacity. The capacity of the other four cells at that time ranged from 35% to 44% of original battery capacity (2.74 AH).

This explanation, however, leads to another question as to the reason why the one cell did so much better than all the others. It is conceivable that the reason for this behavior is that this one cell had a higher capacity than the others initially. Even at the end of battery life, this cell's test-end voltage was 1.13 to 1.15 volts when the battery test-end voltage averaged 0.9 volt/cell. Thus, this cell was never as completely discharged as any of the others, the implication being that cycle-life is increased when the discharges are not carried to low voltages. Substance is lent to this proposal by the data on the BA-30 tests described in the next section.

Except for cell #32 in the above table, there appears to be an interaction between discharge load and cycle life. Cells 30 to 32 were cycled through 2.25 ohm loads, while all other cells were through 4 ohms. Of these three cells, cells #30 and 31 gave significantly lower cycle life than all others except possibly cell #5. Further testing is required to determine whether this is a real effect.

3. Five cells were put on test according to the discharge routine for BA-30's in MIL-B-18B, the military dry battery specification. At the end of each five day week, the cells were allowed to stand 8 hours, were then charged for 24 hours and let stand for 30 hours prior to the next 5 day routine. On this basis, one cell has been cycled 71 weeks, two cells 72 weeks and two other cells 81 weeks. The average discharge voltage during this time has been about 1.24 volts and the weekly ampere-hour output about 1.25 AH. None of the cells has exhibited any decrease in average voltage or weekly output during this time which exceeds 2½%, as long as full charges are administered at the end of every five day routine. At cycle 81, the five cell battery

had lost at least 18% of its original capacity. Although the weekly cycling only withdrew about 50% of the cells' capacity per discharge, it is significant that even after more than 18 months of weekly cycling the characteristics are only slightly different than they were originally.

To equal 81 weeks of use, the required number of BA-30's averaging 17 days life would be 24.

F. Ability to Remain on Float Charge for Long Times.

1. Three cells were tested to determine ability of Hermetac cells to remain on float charge. The test was conducted as follows. The cells were cycled a few times prior to being put on float charge to determine their separate average capacities. They were then put on float for three months and discharged at the end of this time to determine capacity after floating. This procedure was then repeated. The data obtained are given in the table below.

	Cell No.		
	24	25	26
Av.Capacity before 1st Float Chge.-AH*	2.60	2.48	2.65
AH Input during 1st Float Chge.	65.40	33.20	213.20**
AH Output after 1st Float Chge.	2.89	2.80	2.95
Av.Capacity after 1st Float Chge.-AH***	2.34	2.30	2.48
AH Input during 2nd Float Chge.	63.0	63.0	30.3
AH Output after 2nd Float Chge.	2.58	2.51	2.71
Av.Capacity after 2nd Float Chge.-AH****	2.13	2.06	2.38

* Av. of 5 cycles
** This cell discharged after 2 mos. to determine effect of excessive overcharge.
*** Av. of 4 cycles.
**** Av. of 9 cycles.

2. The tests from which the above table was derived are not completed. The reason for the odd behavior of cell #26 has not been determined. The effect of this test on subsequent cycle life has not been determined.

It is noted, however, that in the discharge immediately following each float charge, capacities are obtained which are significantly higher than the average capacities on routine cycles run before or after the float charge. Also to be noted is the fact that the average capacities on routine cycles are lower after each trickle charge. In the eight and ninth routine cycles after the second float charge, the capacities obtained were 10% to 15% higher than those obtained on the first routine cycle after the second float charge. That is, the capacities appeared to be building up. It appears as though float charge maintains capacity as far as the immediately subsequent discharge is concerned, but that capacities on subsequent cycles are adversely affected. The reason for this behavior has not been determined.

G. Gassing Characteristics

1. Three cells, having cycle life ages of 113, 116 and 121 cycles respectively, were tested to determine their rates of gas evolution at 45° C (113°F). Gas volumes were calculated as equivalent volumes at standard temperature and pressure.

2. Gas evolution was measured during charge, discharge, charged stand and discharged stand. In no case did the gassing rate attain a value as high as 1 ml/day. Gassing during discharge was .25 ml/day or less. The charge rates were varied from 0.02 ampere to 0.35 ampere. Gassing rates at normal temperatures would be even less.

3. In view of the above, it can be said that the cell is not truly hermetically sealed, but that the amount of gas which escapes from the cell is trivial under normal service conditions.

IV. Conclusions

From the information described by and given in the discussion above, the following conclusions may be made.

A. The capacity of Hermetac nickel-cadmium rechargeable dry cells is superior to ordinary dry cells at the 20-hour rate and higher current drains. This applies to relatively young Hermetac cells and fresh, natural-ore dry cells.

B. Although at drains below 100 milliamps the Hermetac cell does not give the energy output obtainable from Leclanche cells, the Hermetac cell ampere-hour and watt-hour output is considerably less affected by higher current drains up to about 500 milliamps.

C. A minimum of 50% of original ampere-hour capacity is generally available from D-size cells after a minimum of 120 cycles and a maximum of about 200 cycles. The averaging effect of combining cells into batteries may extend these figures up to 300 cycles to 50% of original capacity.

D. 70% of the initial capacity of Hermetac cells is still obtainable after 6 months of storage at 21°C. This applies to cells which have been cycled less than 110 cycles.

E. The output of Hermetac cells is affected by temperature. No capacity is obtainable at -10°F and below. From about 0°F on up to 70°F, the Hermetac cell is able to deliver a higher percentage of its 70°F capacity than is the Leclanche cell.

F. Although the Hermetac D-size cell is not truly hermetically sealed, the rate at which it evolves gas is less than one milliliter per day under normal use conditions, whether being charged, discharged or standing idle in the charged or discharged condition. Gas evolution is even less while the cell is being discharged, approaching zero gas evolution.

G. The following is a partial list of factors which have not been studied sufficiently to make firm quantitative statements regarding them:

1. The effect of temperature on charging characteristics.
2. The effect of float charging on cycle-life.
3. The effect of cycle-life on charged stand characteristics (shelf-life).

4. The effect of current drain on capacity at temperatures lower than 70°F.

5. The effect of current drain on cycle-life.

HERMETAC D-SIZE CELLS
DISCHARGED TO 0.9 VOLTS
AT 21 °C

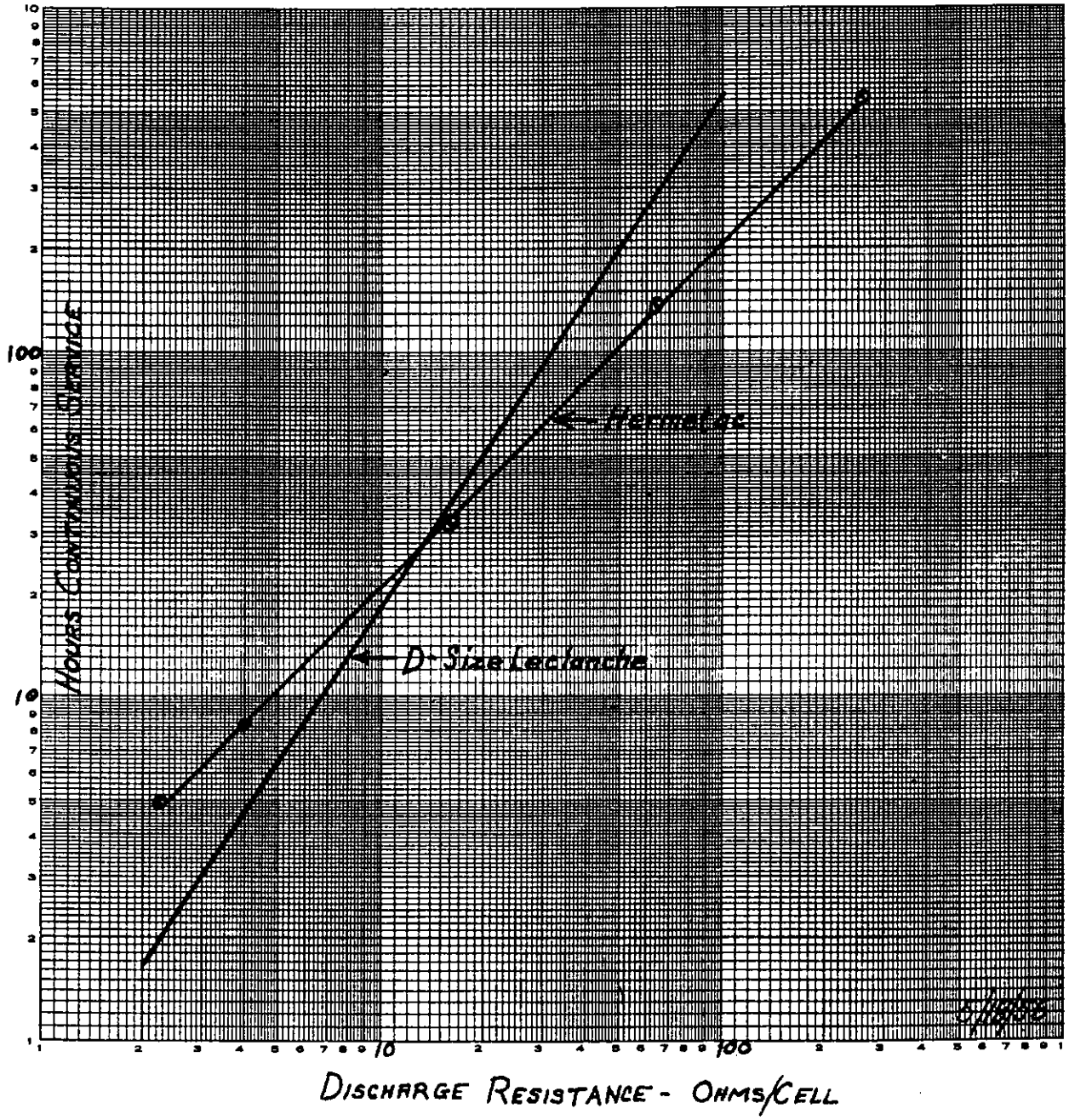


FIGURE 1

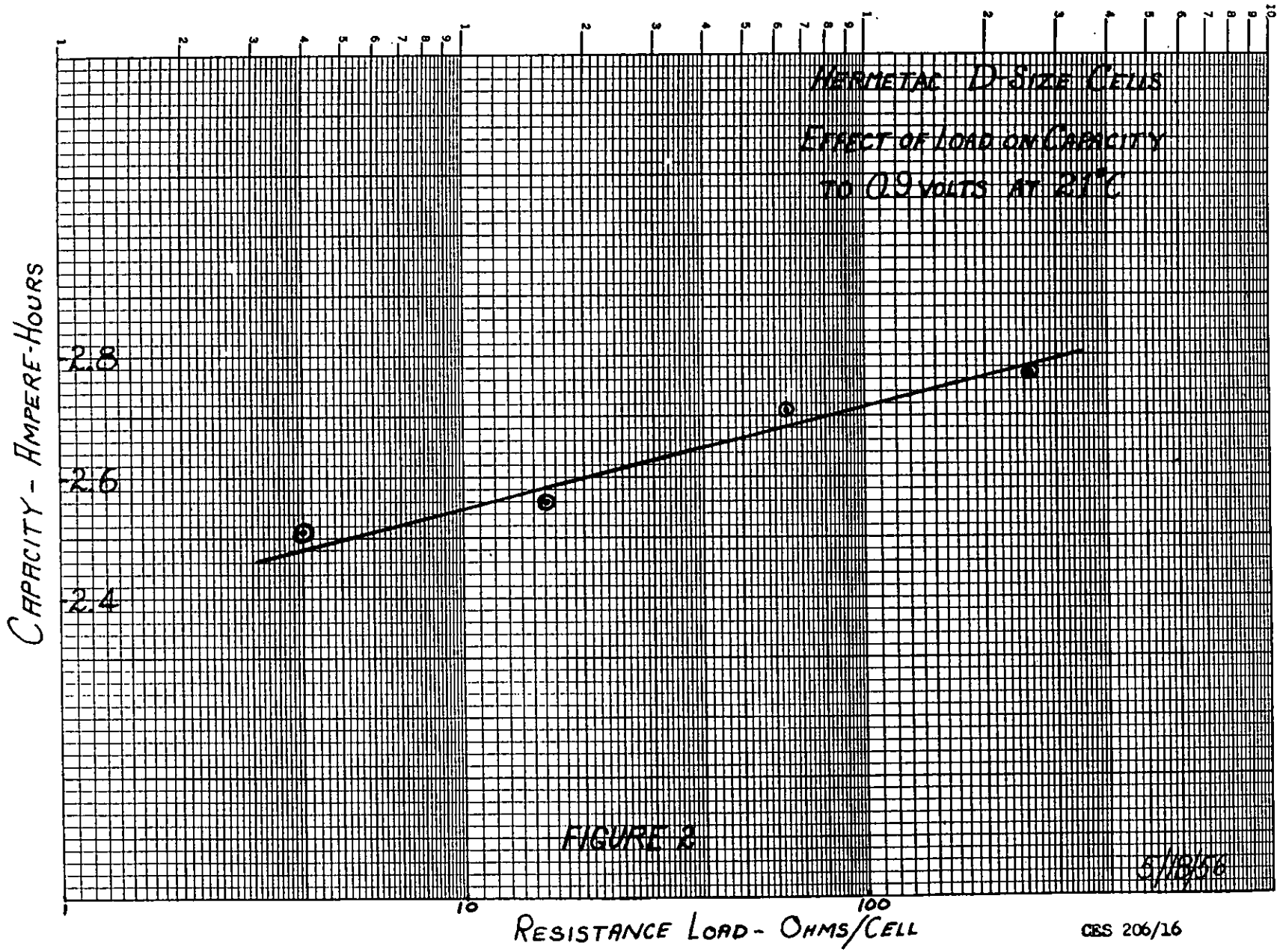


FIGURE 2

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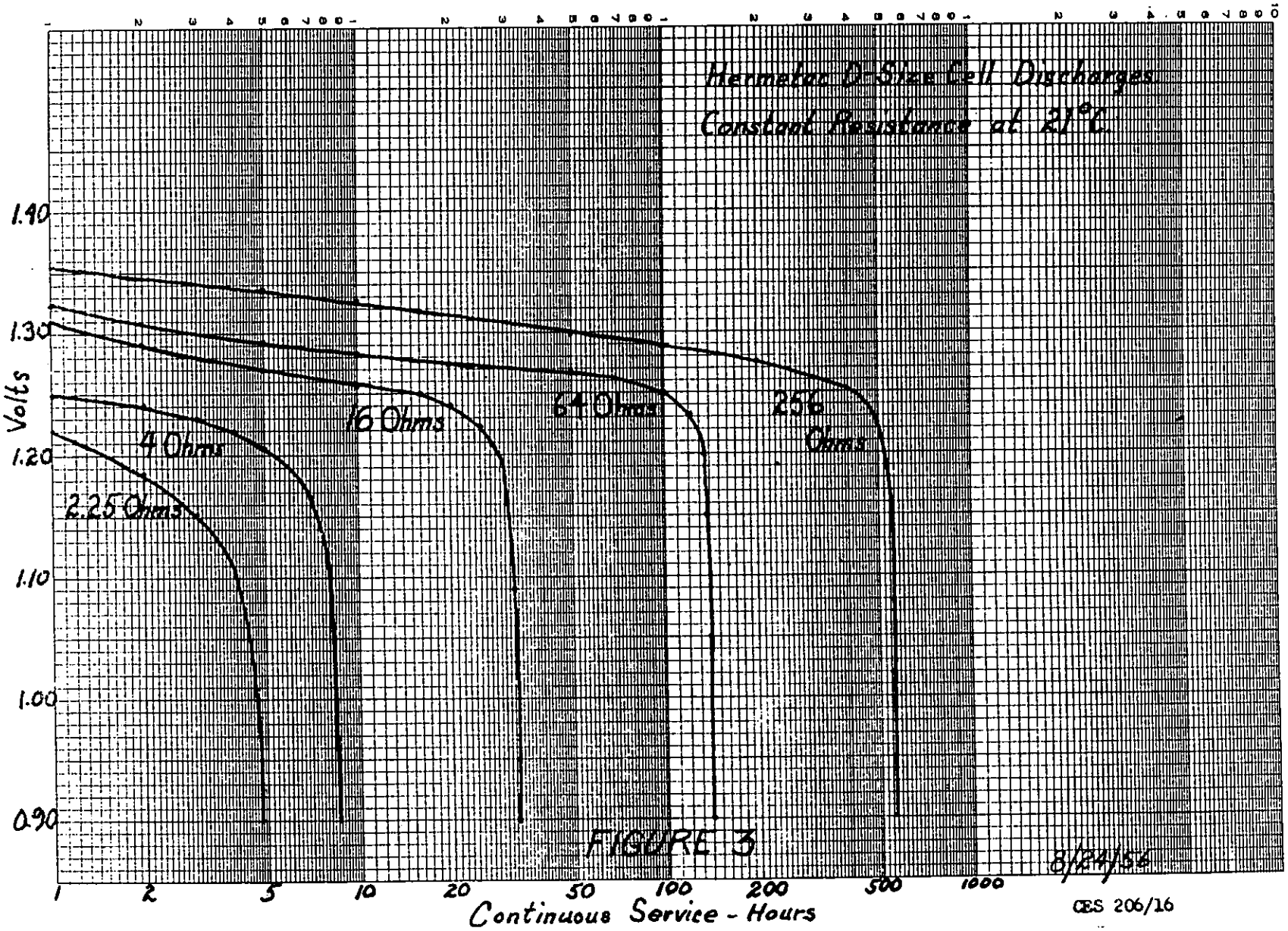
Hermetic D-Size Cell Discharges
Constant Resistance at 21°C.
Volts
1.40
1.30
1.20
1.10
1.00
0.90
2.25 Ohms
4 Ohms
16 Ohms
64 Ohms
256 Ohms
1
2
5
10
20
50
100
200
500
1000
Continuous Service - Hours
FIGURE 3
8/24/56

CES 206/16

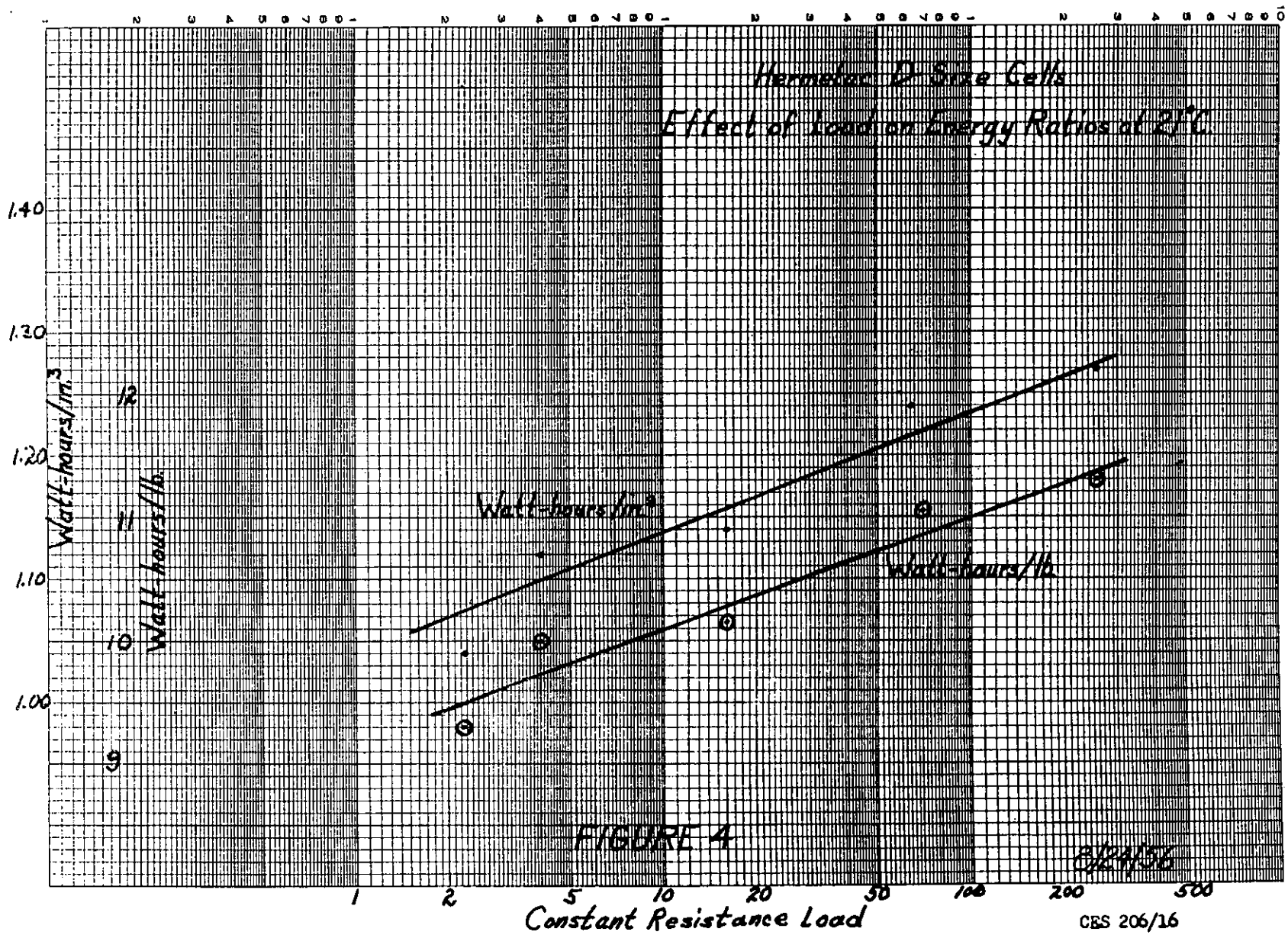

FIGURE 4

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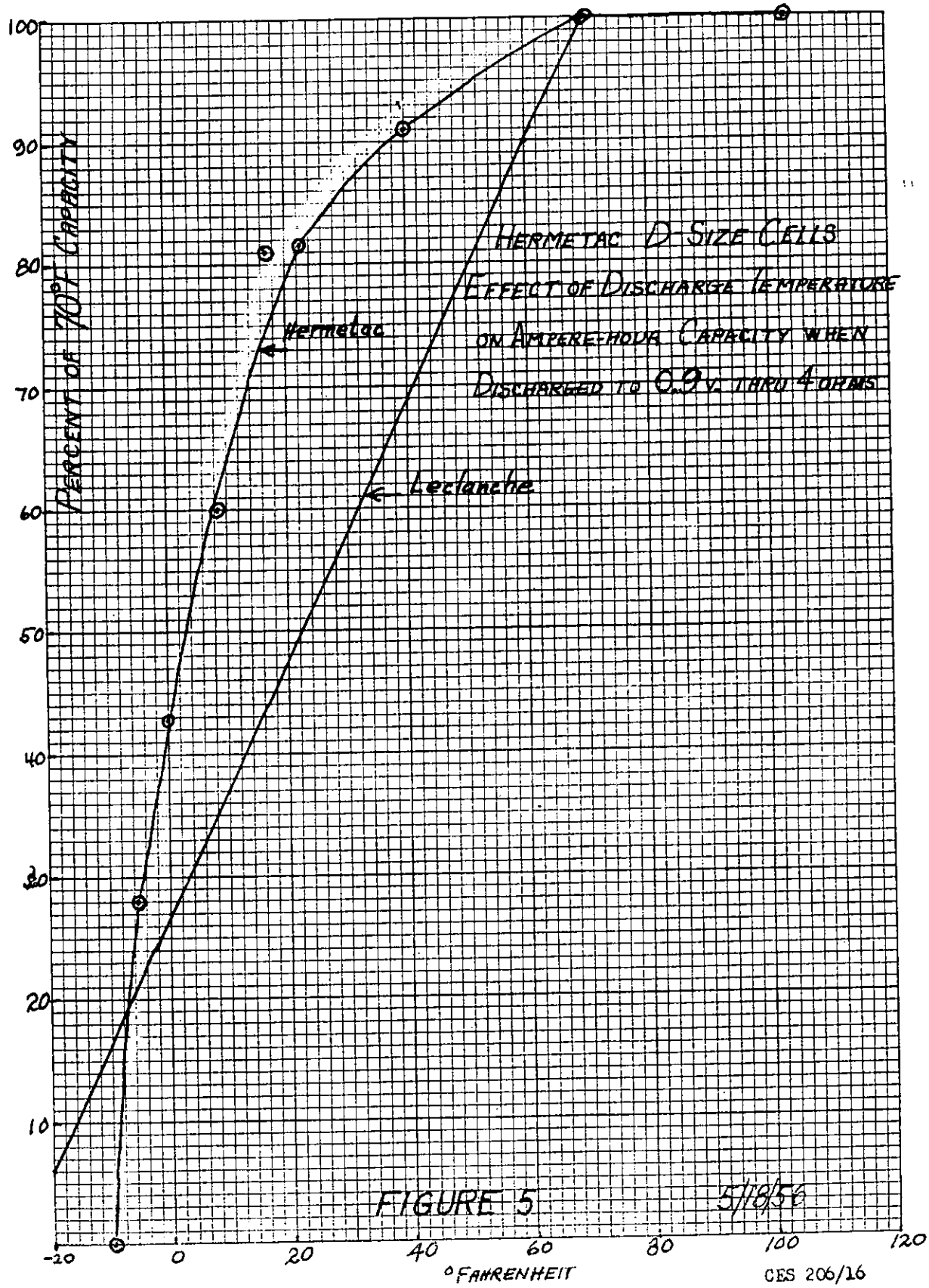

FIGURE 5

CES 206/16

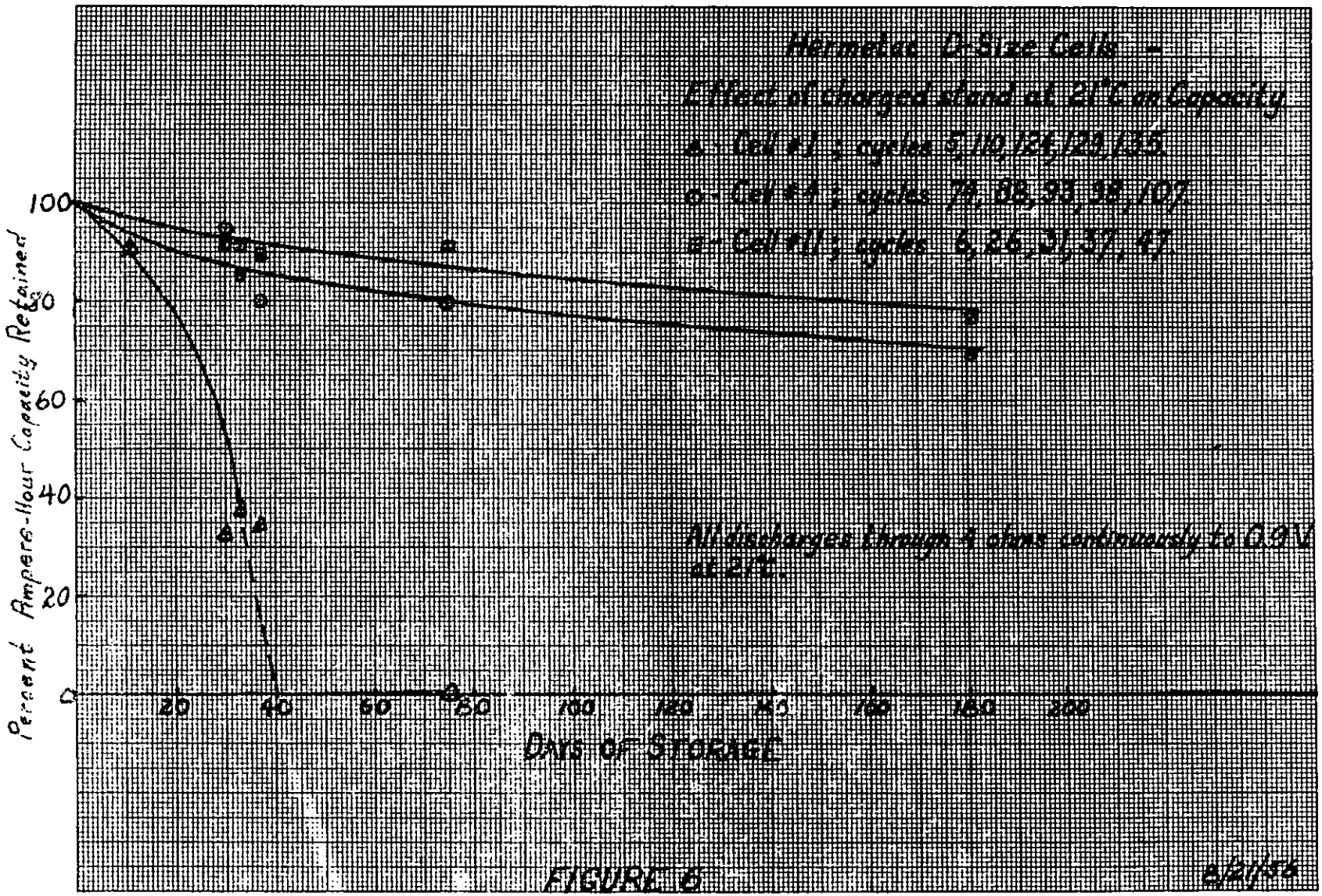

FIGURE 6

CES 206/16

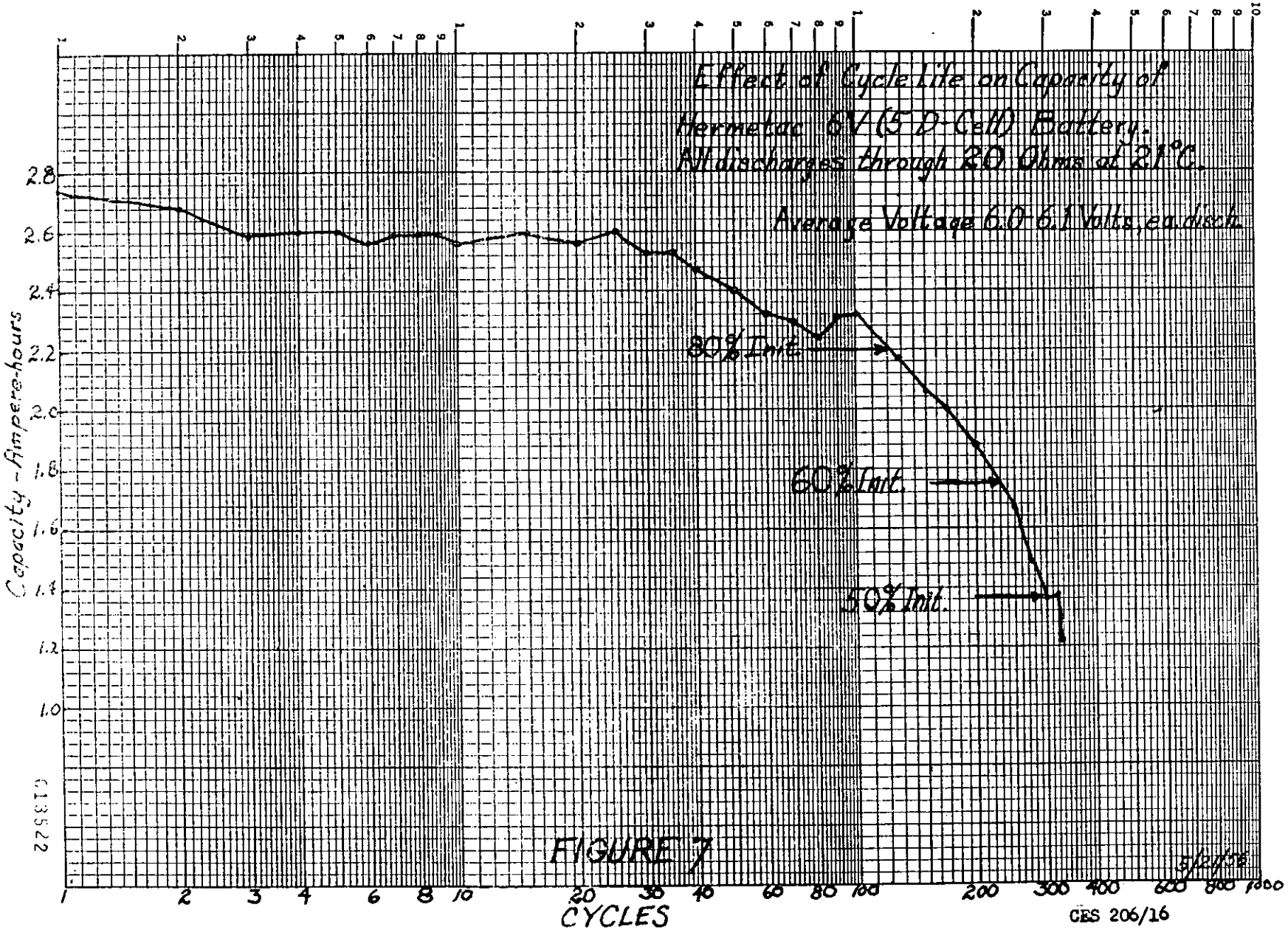

FIGURE 7

CES 206/16

PRESENTED AT THE JOINT BATTERY CONFERENCE MEETING - 12 SEPTEMBER 1956
Sponsored by the Coordinating Committee on Equipment & Supplies
Office of the Assistant Secretary of Defense (R&D)

CES 206/16

LOW-RATE SILVER OXIDE-ZINC SECONDARY BATTERIES

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INTRODUCTION

The theoretical possibilities of the silver oxide-zinc couple have been recognized for many years but early attempts to build a secondary battery satisfactory for wide applications had resulted only in a limited life cell. The unusual electrochemical characteristics of each half of this combination account for both the apparent advantages and some of the problems which arise. For example, the ability of the silver oxide plate to give two faradays of electricity per gram atom of silver plus the low electrochemical equivalent and relatively high emf of the zinc plate suggest a cell of high capacity as compared to the weight and volume. Cycle life was limited, on the other hand, by the ease with which silver oxide was reduced by small amounts of organic matter and also by conditions arising because of the solubility of zinc in the electrolyte. In the latter case, the tendency of the zinc to tree and eventually short through the separators or to fail to reprecipitate on the electrode during charge have been basic problems.

A preliminary study at the Naval Research Laboratory of some of the current production of silver oxide-zinc secondary cells indicates that much progress has been made during the last ten years. The cycle life has been markedly increased and as a better understanding of the mechanism of the cell is gained, additional progress may be expected. A wide range of sizes and types are now available commercially and are being used in varied applications particularly where size and weight are important.

DESCRIPTION

The NRL investigation included only the low-rate type of cells designed particularly for long-life and possible float operation. In addition to these two major considerations, several other characteristics were also studied where time and facilities permitted. In general, groups of four or five cells were worked as a unit. The uniformity of cells is of utmost importance, however, so individual cell potentials were recorded at all times in addition to battery voltage and current. In some instances,

individual plate potential, gas evolution, and temperature measurements were also made on single cells. All the charges and discharges were run at constant current and were cutoff on voltage.

A total of 38 cells representing five or six models developed by two different manufacturers were available for study. Table 1 gives a partial description of these cells.

The majority of the cells spent most of the period on one of two routines which may be broadly classified as a 48-hour cycle or a 30-day float cycle. In the 48-hour cycle, a four-cell battery was discharged at 10 amperes to 5.0 volts (MC-80, MC-100, BB-402) or 5.6 volts (BB-405), immediately recharged at 4 amperes to 8.3 volts (MC-80, MC- 100) or at 6 amperes to 8.6 volts (BB-402, BB-405), and then let stand on open circuit the remainder of 48 hours. The two five-cell batteries on the float routine alternated between normal cycles and float cycles in which the fully charged battery was floated at a constant battery potential of 9.9 volts for 30 days before discharge. These routines were interrupted occasionally to determine other characteristics that would help to explain the mechanism of this cell and the optimum conditions for its operation.

CHARACTERISTICS

Engineering

The charge curve of a silver oxide-zinc cell (Fig. 1) is characterized by three nearly constant potential levels: one at 1.60 to 1.65 volts, one at 1.90 to 1.95 volts, and a third at 2.2 to 2.3 volts (not shown). The potential changes are sharp when they do occur. Although the change in positive-plate potential is responsible for the cell potential rise to the second level, the plate reaching the gassing level first depends on the balance of active materials in the particular cell or model being observed. Little gas is evolved until the end of the charge as normally operated so that a 98 percent ampere-hour charging efficiency is not uncommon.

The characteristic discharge potential generally includes a higher potential portion the first part of the discharge followed by a considerably longer constant potential portion with a sharp

break at the end of the useful discharge (Fig. 2). As was found during charge, the principal cell potential change during discharge reflects a positive-plate potential change. Several factors influence the shape and length of this first part of the discharge curve. The potential changes in both plates often contribute to the break in potential at the end of the discharge, depending again on the particular cell being studied.

The average cell voltage during a 5-hour rate discharge is about 1.5 volts and that during a 48-hour rate discharge about 1.6 volts (Fig. 3). The power output is shown for three batteries in Fig. 4. Similar data on lead acid, nickel iron, and nickel cadmium batteries taken from values reported by their manufacturers in the Journal of the Electrochemical Society, 99, 1952, are included showing watts per pound in part of Fig. 4. Therefore, it would appear that the silver oxide-zinc batteries were 4 to 6 times better than the other well known batteries on the basis of watts per pound.

Life

The useful life of a silver oxide-zinc battery is terminated in two general ways. One of these, the gradual, almost linear loss of capacity with cycling, is illustrated in a form of cycle log in Fig. 5. In other cells, this gradual loss was suddenly aggravated by the development of an internal short circuit as occurred in some cells of the battery capacity plot in Fig. 6. In the latter case, when a cell which had lasted only 15 cycles was opened, it showed a direct growth between two plates near the center of the cell and other places in the separators which indicated advanced breakdown. A cell of a different model battery developed an internal short due to mechanical puncturing of the separator by an imperfect grid. Of course, when a four-cell battery is on the flat part of the discharge curve and one cell fails, it quickly reduces the battery voltage to below the normal battery voltage cutoff. Deep discharges or even short periods of reversal did not appear to cause permanent damage for one cell discharged to an average voltage of 0.72 volt during its lifetime as compared to 1.43 volts for the other three cells of that battery but did not appear to be failing any faster at the end than the other three cells.

Batteries that spent most of the time floating also showed the effect of gradual capacity loss with cycling (Figs. 7 and 8); however, the loss was spread over a longer period of time. Discharges following floats were longer than those following normal charges, but the rate of loss was about the same.

Discharge

Some of the batteries were received dry-charged. The initial discharge of such a battery (Fig. 9) was as long as that of the typical normal discharge shown in Fig. 2 but it differed somewhat in potential. Little of the higher potential part of the discharge curve was present in the dry-charged cell and there was considerably more gas evolution than normally found during discharge. There had also been rapid gas evolution at the time the electrolyte was first added to the dry-charged cell but it tapered off during the soaking period (Fig. 10).

The effect of discharge rate on cell capacity and potential is shown for one cell in the family of curves in Fig. 11. These cells are not particularly designed for high rate work and the performance would vary slightly from one model of battery to another in this respect. However, the curves in Fig. 11 may be considered average for the batteries studied.

Changes in the general shape of discharge curves with cycling may be seen in Fig. 12. In the cell illustrated, the capacity loss appeared more at the lower potential part of the discharge curve but this was not the case with cells of another manufacturer and may not be significant.

In most cases, the particular cell of a battery which limited the battery capacity as a whole changed from time to time. This observation along with the other unexplained variations from cycle to cycle point up the need for additional information and understanding of the charge mechanism for this appears to be the key to the problem of maintaining capacity.

Charge

Since the performance of the silver oxide-zinc battery is considerably dependent on its charge acceptance, it is not surprising that low-rate charges are more effective than higher

rate ones. Normal charges usually take from 15 to 25 hours and thus, by most standards, would be considered low-rate charges. The two families of curves in Fig. 13 show not only the effect of charge rate on potential and charge length but also the effect on the potential and length of the subsequent discharge.

The effect of a partial charge on the potential of the subsequent discharge is of some theoretical interest (Fig. 14). Charging at the higher potential level appears to be necessary to form any of the higher oxide which shows up as the higher potential during the first part of a discharge.

The effect of cycling on charge potential and charge length may be seen in representative charge curves taken throughout the life of one cell in Fig. 15.

Float

The observation of this type of battery under float conditions is still in progress. The New York Naval Material Laboratory made a limited study some years ago on the potential necessary to maintain this type battery. The two five-cell batteries at NRL have been floated only at 9.90 volts per battery, but it was soon discovered that this did not necessarily mean that each cell was being held at 1.98 volts. In fact, cell potentials varied spontaneously and frequently from about 1.9 to 2.2 volts as may be seen in a typical float in Fig. 16. Even in these curves many of the smaller variations have been averaged out. Figure 17 shows the potential of a somewhat less erratic cell along with the gas evolution and battery float current. These data indicate that at the higher potential, relatively little of the charging current is going into the charging of the silver oxide plate as compared to when the potential is low. On the other hand, little of the current is being dissipated as gas evolution at the zinc plate. A much more enlightening picture of this and other aspects of cell characteristics could be had if this work had been done with a single cell rather than in connection with a battery.

Whether one cell of a battery floats at a fairly high potential or at a low one does not necessarily determine the capacity the cell will give when it is discharged following the float. In every case a discharge following a float was longer

than one following a normal charge, but this added capacity can also be put in by means of a low-rate charge and its potential would show the same type of variations towards the end of the charge as it would during float.

In general, the current necessary to maintain the float potential increased with successive float cycles, as shown in Figs. 7 and 8, and corresponded to a downward trend in the amount of charge which it is possible to get into the battery during a normal charge.

Stand

Discharges following short stands often show no measurable capacity loss as illustrated in Fig. 18. The first part of the discharge potential curve, however, indicates that some of the higher potential part of the curve is lost without affecting the total capacity available. With longer stands (Fig. 19), there is a definite capacity loss in addition to a potential change. The capacity loss from stand varied from cycle to cycle and from battery to battery but one battery indicated the loss was on the order of 1 to 3 percent in 14 days; the average loss of several 30-day stands on all the batteries was about 10 percent and the loss on a single battery in 150 days was about 14 percent.

Temperature

All of the work thus far, with but one exception, has been done with the cells in a controlled ambient temperature of 80°F. A thermocouple in the electrolyte just above the plates showed a temperature rise of about 20°F during a normal rate discharge and about 70°F during a four-normal rate discharge (Fig. 20), but much less heat is evolved during most of a charge. While these values are somewhat representative, temperature rise depends on several factors and varied somewhat from one model to another.

A rather specialized high-rate interrupted discharge at 80°, 32°, and 0°F is shown in Fig. 21. The voltage minimum and recovery in the first one-hour discharge, cycle 4, is interesting and probably indicates that the reversal warmed the battery sufficiently to operate the cell as though at a higher temperature where more capacity is available.

Electrolyte Level

The electrolyte level, when observed through the cell case, changes markedly during a cycle of a silver oxide-zinc cell. The type of construction necessary to produce a workable secondary cell apparently requires a multilayer wrapping of one or the other set of plates. This wrapping by its very nature and intent limits the transfer of electrolyte by diffusion. During charge, however, some force such as electroosmosis tends to move the electrolyte away from the silver plate thereby raising the apparent electrolyte level in the cell if the silver plates are the ones that are wrapped. During discharge the reverse action is true. In such a cell, the potential during charge may rise prematurely to the gassing potential and end the charge if the silver plate becomes partially dry. In one cell under study, provision was made for manually moving the electrolyte from one plate to the other; if the cell potential began rising too early during charge, the addition of electrolyte to the positive plates would often lower the potential for another period of charge at about 1.95 volts. The plates are closely packed leaving little room for free electrolyte so that actually the apparent electrolyte level changes do not represent a large amount of electrolyte. Little change may appear if the level is above the top of the plates as seen in Fig. 22, but that is not the normal level for operation.

With cycling the characteristics of the separators probably tend to change since "irrigation" gradually becomes less necessary and less effective. Even the point in the cycle where any make-up water is added is important as evidenced by the improvement in battery capacity beginning at cycle 28, Fig. 8. In this case, adding make-up water at the beginning of the charge rather than at the end made a difference. Actually, if with a single cell the charge is cut off at about 2.0 volts, little water would ever be needed but when cells are operated in series some gas would be evolved and occasional watering would be needed.

Short Circuit

One or more cells of each of two batteries were short-circuited through 1.0×10^{-4} ohm resistance under conditions of maximum and minimum metallic silver content. Figure 23 shows the current and voltage during the first fractions of a

second of short circuits of two cells which had previously been charged and floated for 30 days. Figure 24 shows short-circuit currents of a commercial cell in various other states of charge and discharge, the maximum recorded current being about 1200 amperes.

The voltage rise the first few seconds after the short circuit was removed is shown in Fig. 25 and a little closer look at the initial voltage rise may be had in the tracings of the actual oscillograph record for a cell in each battery in Fig. 26.

CONCLUSIONS

This study has been limited by the time, facilities and number of cells available but it does indicate that, in its present state of development, the silver oxide-zinc secondary battery can give a life of well over 100 cycles. Capacity loss during stand is comparatively small and the battery appears to operate satisfactorily on a float routine. It has maintained or improved its outstanding power output per weight and volume which makes it exclusive for some applications.

Much is yet to be learned about the mechanism of the cell. Problems relating to charging the silver plate and keeping the zinc products in place are recognized.

These batteries are available commercially in capacities from 0.5 to 300 ampere hours although the initial cost is still necessarily high.

TABLE 1

Cell Description

Model No.	No. of Cells	Height (in.)		Length (in.)	Width (in.)	Gross Volume (cu ft)	Weight (lb)	No. of Plates	
		Overall	Less Terminals					Positive	Negative
MC-80*	4	6.4	5.7	3.5	1.5	0.0195	2.22	8	9
MC-100*	4	6.4	5.7	3.5	1.5	0.0195	2.45	10	11
FW-100*	5	11.25	10.25	5.25	1.25	0.0427	5.40	6	7
LR-100*	5	4.8	3.9	2.8	3.4	0.0265	2.97	26	27
BB-402**	8	5.9	5.5	3.6	1.5	0.0319	2.55	7	8
BB-405**	12	5.9	5.5	3.6	1.5	0.0319	2.55	7	8

* Yardney Electric Corp.
** Willard Storage Battery Co.

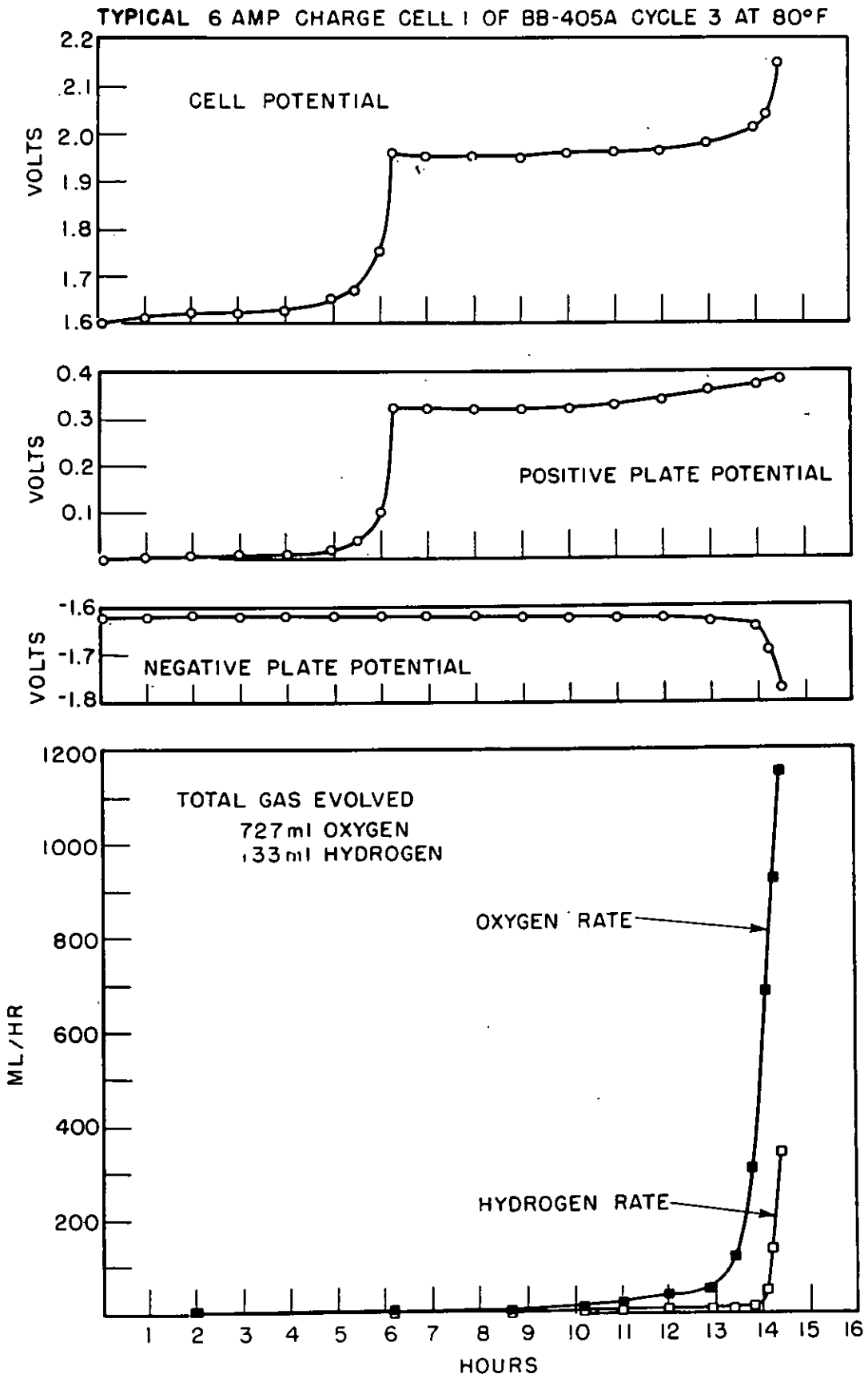


Figure 1

CES 206/16

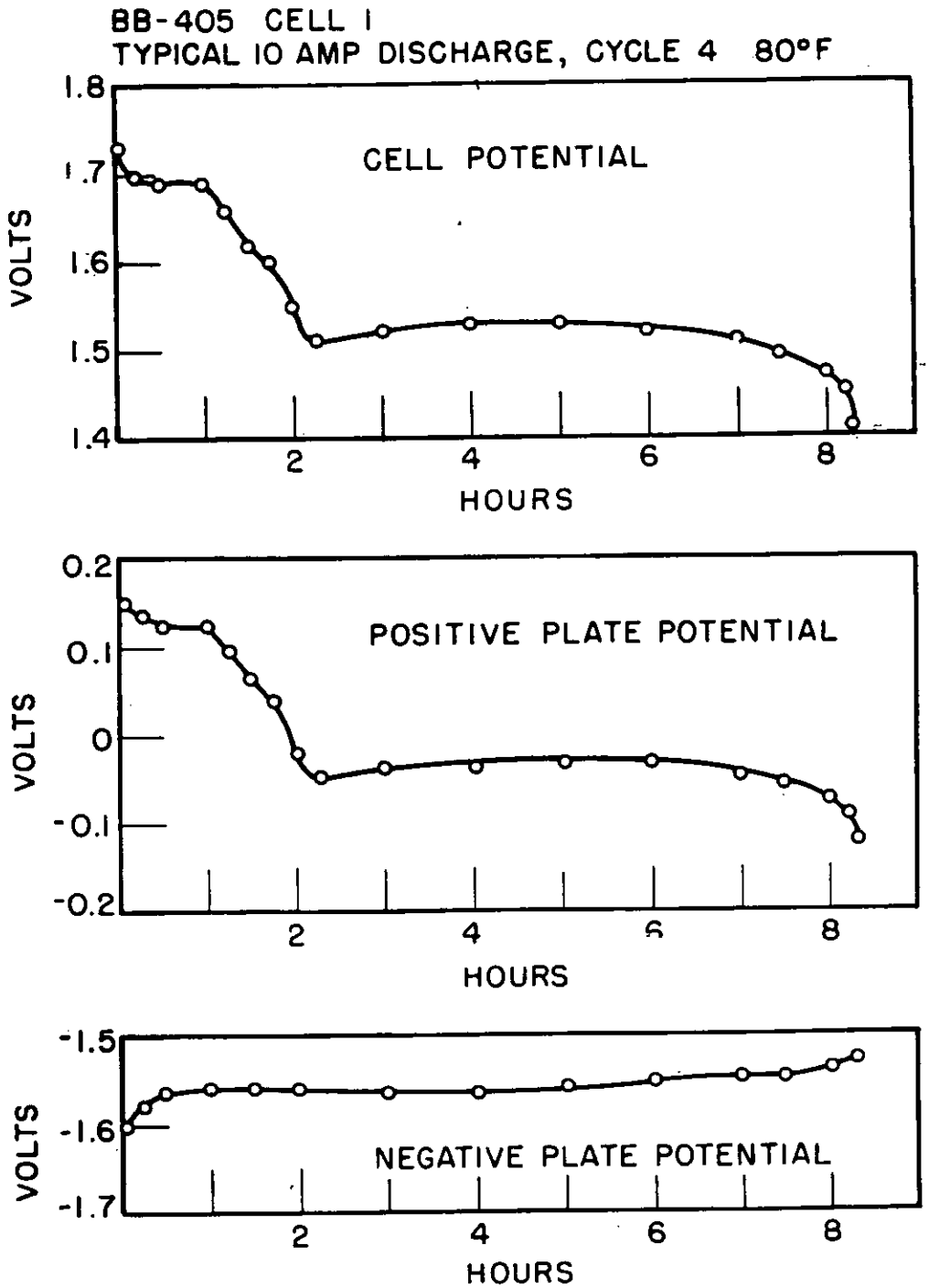

BB-405 CELL I
TYPICAL 10 AMP DISCHARGE, CYCLE 4 80°F
CELL POTENTIAL
VOLTS
1.8
1.7
1.6
1.5
1.4
2
4
6
8
HOURS
POSITIVE PLATE POTENTIAL
VOLTS
0.2
0.1
0
-0.1
-0.2
2
4
6
8
HOURS
NEGATIVE PLATE POTENTIAL
VOLTS
-1.5
-1.6
-1.7
2
4
6
8
HOURS

Figure 2

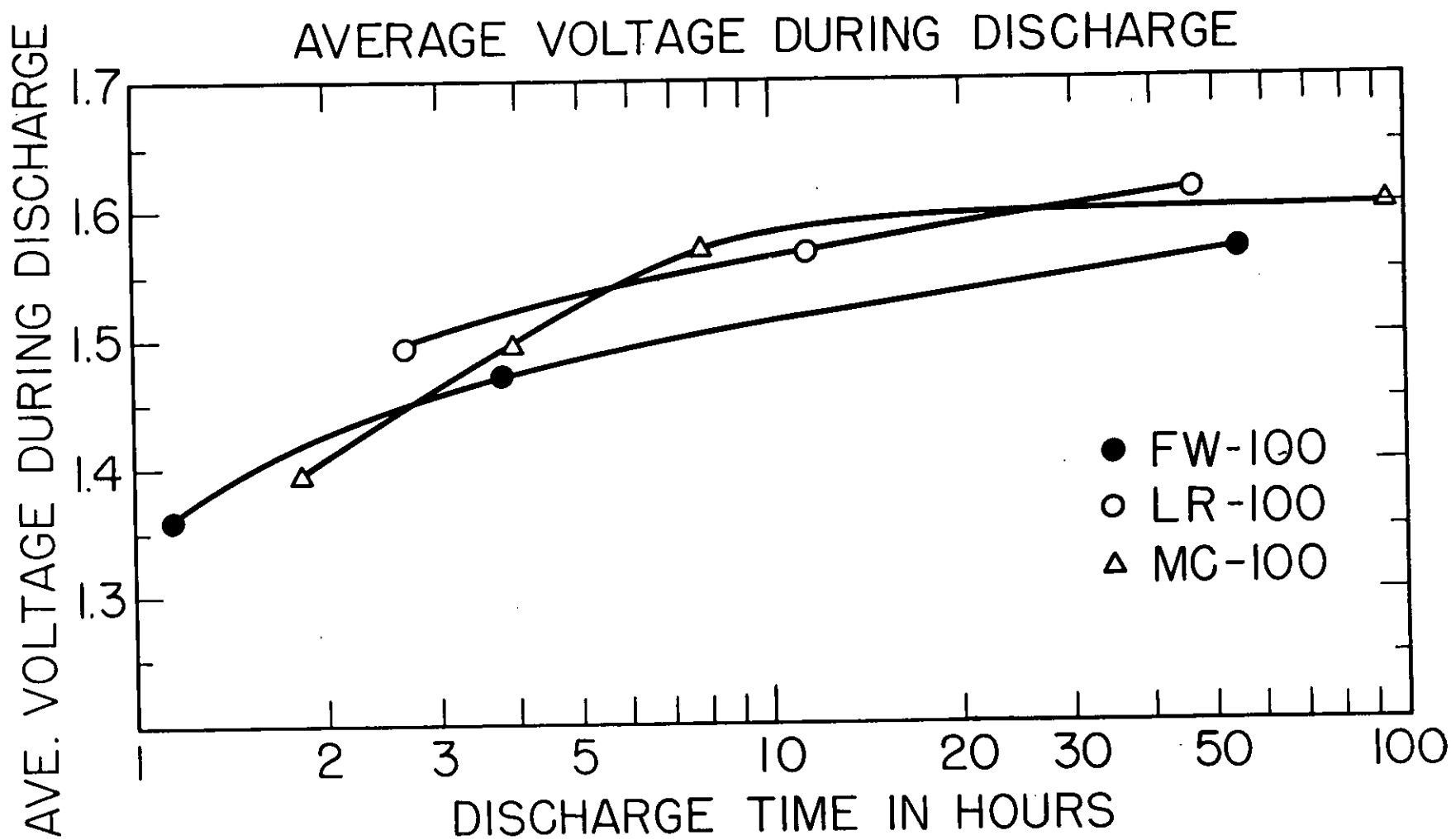
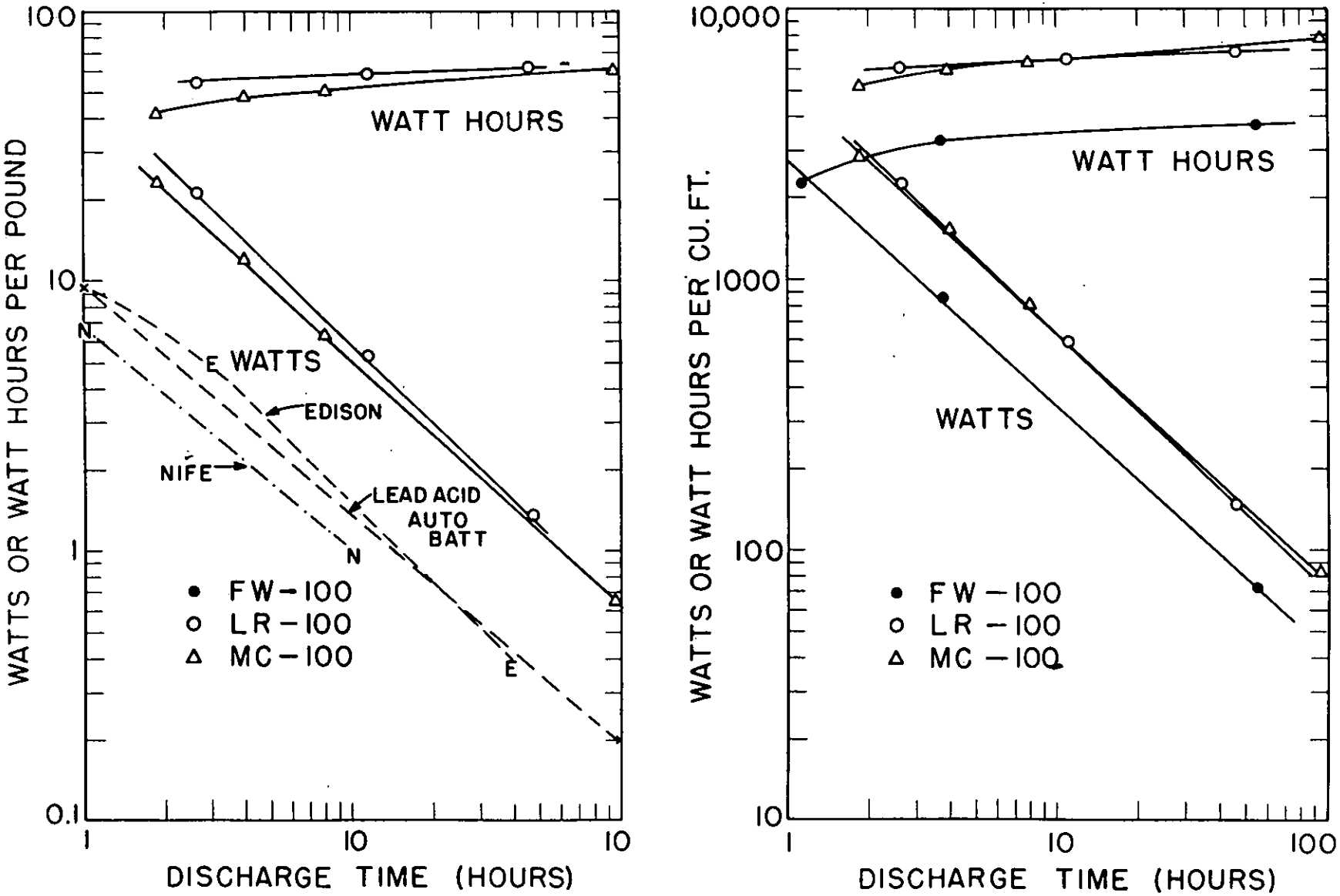


Figure 3

CES 206/16

Figure 4

POWER OUTPUT



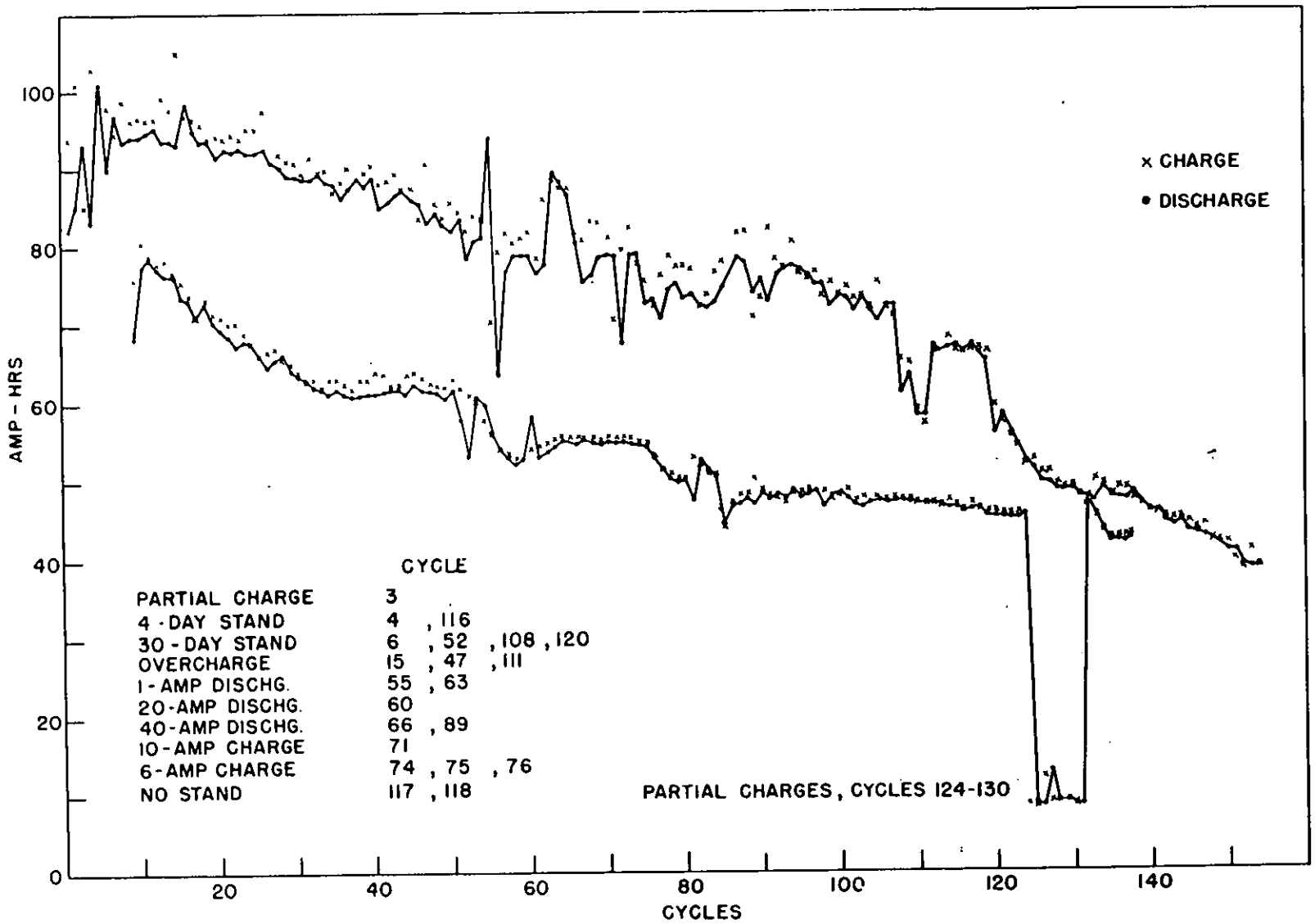


Figure 5

CHARGE AND DISCHARGE CAPACITY WITH CYCLING, MC-100

CES 206/16

BATTERY CAPACITY WHEN DISCHARGED TO 5.6 VOLTS AT 10 AMPERES. 80° F

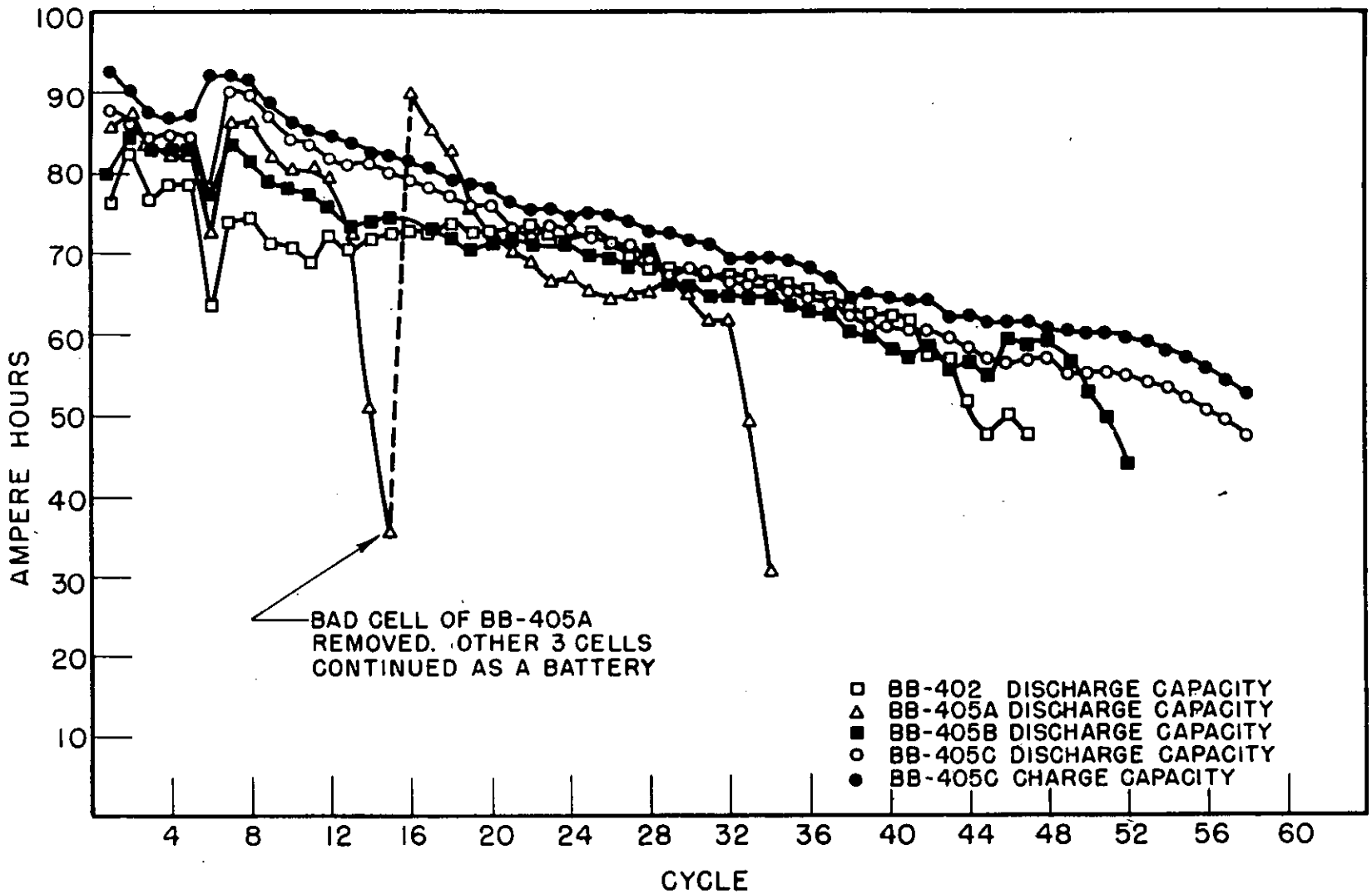


Figure 6

CES 206/16

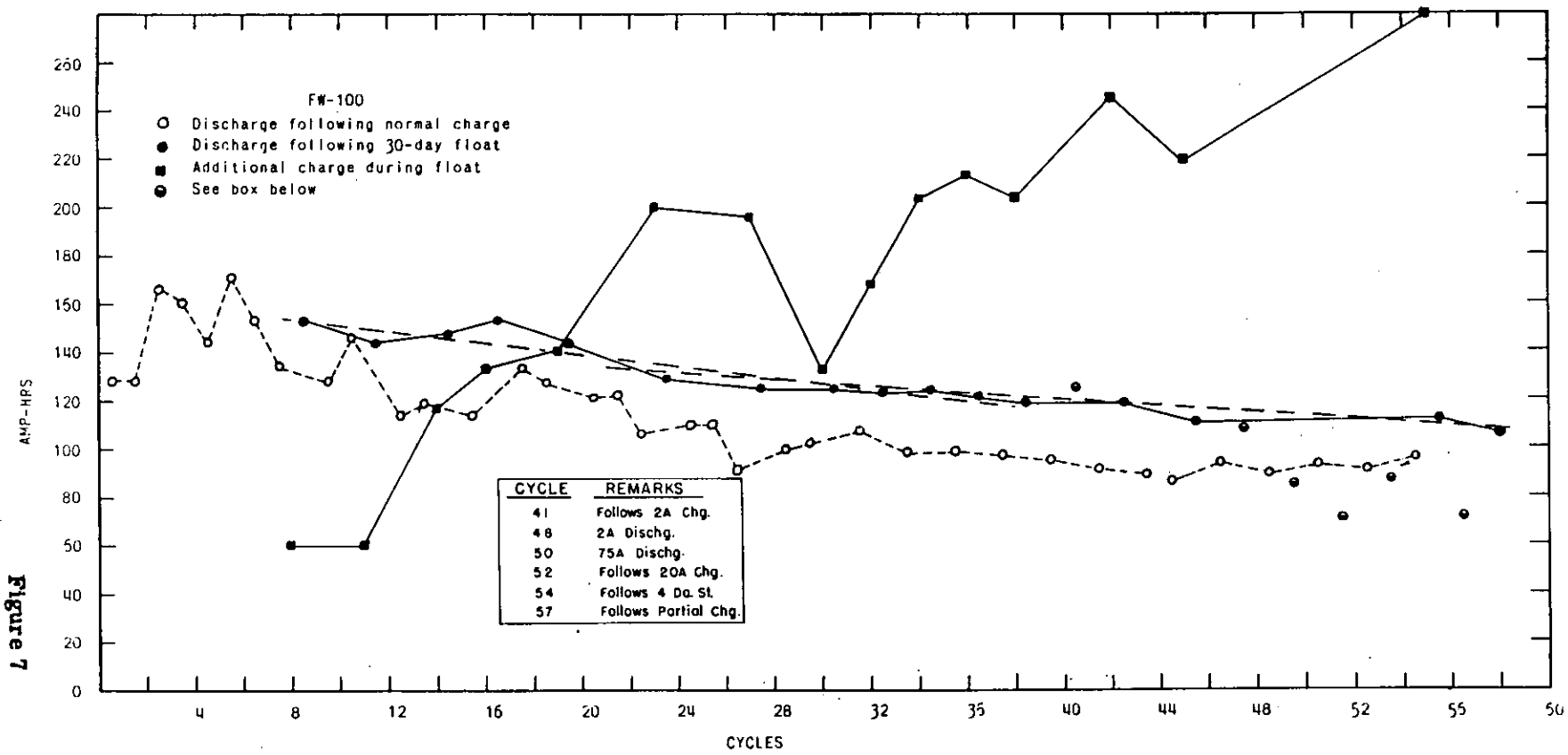


Figure 7

CES 206/16

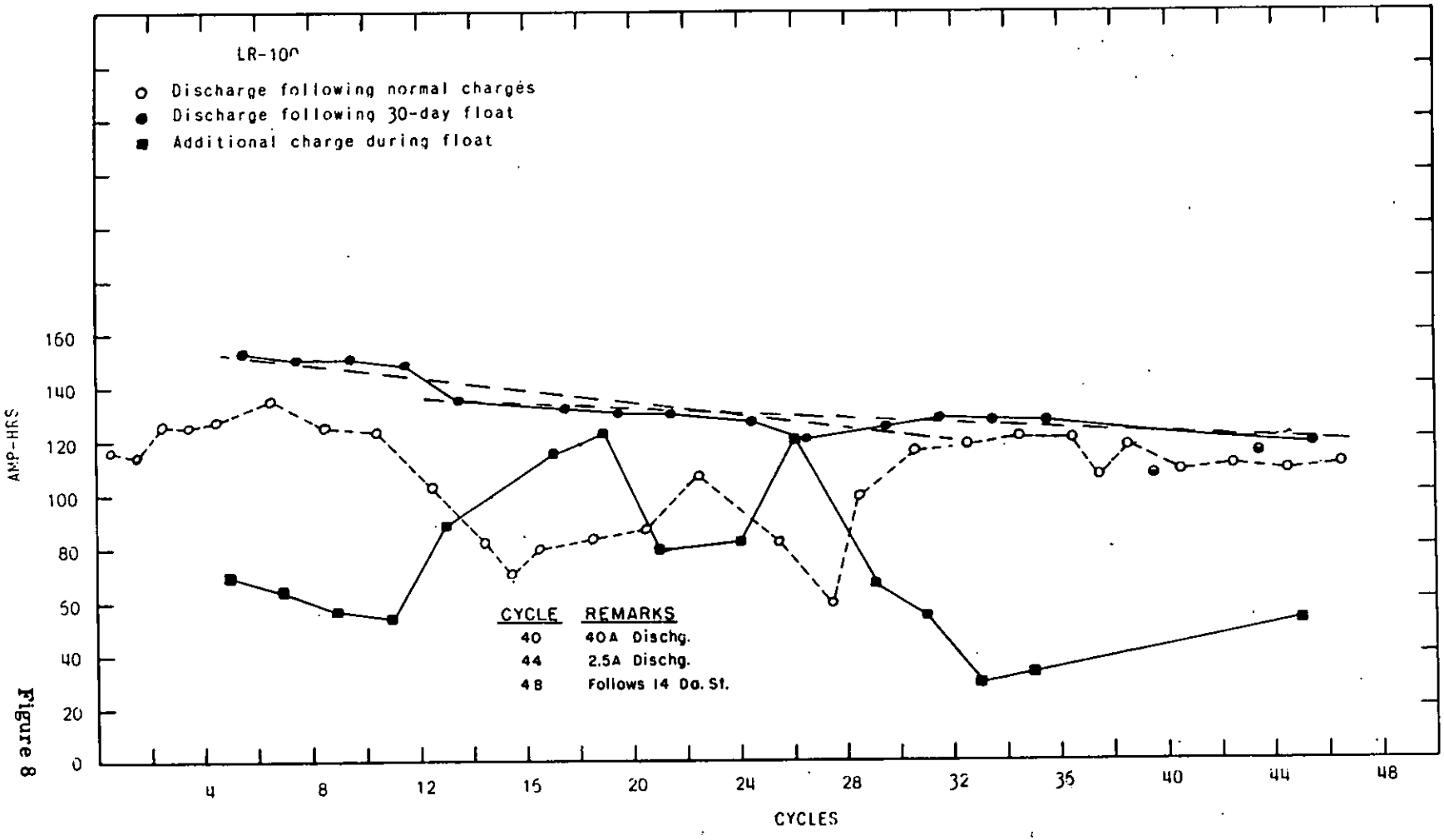


Figure 8

CES 206/16

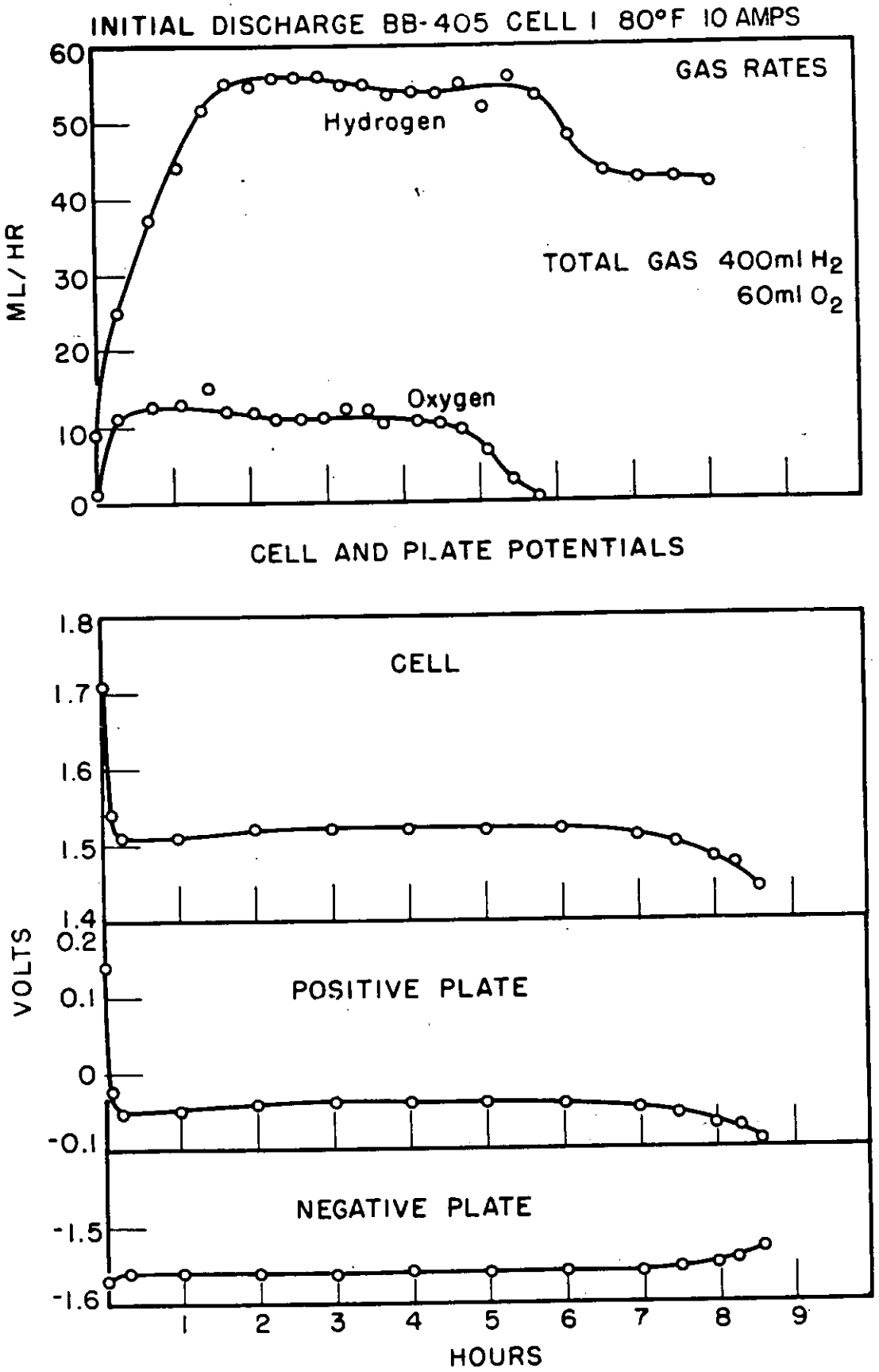
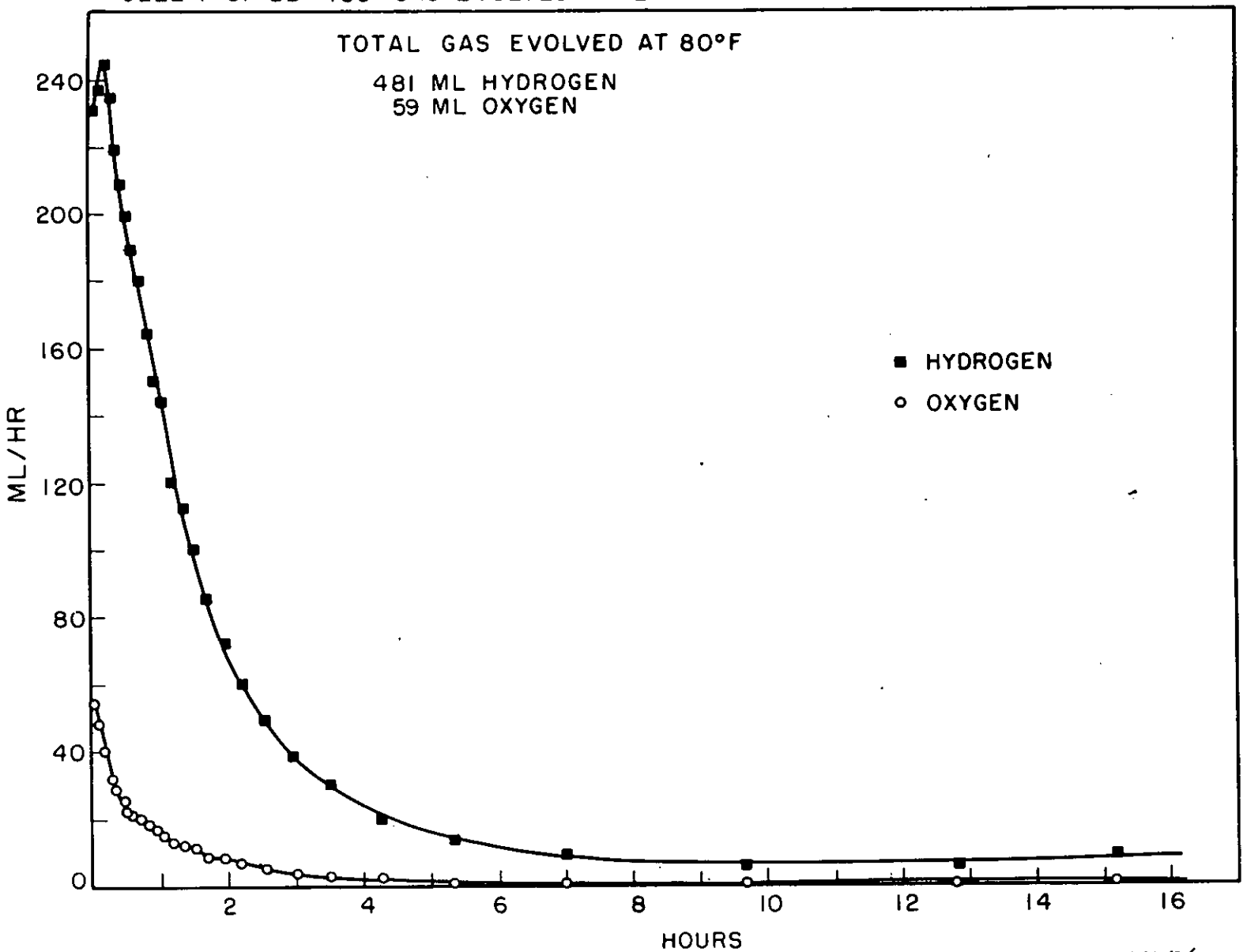

INITIAL DISCHARGE BB-405 CELL I 80°F 10 AMPS
GAS RATES
Hydrogen
Oxygen
TOTAL GAS 400ml H2
60ml O2
ML/HR
60
50
40
30
20
10
0
CELL AND PLATE POTENTIALS
CELL
POSITIVE PLATE
NEGATIVE PLATE
VOLTS
1.8
1.7
1.6
1.5
1.4
0.2
0.1
0
-0.1
-1.5
-1.6
1
2
3
4
5
6
7
8
9
HOURS

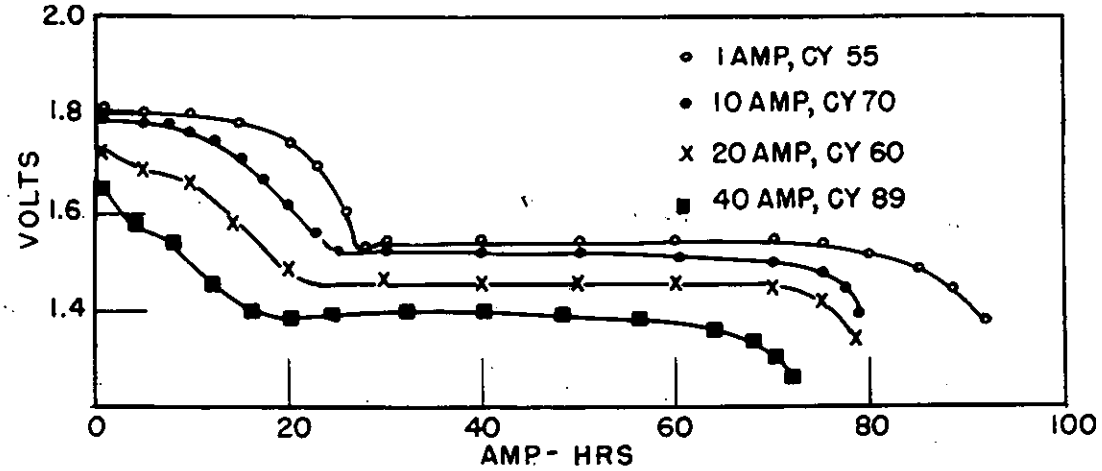
Figure 9

CELL I OF BB-405 GAS EVOLVED AFTER ADDING ELECTROLYTE TO DRY CHARGED CELL

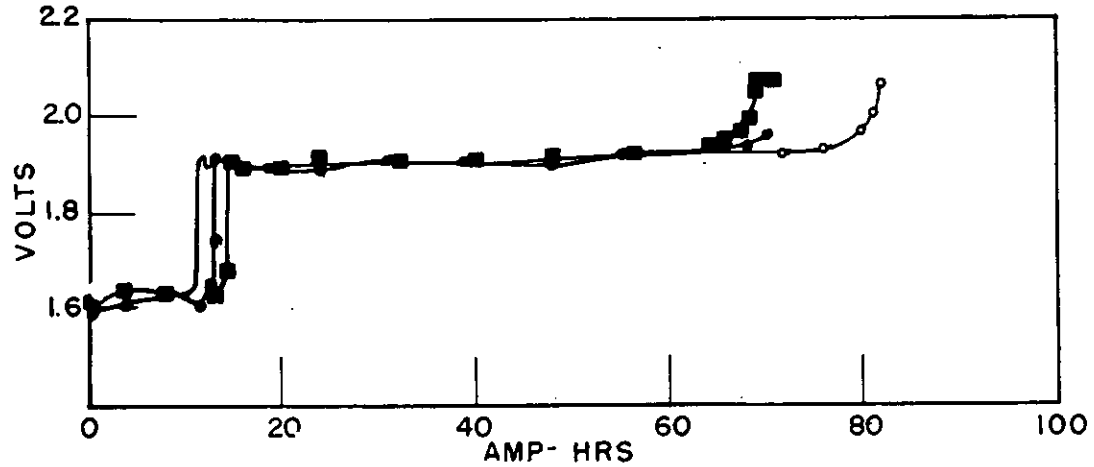


CES 206/16

Figure 10

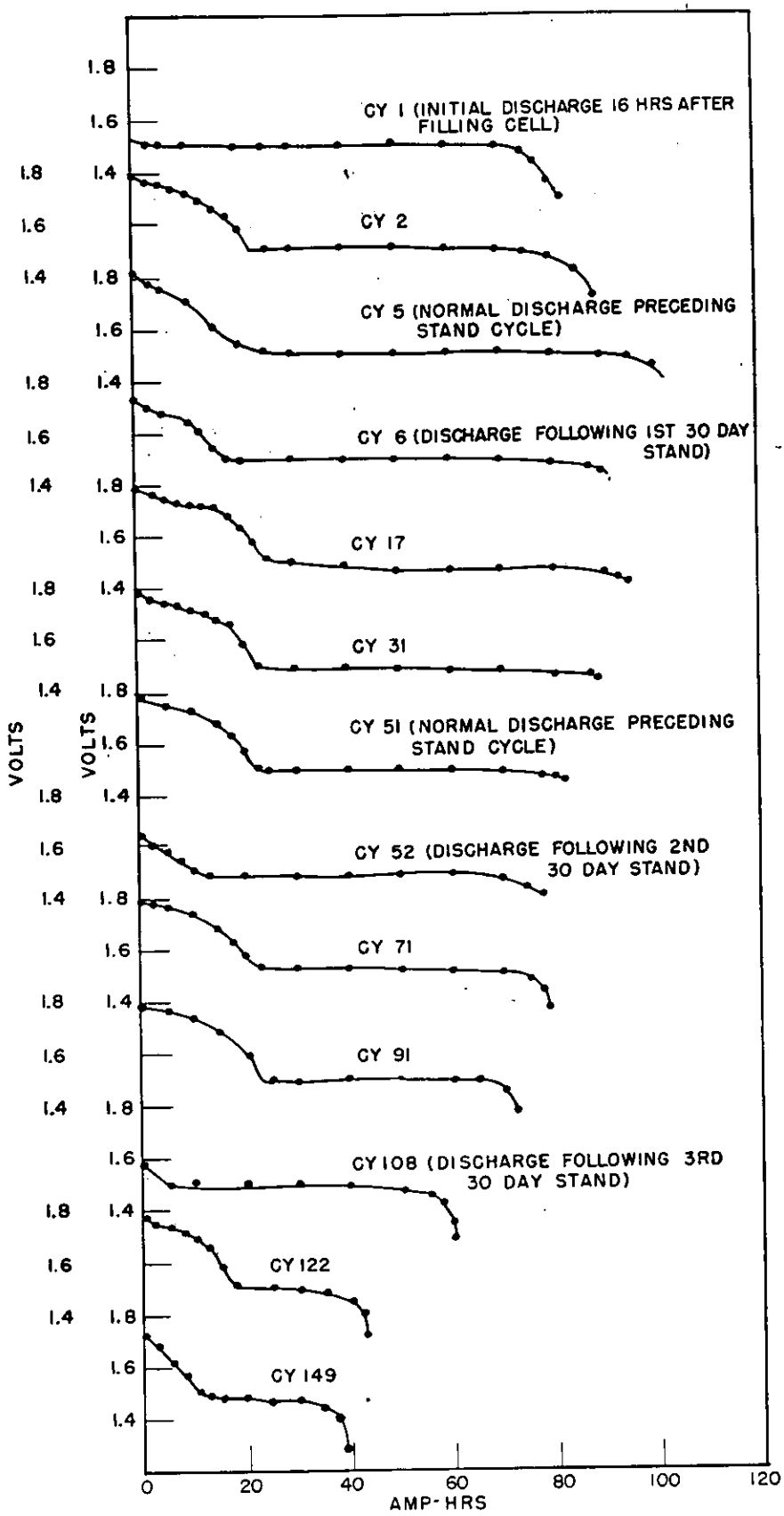


1-, 10-, 20- AND 40 AMP RATE DISCHARGE MC-100, CELL 20



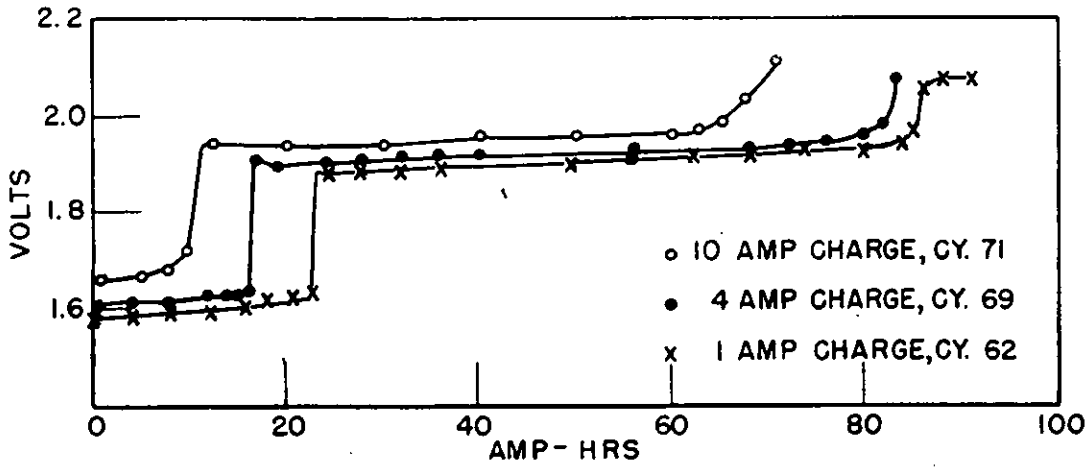
4-AMP RATE CHARGES FOLLOWING VARIOUS RATE DISCHARGES, MC-100 CELL 20

Figure 11

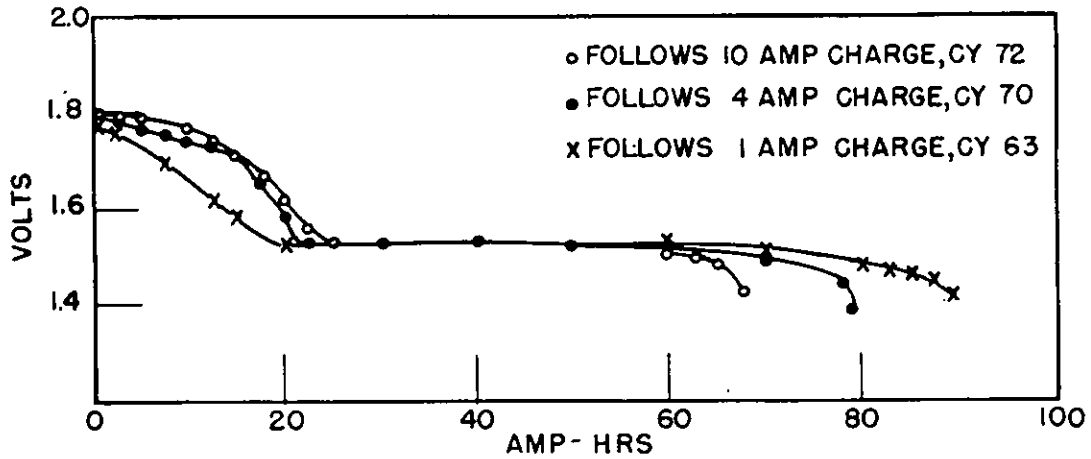


TYPICAL DISCHARGE POTENTIALS, MC-100, CELL 20

Figure 12

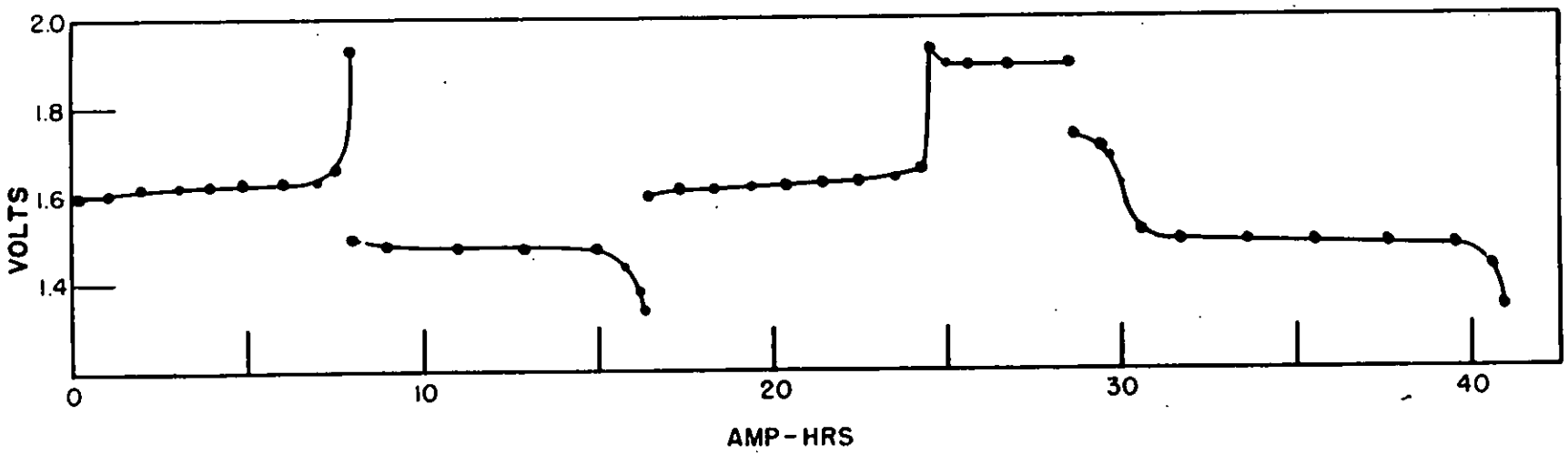


1-, 4- AND 10 AMP RATE CHARGES MC-100, CELL 20



10 AMP DISCHARGE FOLLOWING CHARGES @ 1-, 4- AND 10 AMP RATE
MC 100, CELL 20

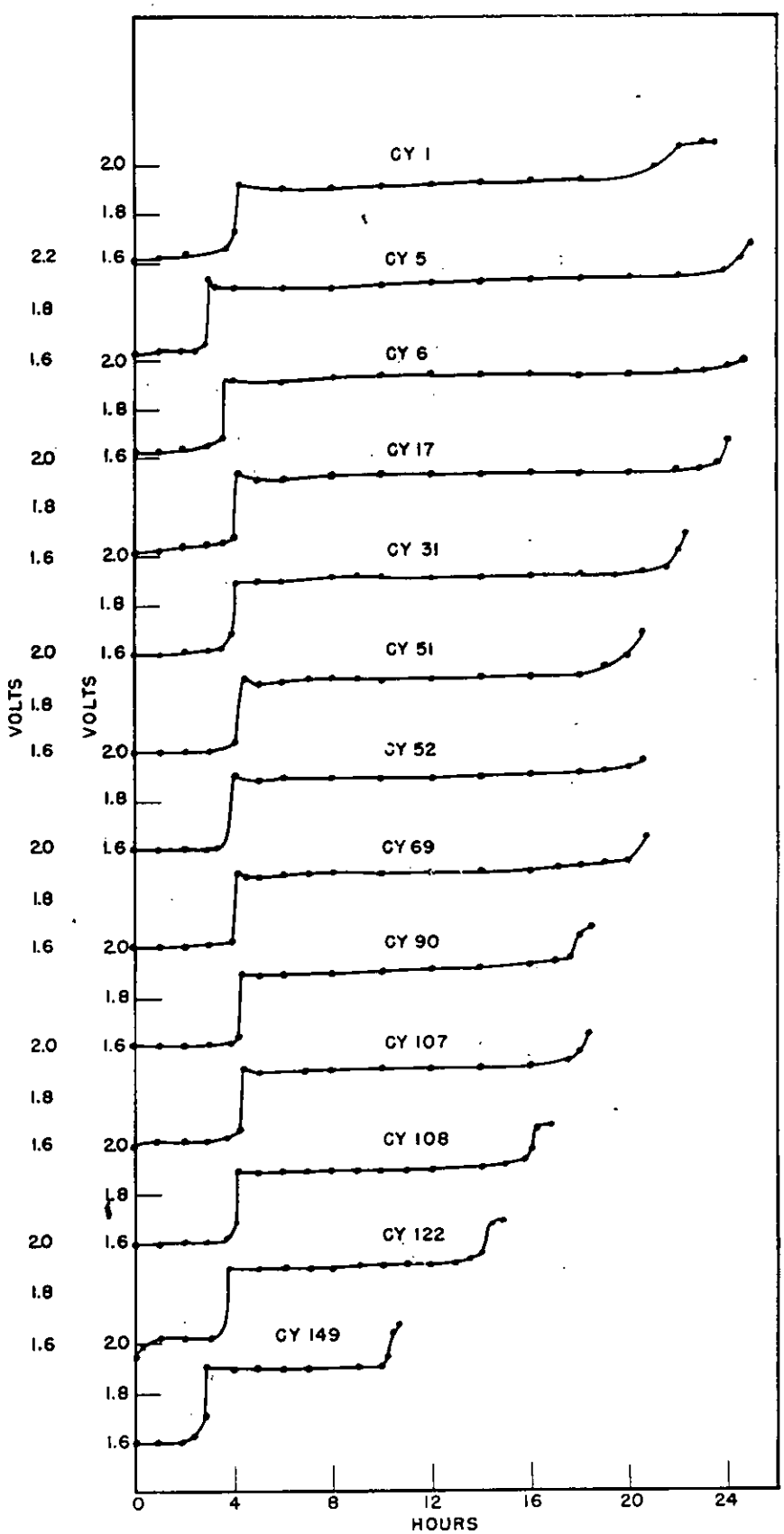
Figure 13



PARTIAL CHARGES AND DISCHARGES MC-80, CELL NO.16, CYCLES 126, 127

Figure 14

CES 206/16



TYPICAL CHARGE POTENTIALS, MC-100, CELL 20

Figure 15

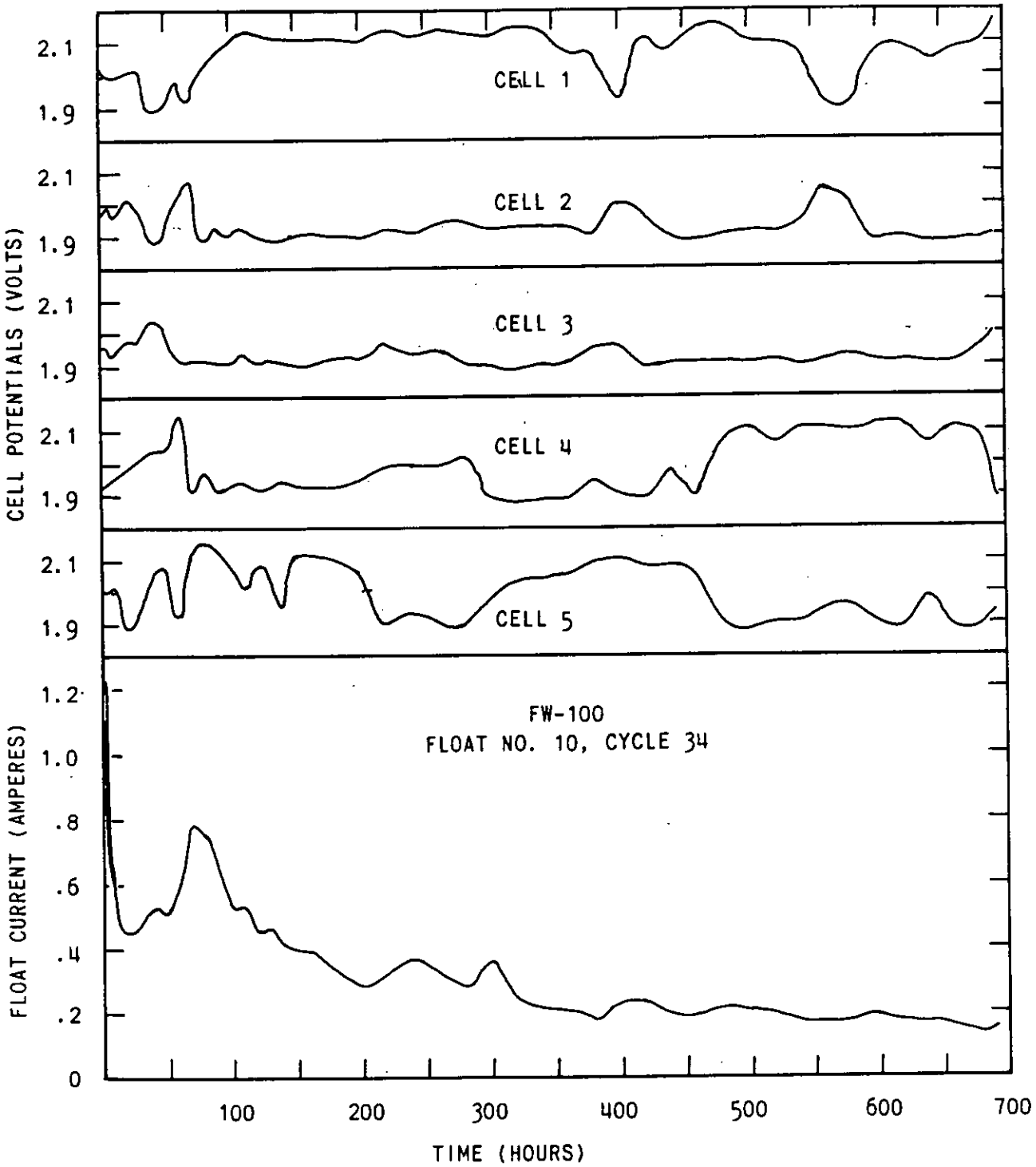


Figure 16

CES 206/16

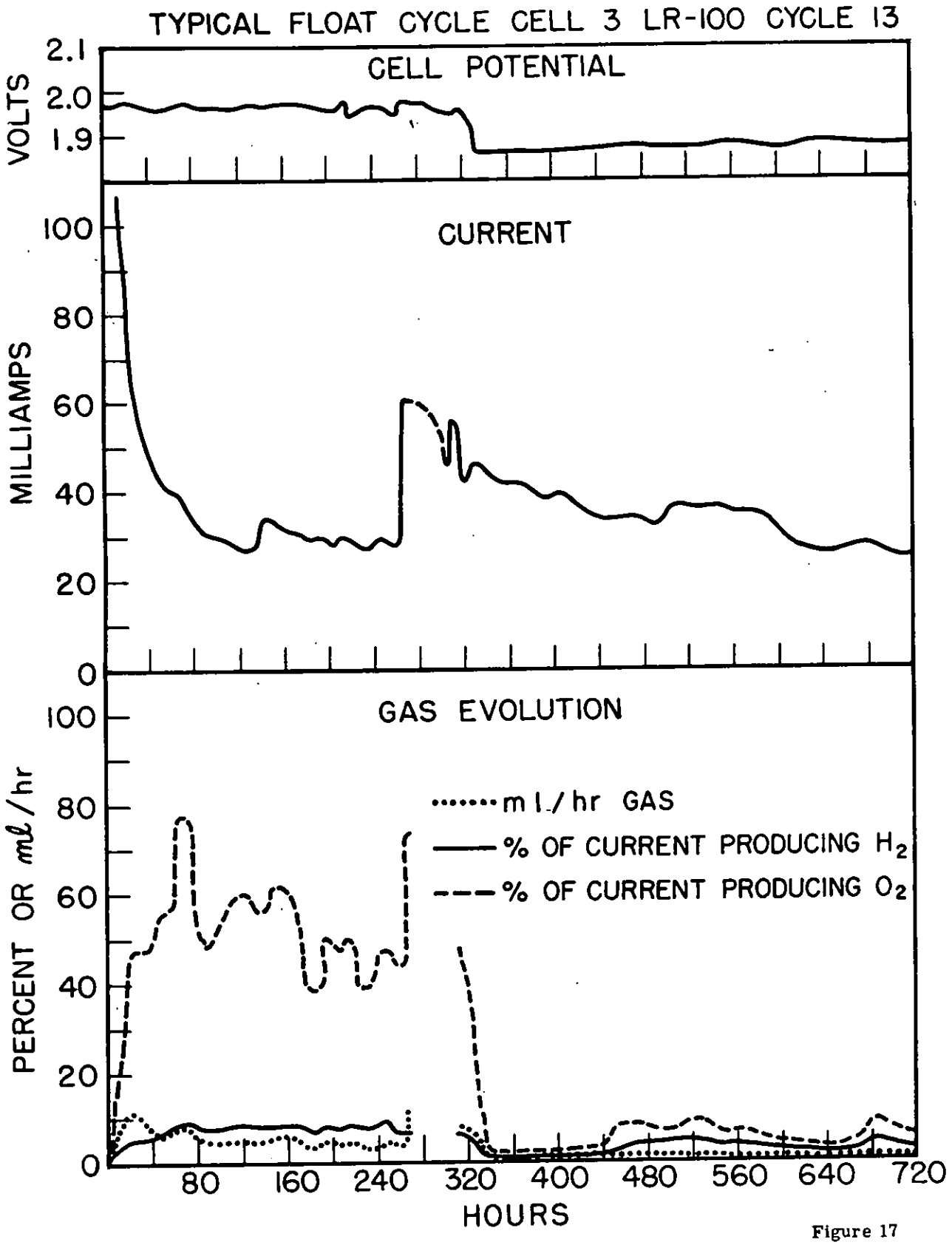
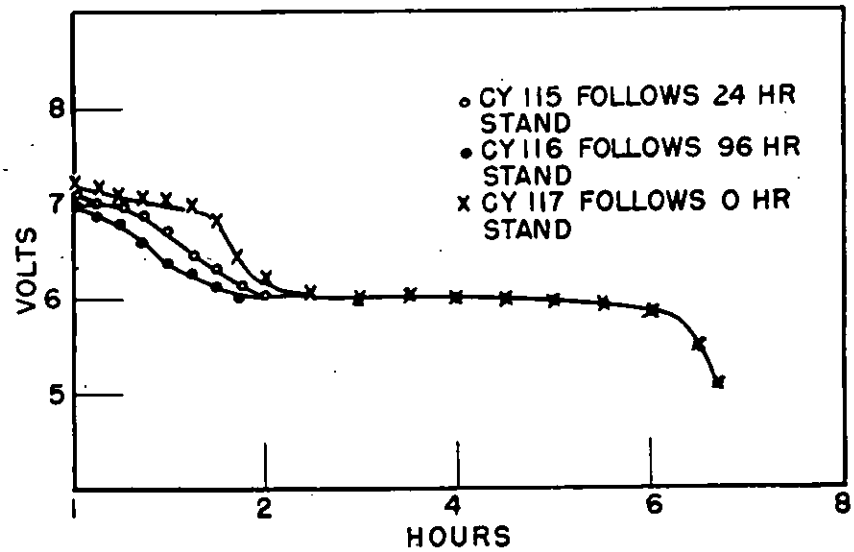


Figure 17

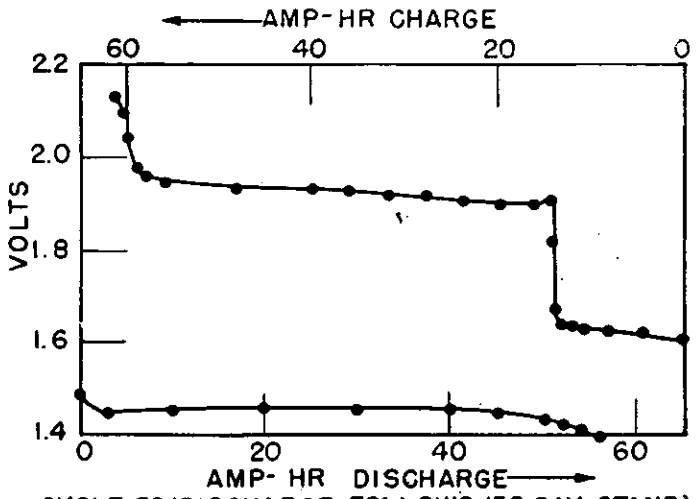
CES 206/16



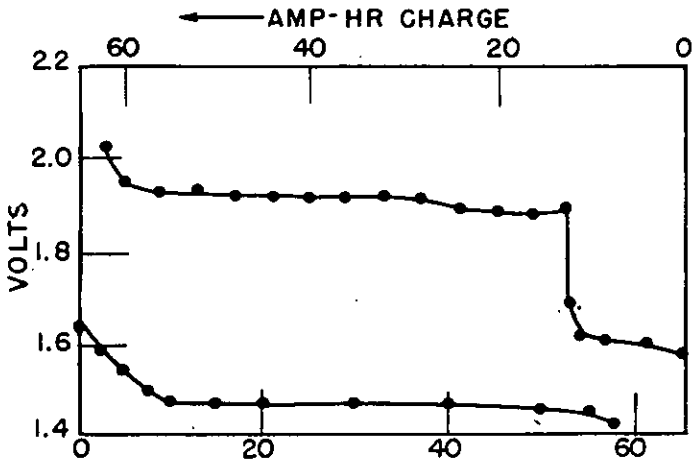
DISCHARGES FOLLOWING 0-, 24- AND 96 HR STANDS, MC-100

Figure 18

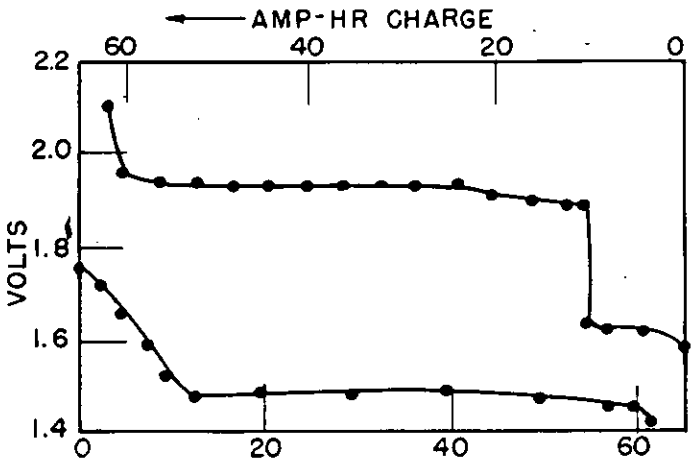
CES 206/16



CYCLE 52 (DISCHARGE FOLLOWS 150 DAY STAND)



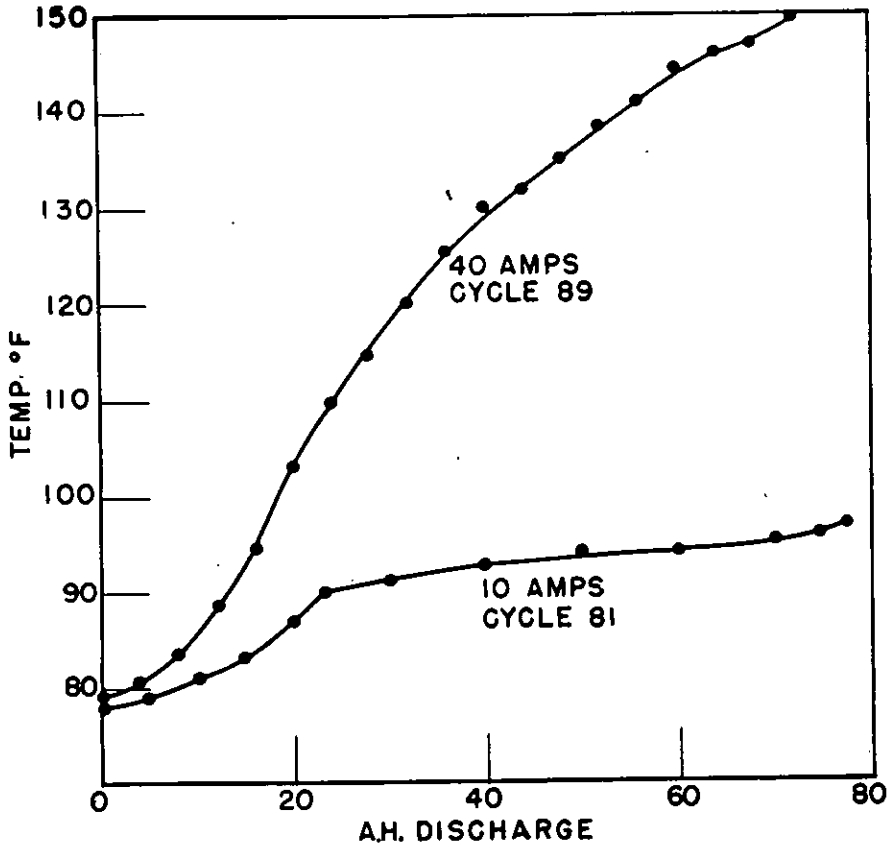
CYCLE 51 (DISCHARGE FOLLOWS 30 DAY STAND)



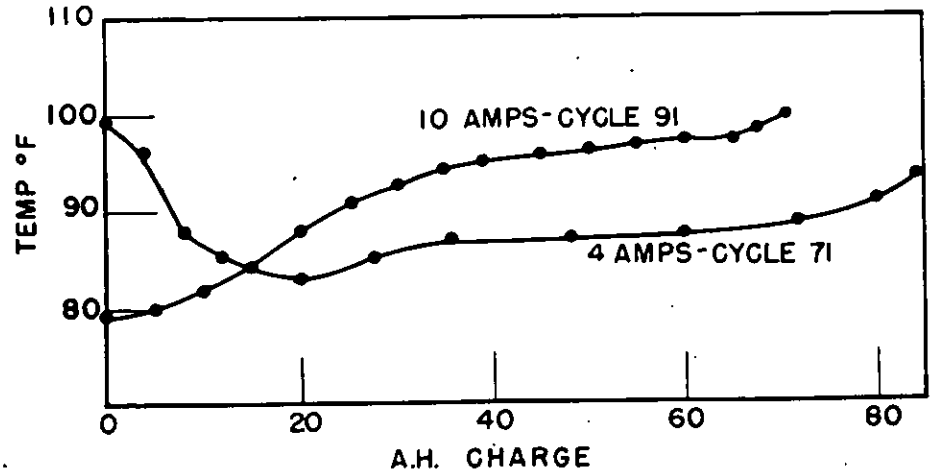
CYCLE 50-(NORMAL CYCLE)

DISCHARGE AND CHARGE POTENTIALS MC-80, CELL 16

Figure 19



CELL TEMPERATURE DURING 1- AND 4- NORMAL RATE DISCHARGE, MC-100, CELL 21



CELL TEMPERATURE DURING 1- AND 2.5- NORMAL RATE CHARGES, MC-100, CELL 21

Figure 20

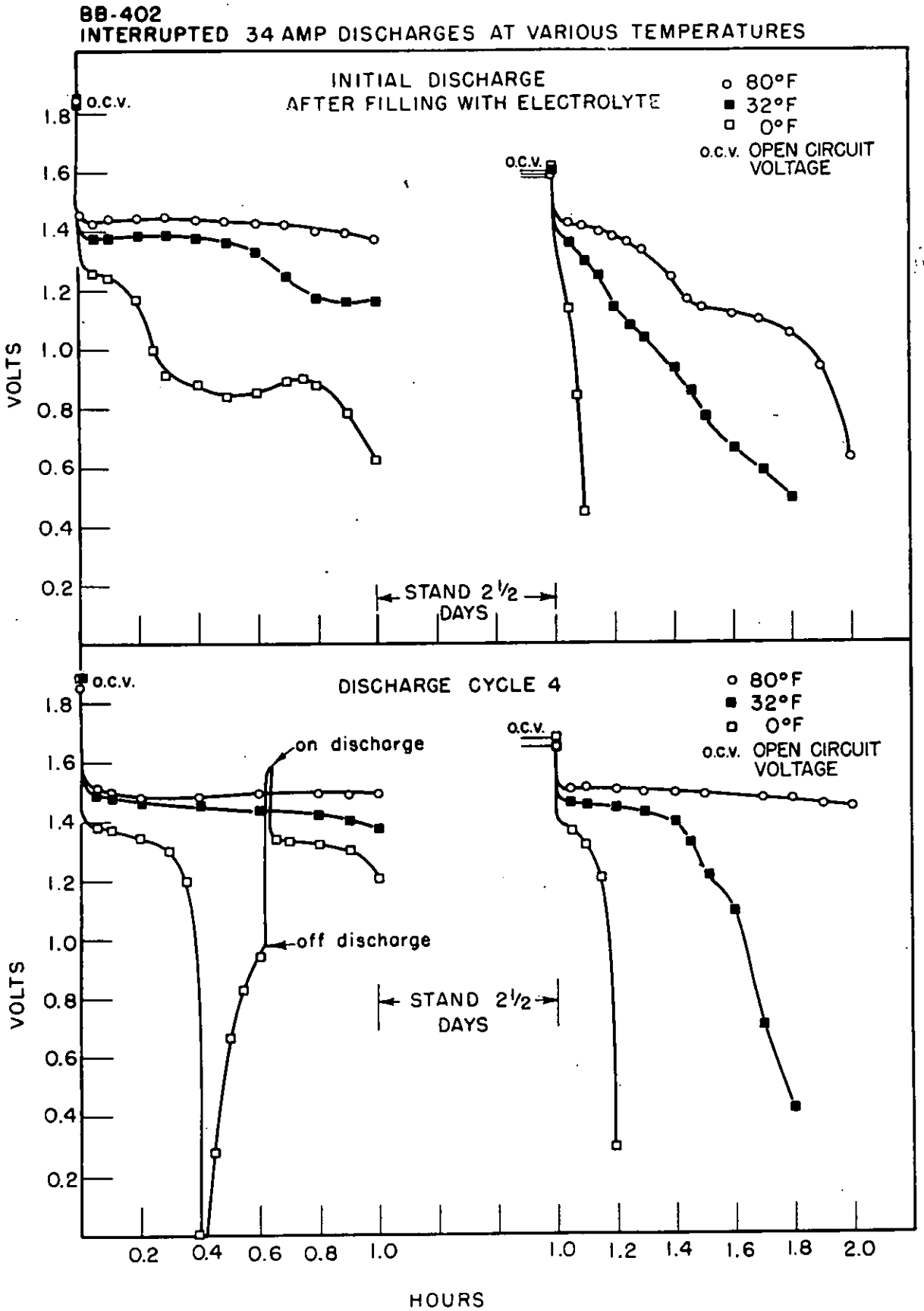

BB-402
INTERRUPTED 34 AMP DISCHARGES AT VARIOUS TEMPERATURES
INITIAL DISCHARGE
AFTER FILLING WITH ELECTROLYTE
o 80°F
■ 32°F
□ 0°F
o.c.v. OPEN CIRCUIT VOLTAGE
o.c.v.
STAND 2 1/2 DAYS
DISCHARGE CYCLE 4
on discharge
off discharge
VOLTS
HOURS
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0

Figure 21

BB405 CELL 10. ELECTROLYTE LEVELS AND CELL POTENTIALS DURING A DISCHARGE 80°F 10 AMPS

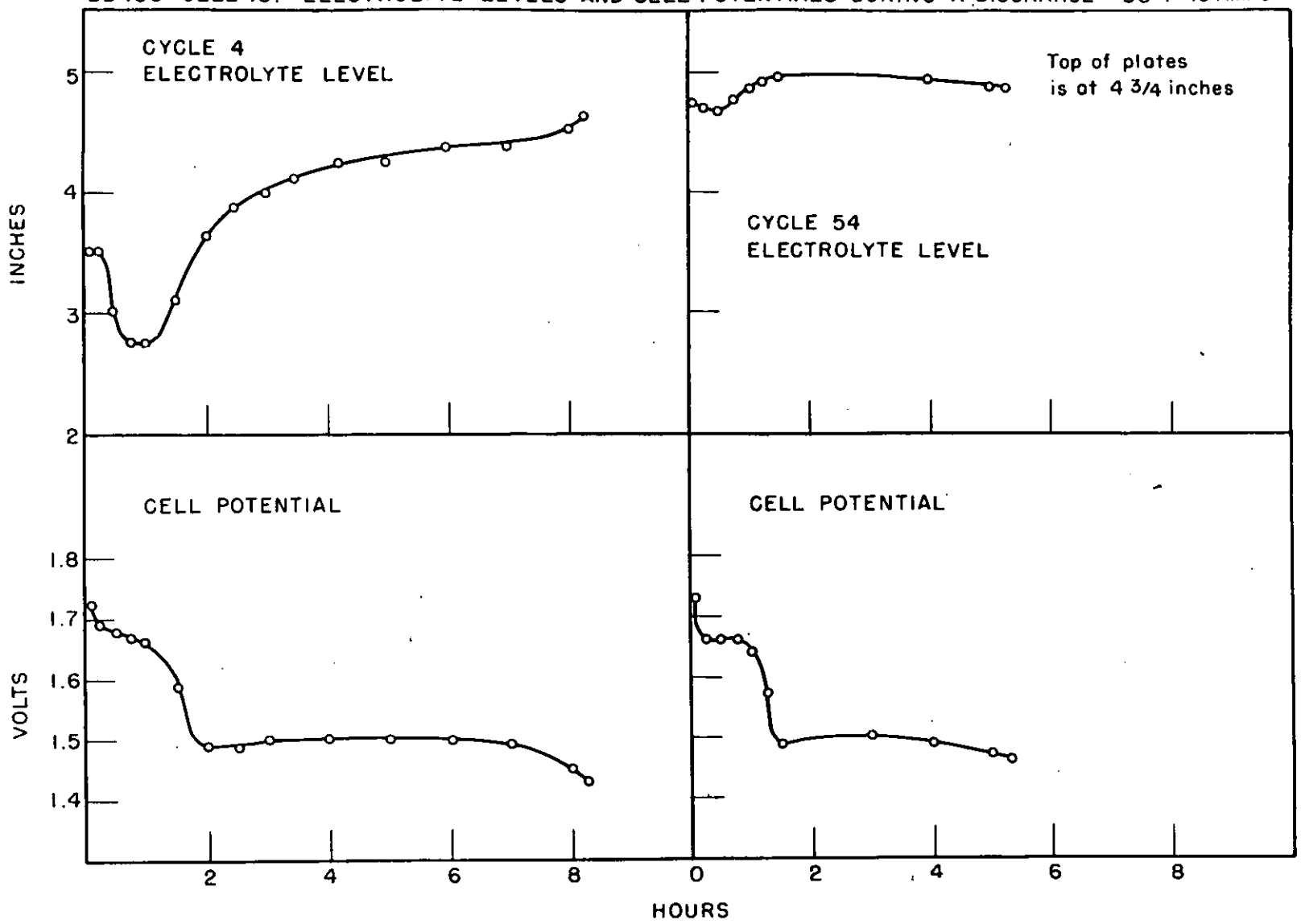
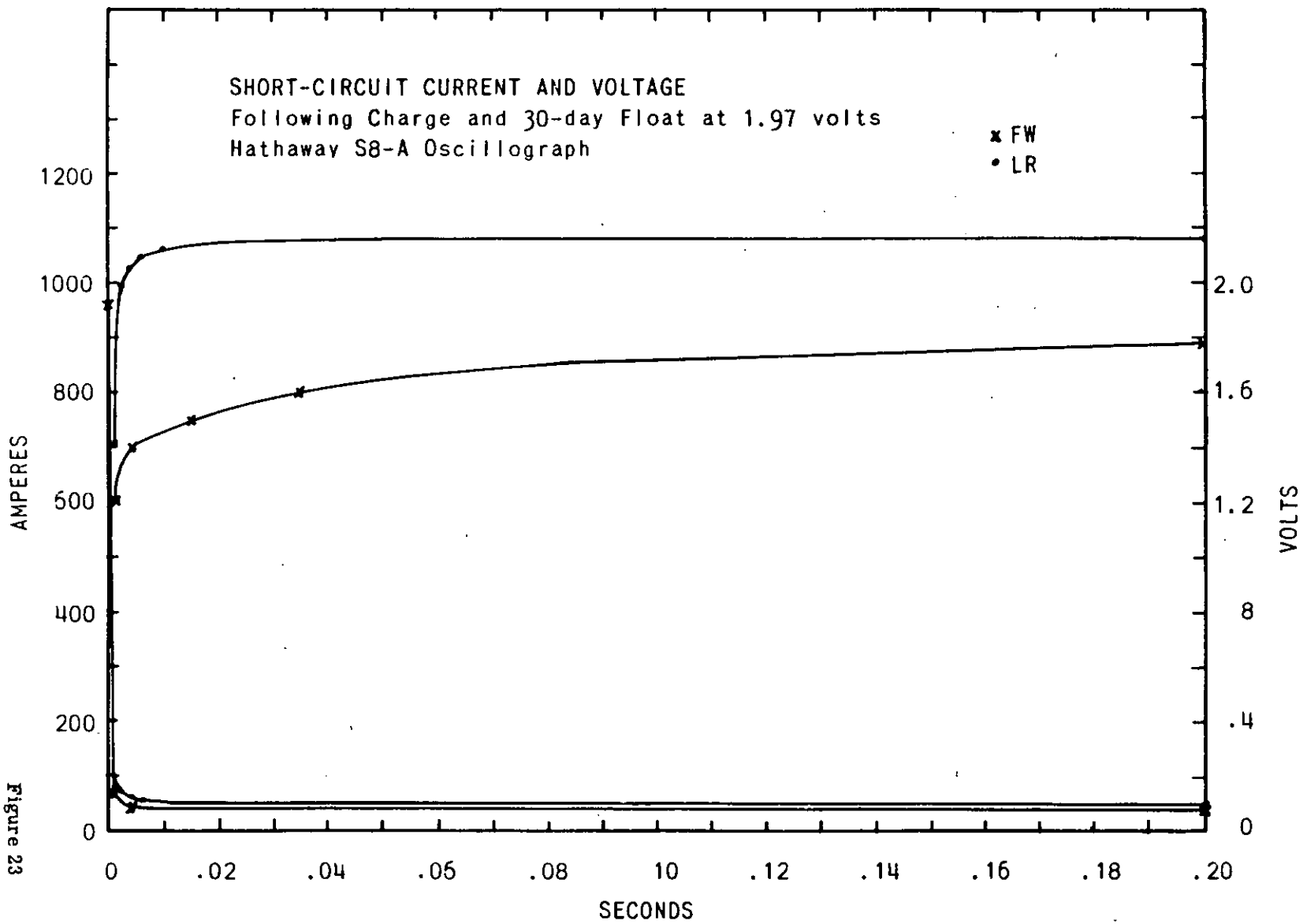


Figure 22

CES 206/16

SILVER OXIDE-ZINC ALKALINE STORAGE BATTERY



CES 206/16

Figure 23

SILVER OXIDE-ZINC ALKALINE STORAGE BATTERY

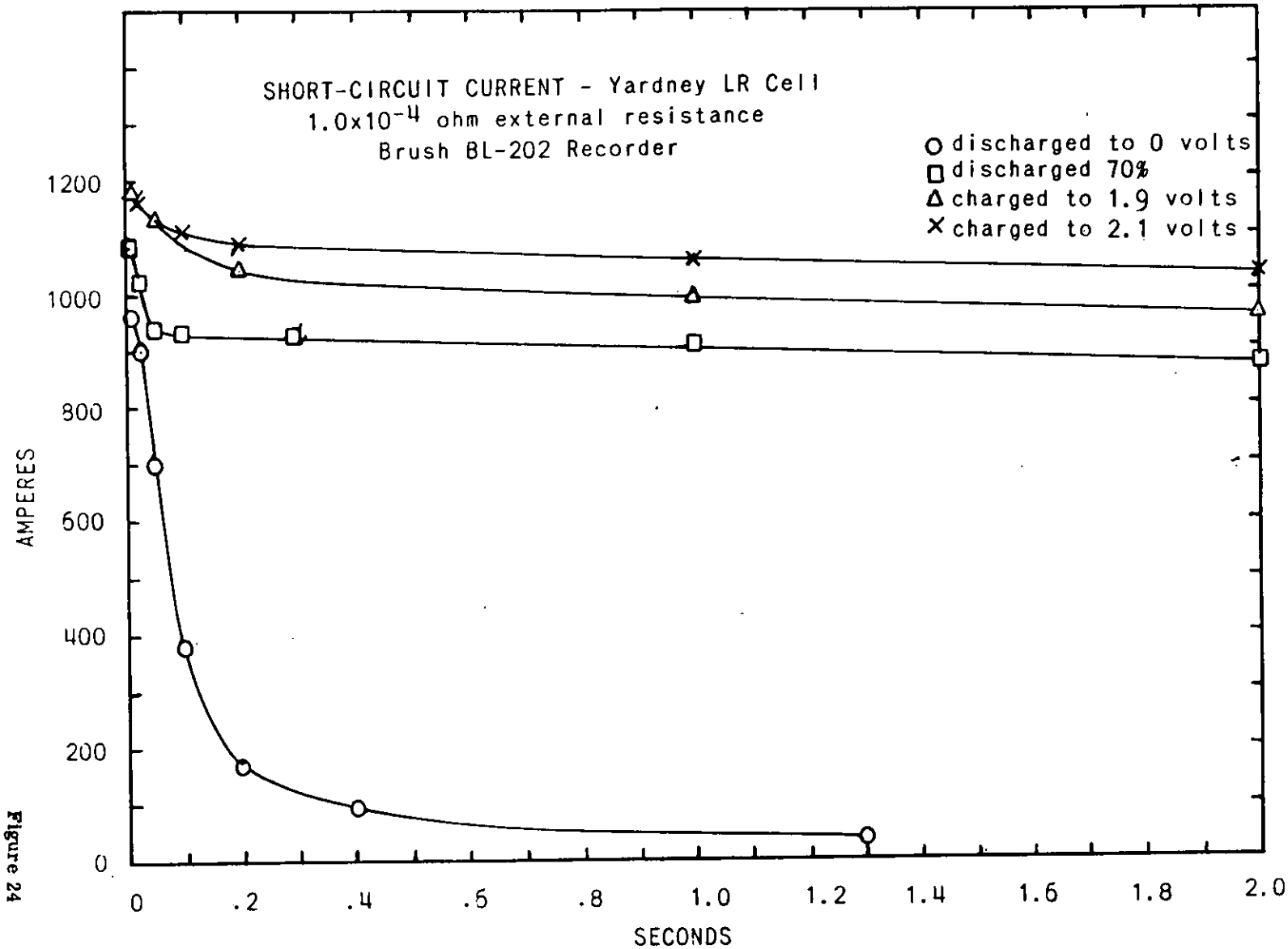
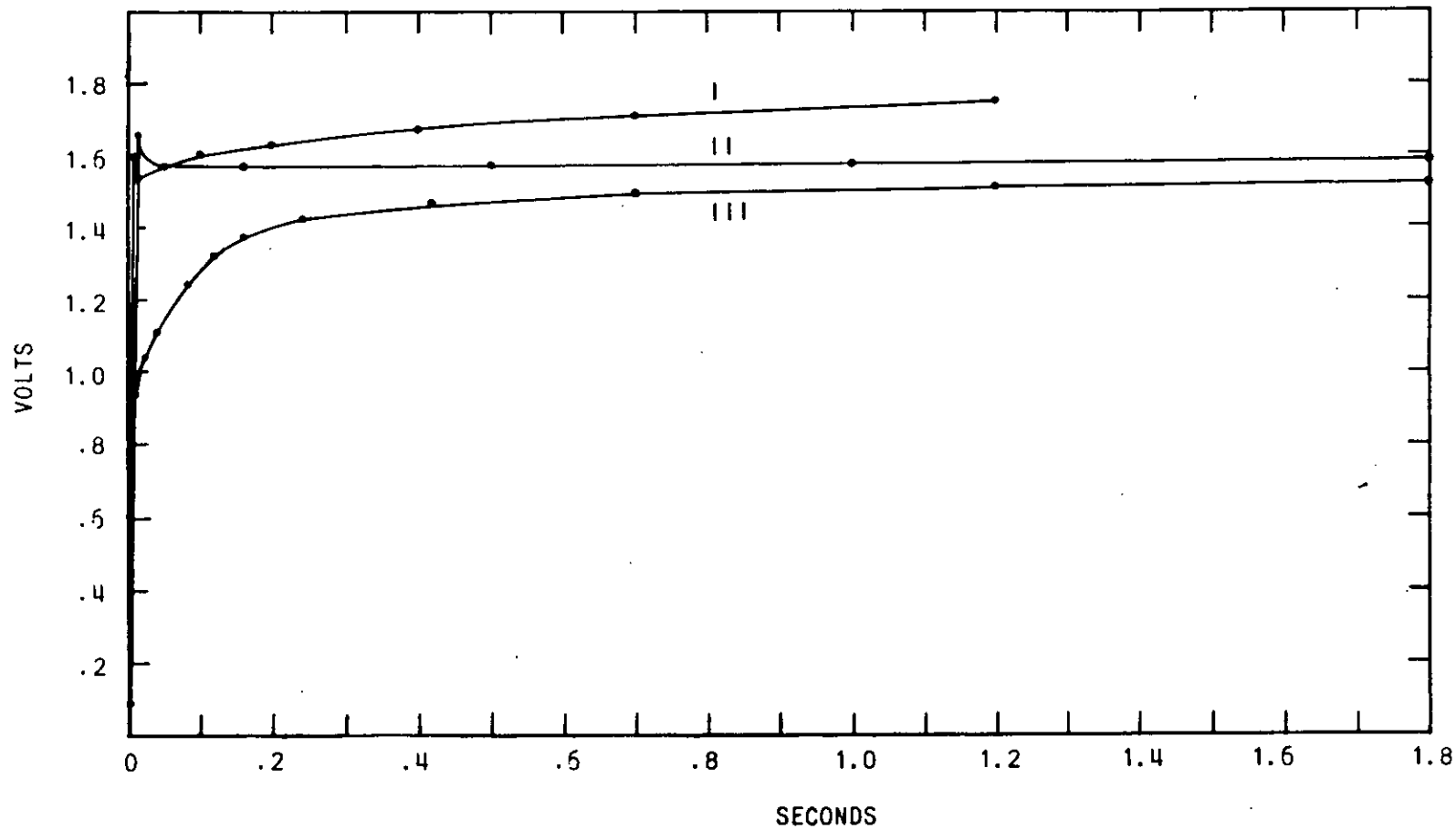


Figure 24

CES 206/16



CELL VOLTAGE RISE WHEN SHORT CIRCUIT IS REMOVED, FW-100, 80°F.

Curve I follows charge, 30-day float and 0.7-second short circuit, Cell 1 (Hathaway Oscillograph)

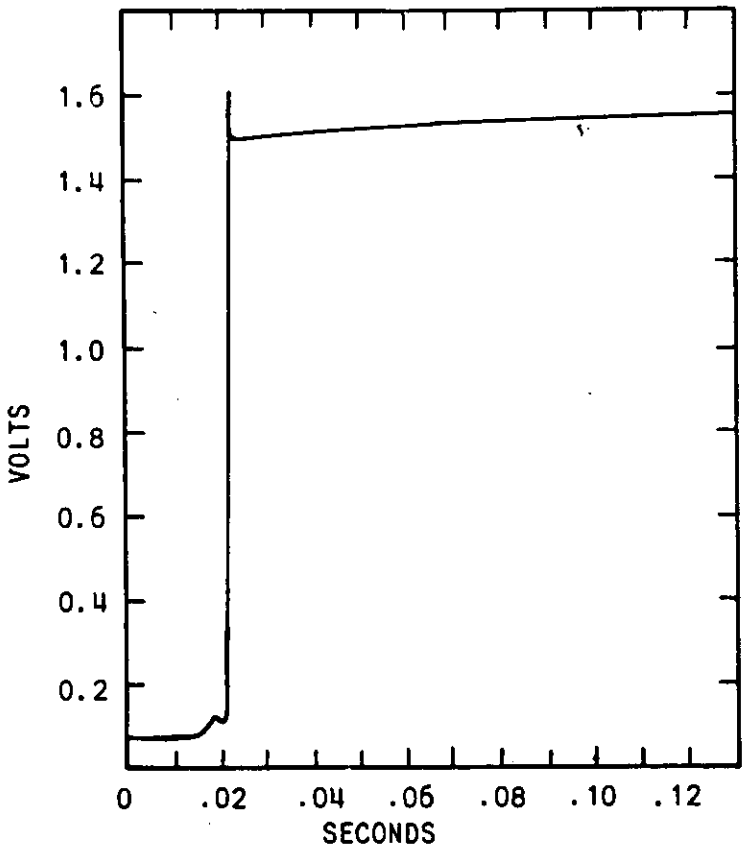
Curve II follows partial charge and 2-second short circuit Cell 4 (Brush Recorder)

Curve III follows normal discharge to 1-volt and 2-second short circuit, Cell 1 (Brush Recorder)

CES 206/16

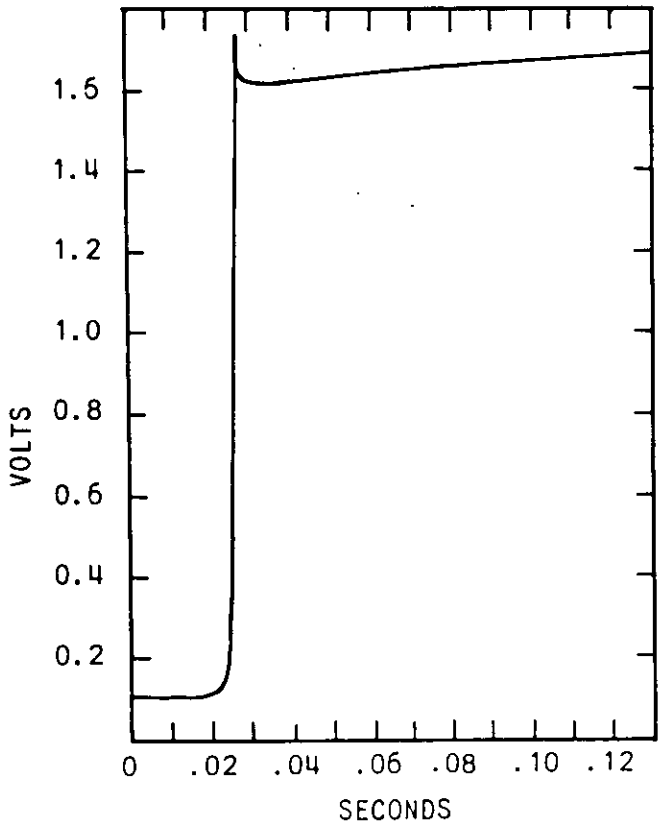
Figure 25

CELL VOLTAGE RISE WHEN SHORT CIRCUIT IS REMOVED,
FW-100 AND LR-100



FW-100, Cell 1

Follows charge, 30-day float and three brief short circuits. OCV before last short circuit was 1.78 volts.



LR-100, Cell 2

Follows charge, 30-day float and one-second short circuit. OCV before short circuit was 1.92 volts.

Figure 26

PRESENTED AT THE JOINT BATTERY CONFERENCE MEETING - 12 SEPTEMBER 1956
Sponsored by the Coordinating Committee on Equipment & Supplies
Office of the Assistant Secretary of Defense (R&D)
Washington, D. C.

CES 206/16 RESULTS OF BUREAU OF SHIPS TESTS OF LEAD-ACID BATTERIES WITH CALCIUM-LEAD GRIDS

BY

SAMUEL EIDENSOHN, BUREAU OF SHIPS, CODE 560S

Introduction

Lead acid storage battery plates are usually made by applying the active material, in paste form, to a metallic grid. The grid is usually an alloy of lead with antimony and possibly other ingredients. Antimony may be present in percentages up to 12%. Such alloys make good castings but are not desirable electrochemically because of the harmful effects of antimony in promoting self discharge. An alloy of lead and calcium has been developed for grids, largely by the efforts of the Bell Telephone Laboratories, which has made it possible to reduce the self discharge of lead batteries by a very large amount. Batteries with calcium-lead grids have been used successfully in floating service but are generally believed to be unsuitable for cycling. The Bureau of Ships has been investigating the characteristics of batteries with calcium-lead grids in cycle service because of the evolution of hydrogen which is explosive, and the evolution of stibine which is toxic, from submarine batteries with antimonial-lead grids. The results of the tests conducted by the Material Laboratory, C & D Batteries, and the U.S. Naval Research Laboratory are presented in the following text. These tests included cells with positive grids of .250, .135 and .090 inch thick.

Theoretical Considerations

The lead-acid storage battery, using only the active materials has been determined to be highly reversible. This means that the rate of chemical reaction between the active material and the electrolyte, is strictly proportional to the current flowing. Chemical reaction on open circuit is extremely slow under normal conditions of temperature and electrolyte concentration.

Practical cells, however, do not use the active materials only. In addition to the active materials, the practical cell contains antimony, carbon, barium sulfate, organic materials, and significant amounts of other materials. With respect to antimony, the amount in the cell may be as much as 12% of the weight of the battery grids. Experiment has shown that the antimony is responsible for self discharge both at the positive plate and the negative plate.

An alloy of lead and calcium, containing .085% calcium has been found to be very similar to pure lead in density, melting point and conductivity while being far superior to pure lead in tensile strength. Actually, this calcium lead aloy is at least as good as 12% antimonial-lead in tensile strength.

The calcium-lead alloy has been widely used in telephone systems batteries which are floated on a constant potential line. However, it has been generally considered that the cells with this alloy are not suited for ordinary cycling and are more easily damaged by over charging.

Test Results - Thick Plate Cells

The Bureau procured six, 6 volt batteries, C & D Type 3-CXH15-W, on Contract NObs-50289, which were shipped to the Material Laboratory in August 1951.

Descriptive details are as follows:

AH (10-hour rate)	200 AH
Service Weight	180 Lbs.
Dimensions of Tray	21-5/8 inches long - overall 7-9/16 inches wide 18-5/8 inches high - overall
Cell Dimensions	6.85 Long 6-5/16 Wide 16-1/2 High - overall
Plate Thickness	.250 inches positive

One battery was put on life test, in accordance with the standard procedure of MIL-B-15072, Test IV. Routine discharges consist of a discharge at 65 amperes for two hours (130 AH) or to prior limiting voltage of 4.80. Routine charges are 36 amperes for 3 hours (108 AH) followed by 16 amperes for 3 hours, totalling 156 AH. This averages 20% overcharge. Capacity tests were preceded by an equalizing charge, finished at 10 amperes. Capacity was determined at the 10-hour rate at cycles 10, 20, 30, 40, 50, 60, 70, 72, 83, 92, 100, 150, and at 50 cycle intervals thereafter. Capacity was determined at the 5 minute rate at cycle 51, 1041, and after failure at the 10-hour rate.

It was found that the capacity at the 10-hour rate was about 240 AH or 120% of rating for over 1000 cycles. Total cycle

life to failure was 1610. Failure was apparently caused by moss short-circuits in one cell. Five minute rate (500 amperes) tests gave 47.5 AH at cycle 51, 56.25 AH at cycle 1041, and 52 AH after failure. This last test was made on two cells, in February 1954. Rated capacity is 41.7 AH at 500 amperes.

Hence it was determined that the cells were capable of lasting 42 months on test involving 1610 cycles. This is as good as the cycle life of high quality antimonial-lead batteries.

It will be noted that the charging of the battery was performed by a two step, constant current, charge. This gave 120% charge. The manufacturer does not recommend this kind of charge. He recommends a constant potential charge and a minimum of overcharge. This recommendation is believed to have a sound basis for two reasons:

(a) The cells do not need 20% overcharge

(b) Overcharging a calcium-lead cell battery will soften the positive paste sooner than would occur with antimonial-lead grid cells.

However, equipment for this kind of charging was not available.

Long time stand tests were scheduled for four batteries. Results of capacity tests are now available for 1, 2, and 3 years stand. Four years of stand will be completed in December 1956.

The tests were performed as follows:

Each battery was charged and then discharged at the 10-hour rate. This is cycle #1.

Each battery was then recharged and put on shelf for 12, 24, 36, and 48 months.

The batteries were discharged after the specified shelf period. This is cycle #2.

The batteries were then recharged and then discharged immediately after charge. This is cycle #3.

Results were as follows:

	1 Year Shelf	2 Years Shelf	3 Years Shelf
(1) Discharge #1	242 AH	245 AH	260 AH
(2) Discharge #2	217	206	140

	1 Year Shelf	2 Years Shelf	3 Years Shelf
(3) Discharge #3	226 AH	266 AH	233 AH
(4) Average #1 & #3	234	251	246
(5) Loss of Capacity (4-2)	17	45	106
(6) % Loss	7	22	43
(7) % Loss/Year	7	11	14

The procedure used in calculating per cent loss follows that used by A. C. Zachlin in his article "Self Discharge in Lead-Acid Storage Batteries" Journal of Electrochemical Society, Vol 92, 1947. He considers that averaging the capacity just before the stand and just after the charge following the stand, takes into account the trend of cycling and avoids undue emphasis on the cycle just before the stand.

Zachlin's data was obtained with plates .250 inch thick with grid compositions ranging from pure lead to 12% antimonial-lead. Extrapolation of Zachlin's data on 6 month stand test to 1.210 sp.gr. electrolyte indicates a loss of about 1% per month with pure lead grids. This is in fair agreement with the Material Laboratory results with calcium-lead alloy grids. This is to be expected since the calcium-lead alloy is practically equivalent to pure lead i.e. 99.9% lead, .1% calcium.

Cells with antimonial-lead alloy grids, on the basis of Zachlin's data, show much greater stand loss.

On stand for 100 days at 80°F, cells with pure lead grids lost 7% capacity whereas cells with 9% antimonial-lead grids lost about 45% of initial capacity, according to Zachlin. This was determined for nearly new cells. As the cells age, pure lead or calcium-lead grid cells show no significant change in self discharge. Antimonial-lead grid cells, on the other hand, may increase enormously in this respect. Antimonial-lead cells also tend to show much higher self discharge if maintained on a program of low overcharge, or high per cent of idle time.

Another indication of capacity loss on stand of lead-acid batteries is the drop in electrolyte specific gravity. The results obtained for the batteries on shelf for 1, 2, and 3 years, averaging the 3 cells in each battery were as follows:

Specific Gravity Drop During Room Temperature Stand

Stand (years	1	2	3
Sp. Gr. drop	.005	.015	.058
Sp.Gr. drop per year	.005	.0075	.018

This may be contrasted with a normal drop of about .001 per day for antimonial-lead batteries.

Plotting total sp.gr. drop against AH loss gives a straight line whose slope is 2.3 AH/point (.001 sp.gr.). This is in good agreement with the specific gravity drop on 10-hour rate discharge, which averaged 2.3 AH/point.

In conclusion, it has been established that calcium-lead alloy grid cells, with .250 inch positives and efficient active material retention, in electrolyte of 1.210 sp.gr., have as good cycle life under normal overcharge as antimonial-lead grid cells of high quality. In addition, the cells are capable of long stand periods, up to 3 years at room temperature, with a retention of charge greater than 50% of initial capacity. The cells can be recharged after 3 years stand and discharge, with restoration of normal capacity.

Test Results - Thin Plate Cells

On Contract NObs-65261, C & D Batteries endeavored to develop a battery with .090 thick positive grids, to meet the requirements of the Navy standard diesel engine starting battery BB257/U. Considerable effort was required to develop a technique of casting suitable for such grids. However, good homogeneous grids were finally cast.

Life tests were conducted in accordance with Test V of Specification MIL-B-15072A. This provided considerable overcharge, averaging about 25%. Requirements are 150 cycles, minimum.

Results of tests of six batteries were not satisfactory. All batteries developed internal short-circuits before cycle 100. In addition, the positive material softened and the cells lost capacity at the 10-hour rate.

The major problem seems to be the need for a effective retainer which is thin enough for these cells.

Retainers used in the six batteries were as follows:

(1) Non-woven felted mat of Dynel fibers folded over the bottom of the positive plates.

(2) Unidirectional glass fiber mats plus perforated sheet retainer.

(3) .015 inch jackstraw glass mats.

All batteries used microporous separators, as well.

Results of Capacity Tests were as follows:

Cycle	Rate (Amps)	Spec.	Discharge Time (Hours unless otherwise stated) #1	#2	#3	#4	#5	#6
1	17.5	10	10.9	11.3	11.38	11.25	12.15	10.25
2	100	1	1.23	1.3	1.45	1.35	1.48	1.2
3	650(X)	3.3	4.1	4.25	5.3	2.15	2.15	1.5 Min.
49	100	1-	1.07	1.38	1.43	1.02	1.3	1.03
50	17.5	10	7.7	8.9	8.9	4.8	6.6	8.33
52	17.5	10	--	9.98XX	--	2.0	5.7	5.6
99	100	1	--	1.05	--	--	--	--
100	17.5	10	--	5.25	--	--	--	--
101	650(X)	3.3	--	3.1 Min.	--	--	--	--

(X) discharged at zero F to 3 volts final

(XX) separators were replaced after cycle 50

Thus three of the batteries met or exceeded the specification initially and through cycle 49. However a sharp decline in 10-hour rate capacity occurred at cycle 50. The best battery, #2 showed about 50% of 10-hour rating at cycle 100, 105% of 1-hour rating at cycle 99, 93% of rated capacity on cold test at cycle 101.

Inspection of the batteries after cycling disclosed the following:

positive material was soft and mushy
internal shorts, generally across the bottom of the plates
penetration of grid by oxide formation was slight.

The fact that the low rate capacity fell so sharply is attributed to the loss of available positive material. This loss is believed due to two factors:

(a) Under continued overcharge, the residual sulfate which binds the lead dioxide tends to be completely eliminated. Ordinary

antimonial lead grids have the effect of preventing the complete conversion of lead sulfate to lead dioxide. In the absence of antimony, this conversion can apparently go to completion. Consequently, the calcium-lead cell is more easily damaged by overcharge than the antimonial-lead cell. On the other hand, it does not need very much overcharge. This point seems well established by the excellent results reported for batteries on float. However, it remains to be seen how the batteries perform in cycle service when the overcharge is minimized.

(b) The close spacing between plates in the engine-starting batteries limits the retainer to about .015 inch thickness. With available retainer materials, under overcharge conditions, the mats become saturated quickly and then permit rapid erosion of the active material.

It is concluded that further development is needed along the following lines:

(a) More effective material retention under overcharge.

(b) Determination of optimum charging procedure to minimize overcharging on cycle tests.

With respect to (b), some preliminary work at the U.S. Naval Research Laboratory on cycle tests without overcharge, on cells with about .090 inch positives, is of interest. In this test, the cells used five plates, 5-1/2 x 5-5/8 with .08% calcium-lead alloy grids. Separation was accomplished by microporous separators .035 inch thick with the flat side against an .010 inch glass fiber mat which pressed against the positive. A thin glass mat was placed between the separator ribs and the negative plates.

The cycle consisted of a discharge of 3.7 amperes for 4 hours, 11 minutes (940 amp. minutes) followed by a two step charge totalling 940 amp-minutes. Charge rates were 6.9 amperes for 1.48 hours then 1.8 amperes for 1.56 hours.

The absence of overcharge was found to produce electrolyte stratification and poor charge acceptance at the bottom of the plates. After 25 cycles, air agitation was employed to eliminate stratification. Capacity tests were made after an over-night charge at 0.5 ampere.

Results of capacity test of cells in 1.280 sp.gr. electrolyte, were as follows:

Cycle	Capacity (Amp-Min)	% Rating
8	1340	96%
21	1390 (Air agitation after cycle 25)	99%
42	1460	105%
70	1520	109%
123	1530	109%

It is clear that these results are entirely different from the results reported by C & D Batteries for cycle tests with 120% overcharge. The contrast becomes sharper when it is realized that the U.S. Naval Research Laboratory plates were made by C & D for their experimental work.

U.S. Naval Research Laboratory also determined the growth and the penetration of the positive grids during the test. Results reported were:

Cycle	% Growth
10	.3
25	.55
120	1.5

These results would indicate that the growth of the grids did not cause any loss of capacity at moderate rates of discharge.

Inspection of the cells after cycle 123 showed that the positive material was firm and in good condition. Grid growth was 1.5% in width and the peroxide penetration was only .006 cm.

The difference between the results of tests of the six batteries at C & D and the cells at U.S. Naval Research Laboratory may be attributed, in part, to a more effective retainer system and, in part, to greatly reduced overcharge. Continuation of this work will be necessary to determine whether thin plates (.090 inch) with calcium-lead grids can be built to meet the life requirements of MIL-B-15072A. In this connection, it should be noted that present

antimonial-lead cells last 2-3 times as long as the minimum requirement of MIL-B-15072A for the BB257/U.

Intermediate Thickness Plates

Submarine battery cells have been built and are on test to determine performance under simulated service conditions. These cells were built by The Electric Storage Battery Company and by Gould-National Batteries, Inc. Each cell weighs about 1000 pounds and is rated at 6850 AH at the 10-hour rate, 4340 AH at the 1-hour rate. The Electric Storage Battery Company cast the grids by top pouring. Gould cast the grids by bottom pouring. Both claim satisfactory grids can be cast by their procedures. However, it is believed that bottom pouring in which the molten metal rises in the mold and the leading portions contact air, is less liable to dross inclusions than top pouring.

Because of very close weight tolerances for submarine cells, the differences in density between antimonial-lead and calcium lead required modification of the standard grid mold. (8% antimonial-lead weighs .388 pound per cu.in., calcium-lead weighs .410 pound per cu.in.)

Several other production problems were encountered. The calcium-lead alloy is much more difficult to "burn" i.e. weld than antimonial lead. In addition, the bond between the alloy and the copper inserts in the terminals required special techniques. However, these problems were solved, and cells were produced without any antimony.

In the submarine cell, the positive plate is .135 inch thick by 12 x 30. The negative plate is .098 inch thick by 12 x 30. Electrolyte specific gravity is 1.265.

Results obtained thus far at the Material Laboratory on Gould cells on a simulated Submarine Service Life Test are as follows:

		Capacity	
Cycle	Rate	Hours	% of Rating
6	165	44.75	93.2
7	685	9.63	97.0
8	4340	0.89	89.9
9	6775	0.44	90.0
96	165	47.83	97.7
97	685	11.12	108.4
98	4340	1.08	103.4
99	6775	.53	100.0

Hydrogen evolution on stand, fully charged, at 100°F, averaged 62 cc/hour at cycle 52: 55 cc/hour at cycle 95. To appreciate how small this is, note that it is equivalent to a current of about 20 milliamperes for a 1000 AH cell. It is actually 3 cc/hour per 1000 sq.in. of plate area.

For an extreme comparison, Crennell & Milligan, "World Power", June 1932 reported that tests of hydrogen evolution from charged antimonial-lead negative plates in 1.260 sp.gr. electrolyte, at 35°C (95°F) showed a rate of about 10 cc/hr x sq.cm. or about 60 cc/hr x sq.in. This is 20,000 times as great.

Submarine battery cells with antimonial-lead negatives are usually much better than the results reported by Crennell & Milligan would indicate. However, as they age, the hydrogen evolution increases slowly at first and then rises sharply at about the time the capacity begins to fall. It is expected that the calcium-lead cells will not show appreciable increase in hydrogen evolution during life.

Hydrogen evolution from antimonial-lead grid cells otherwise the same as the calcium-lead grid submarine cells whose hydrogen evolution was given above, has been measured with the following results:

Cycle	Hyd. Evolution (cc/hour x cell)	Ratio to Ca-Pb
47	162	2.7
137	263	4.4
226	524	8.7
317	746	12.5
407	1600	27
497	2540	42
587	3510	88

Tests of stibine evolution have not been made on cells with calcium-lead grids. It is expected that stibine will not be found. This is an important consideration among the factors that led the Bureau to install a battery of cells with calcium-lead grids in the nuclear powered submarine, the USS SEAWOLF.

In addition to the Exide and Gould submarine battery cells on test at the Material Laboratory, a group of 12 cells including 3 with calcium-lead grids were put on a special life test at the Electric Storage Battery Company, as specified in Contracts NObs-65221 and NObs-72005. The life test was designed to simulate an anti-submarine (SSK) patrol which differs from the normal submarine life test in that the cells are most frequently discharged 7 hours at 105 amperes, then charged for 1 hour starting at 1200 amperes. This partial discharge and charge is typical of SSK operation. It results in a slight charge deficit which is made up periodically. Results obtained on capacity and hydrogen tests with cells built with .08% calcium-lead alloy grids were as follows:

Lab Cycle (Approx)	% Rated Capacity 6-hr rate	1-hr rate	Hyd. Evolution cc/hour x 1000 AH
Initial	105.7	101.5	18.9
118	104.3		
210	113.6		
212, 213	105.3	109.3	20.0
314	121.7		
417, 418	100.9	93.3	34.0
610	106.1		
613, 614	86.9	73.3	16.7

Failure was due to grid corrosion. It will be noted that the hydrogen evolution did not rise at the failure point, which usually occurs with antimonial-lead grid cells. Total life was about 18 months on this test. This is considerably less than shown by the antimonial-lead cell groups on the same test. However, in the performance of this test which began in June 1954, The Electric Storage Battery Company operated the entire group of 12 cells in series. This subjected the calcium alloy cells to the same overcharge as the antimonial-lead cells. It is possible that the life of the calcium cells might have been extended if they had been operated as a separate group. In addition, the grids were cast by techniques which may not have been optimum. However, pending results of the Material Laboratory tests, the Bureau is not approving calcium-lead for submarine batteries in diesel-electric submarines.

REFERENCES

Bureau of Ships projects on storage batteries with calcium-lead grids.

(a) New York Naval Shipyard (Material Laboratory)
Project 4433-127 -
Evaluation of submarine battery cells, Gould TPX-C-67 with calcium alloy positive grids and pure lead negative grids
Status - 99 cycles on 5 May 1956

(b) New York Naval Shipyard (Material Laboratory)
Project 4433-132 -
Evaluation of submarine battery cells, ESBCO type MAW-67E with positive and negative grids of lead-calcium alloy .065 - .08% calcium.
Status - 4 capacity test cycles reported in June 1956

(c) New York Naval Shipyard (Material Laboratory)
Project 5311-C-1 -
Evaluation of 200 AH portable storage batteries with calcium-lead grids, C&D type 3-CXSH15-W, furnished on NObs-50289.
Status - Cycle life test completed
3 year stand test completed December 1955
4 year stand in December 1956

(d) Contract NObs-65261 with C & D Batteries, Inc.
Development and testing of a battery with calcium-lead grids to meet the specifications for the standard Navy portable engine starting battery (6V-SBM-130 AH - BB-257/U).
Status - Contract completed but results unsatisfactory.

Other related projects are:

Contracts NObs-65221 and NObs-72005 with The Electric Storage Battery Company

Special grid alloys for submarine cells on SSK service life test.

This contract covers the construction and testing of four (4) groups of GUPPY submarine battery cells on a program simulating service in an anti-submarine submarine.

	Positive Grid	Negative Grid
Group 1 -	8% antimony, Lead-plated	Pure lead
Group 2 -	4% antimony, .1% silver	Pure lead
Group 3 -	.08% calcium	.08% calcium
Group 4 -	3% antimony, 1.5% tin, .03% selemium	Pure lead

Work started in June 1954 and is continuing.

C13523

PRESENTED AT THE JOINT BATTERY CONFERENCE MEETING - 12 SEPTEMBER 1956
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Office of the Assistant Secretary of Defense (R&D)

CES 206/16

AIRCRAFT STORAGE BATTERIES
NICKEL-CADMIUM AND SILVER ZINC

By Paul C. Donnelly
Bureau of Aeronautics

The aircraft battery prior to the introduction of jet aircraft was used in a dual capacity for both engine starting and as an emergency electrical power supply. In today's high performance aircraft equipped with jet engines, batteries are no longer required for starting power; however, their importance as an emergency power system has been greatly increased.

There can be no dispute to the statement that the electric system has a more important role in the flight of modern military aircraft than ever before. The electrical power requirements of todays military aircraft have increased approximately three fold over that of our World War II aircraft. This increase is especially true in regard to the emergency or essential bus. Today an emergency load of 75 to 100 amperes for periods of time up to 30 minutes is not uncommon. Batteries with increased capacity must be developed to handle these emergency loads. The Bureau of Aeronautics is cognizant of this fact and has embarked on the development and evaluation of nickel-cadmium and silver-zinc aircraft batteries capable of meeting these requirements.

Before any new battery can be installed in a military aircraft, long and careful laboratory evaluation must take place. Learning all the characteristics of the battery improving its shortcomings, searching for hidden deficiencies, and modifying if necessary the aircraft electrical configuration to accomodate any peculiarities of charge or discharge of the battery must be undertaken.

Briefly, the construction and the electro-chemical reaction of the nickel-cadmium battery is as follows: Carbonyl nickel powder is pasted on thin strips of nickel plated steel sheets and then sintered under high temperature. The positive plates are saturated with nickel hydroxide and the negative plates are saturated with cadmium hydroxide. Nylon cloth is normally used as a separator material and potassium hydroxide employed as the electrolyte. In order to minimize the gassing all the plates and separators are tightly compressed into a stainless steel container. On charge nickel oxide is converted into nickel dioxide and cadmium oxide is reduced to cadmium. On discharge the process is reversed.

$$NiO_2 + Cd \rightleftharpoons NiO + CdO$$

During charge there is no release of any gas until the plates approach a full charge condition, at which time oxygen is released by the positive plates and hydrogen by the negative resulting from the electrolysis of water in the electrolyte. In the aircraft storage batteries being procured the gas is quite easily recombined due to the large surface area of the plates and the limited amount of electrolyte resulting from tightly compressing the plates. Actually, if the charging rate is reduced sufficiently at the end of charge a point of equilibrium is reached where charging can be conducted indefinitely without any measurable release of gasses.

The construction and electro-chemical reaction of the silver oxide-zinc battery is somewhat similar. The silver battery is composed of silver oxide positive plates and negatives of zinc. Because of the absence of heavy supporting grids in the plates, the close packing of the plates, and the fact that the reactions of the cell do not involve overall electrolyte concentration changes, thus allowing a minimum quantity of electrolyte, the silver battery is a very compact unit on a weight to volume basis. The extent of usage of the active materials is unusually great which also contributes to small size and weight.

The effective overall electro-chemical reactions of the system may be stated as:

$$Zn + 2(OH) \rightleftharpoons ZnO + H_2O + 2e \qquad (1)$$

$$Ag_2O + H_2O + 2e \rightleftharpoons 2Ag + 2(OH) \qquad (2)$$

When silver is oxidixed electrochemically, it may attain a higher valence state than it does in the more familiar chemical reactions in which silver has a valence of one. Research has indicated that in the silver battery silver reaches a state of oxidation greater than is represented by Ag_2O. In this case the reactions are:

$$Zn + 2(OH) \rightleftharpoons ZnO + H_2O + 2e \qquad (3)$$

$$2AgO + H_2O + 2e \rightleftharpoons Ag_2O + 2(OH) \qquad (4)$$

The conductivity of the negative plate is high even though zinc oxide, the product of discharge, is an insulating material. The negative conductivity does not restrict the discharge rate. As seen in half reaction (4), the positive plate is in a highly oxidized condition at the start of discharge. Since silver oxides are fair conductors, and the positives contain residual silver even in a fully charged condition, the conductivity of the positives is understandably high from the beginning of a high rate discharge and improves as the plate is reduced to metallic silver. The good performance on discharge of the silver battery may be attributed to:

a. Excellent plate conductivity.
b. High active material efficiency.
c. Lack of concentration polarizations due to the almost unchanging composition of the electrolyte during discharge.

The silver-zinc and nickel-cadmium aircraft batteries have been developed along the lines of present lead-acid aircraft batteries as regards size, weight, and dimensions. This has been done in the interest of standardization and interchangeability. The nickel-cadmium battery does not have an electrical output appreciably more than that of the lead-acid battery. Its

improvement, or advantage, over a lead-acid battery is due to the fact that during the life of the battery no battery maintenance is required, no objectionable gasses are released, and a slightly higher wattage output of the battery at high rates is obtained. It is hoped that a longer battery operating life will result, however, only through service evaluations can this fact be ascertained. The silver battery holds a distinct advantage over both the nickel-cadmium and the lead-acid batteries in relation to watt-hours per pound. For example, a 30 pound silver battery can furnish the same capacity as an 80 pound lead-acid battery under normal conditions.

Although both the nickel-cadmium and the silver batteries have been given extensive publicity as a major improvement over lead-acid batteries, there are still several obstacles to be overcome, some of which are serious while others can be corrected easily.

The difficulties encountered by this bureau in its evaluation of the nickel-cadmium battery have been:

(1) Susceptibility to go into a "vicious cycle" caused by high temperature and or high charging voltage.
(2) Failure of safety relief valves to operate, due to poor design.
(3) General poor mechanical construction as regards the battery container and the method of securing the cells in the container.

It is hoped all these discrepancies will be overcome by the following design improvements: The addition of a reliable over-temperature relay to prevent overcharging; an improved pressure relief valve; and a better designed battery container and method of securing the cells in the container.

The difficulties with the silver battery are more complex. Evaluation tests have shown that this battery cannot be efficiently charged from a DC generator and also it has a short cycle life. This bureau is presently engaged in the development of a compatible charging system for these batteries and also investigating means of increasing it's cycle life.