

LEAD ACID BATTERY
PULSE DISCHARGE INVESTIGATION

FINAL REPORT

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MASTER

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WITH BATTERY EXAMINATIONS

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Principal Findings

1a. Electric vehicle lead acid batteries of the improved golf cart type produce about 5 to 10% less energy under pulsed conditions relative to the same average d.c. current after the first twenty deep discharge cycles. The pulse characteristics were a peak to average amperes ratio of 300/150 and 50% duty cycle within a frequency range of 16 to 333 hertz.

1b. Pulsed discharge energies approached the d.c. energies at the same average currents above 333 hertz.

2. Frequencies and duty cycles characteristic of electric vehicle controllers produce ampere-hour capacities similar in magnitude to d.c. discharges of the same average currents. The voltage termination circuit compensated for battery internal voltage drops. This approximates actual operation guaranteeing a return at slightly reduced performance in extreme cases.

3. At the frequencies evaluated (d.c., 17, 83, 167, 333, 500 and 1000 hertz) a discharge energy minimum occurred at 83 hertz.

4. The amount of positive plate corrosion under pulsed conditions was about twice that of the unpulsed. This was most noticeable at the interface region between the active material and the grid.

5. Unusually large lead sulfate crystals were found in isolated colonies in both the positive and negative pulsed plates, whereas a battery that had been

discharged each cycle at an equivalent steady state did not show these large crystals.

a. In the negative plates, the large lead sulfate crystals gave evidence of having become detached from the cell circuit.

b. In the positive plates the large lead sulfate crystals reconvert to the lead dioxide structure during prolonged charges.

Recommendations

1. A 300 amperes d.c. set of at least 70 cycles should be run on three battery modules connected electrically in series. This is necessary in order to determine whether the increased corrosion and/or large sulfate crystals are related more to the pulse regime or to the peak current.
2. At least 70 cycles of a pulse regime of 50% duty cycle but of a higher frequency, 500 hertz for example, would help determine whether the pulse frequency affects the rate of corrosion and/or large sulfate crystal growth.
3. One cell should be removed from each battery module before tests in the future. The cell should be examined before the test to assure that its plates, separators, etc. are in good condition and to establish a reference for subsequent evaluations of the remaining two cells in the battery module. This is absolutely necessary since it is impossible to assure that all batteries are from the same batch or were made in exactly the same way. The remaining two cells of a three cell battery module should be similar in microstructure since they should have been manufactured by the same process and materials and about the same time as the reference cell. A high current terminal would be added to the intercell connection which was connected to the removed reference cell. Three of these two cell modules would be connected in series for cycling.

Introduction

The effects of high current pulses caused by electric vehicle Silicon controlled rectifier (SCR) and transistor chopper controllers on battery energy, life and microstructure has been uncertain in the past. Such high current pulses may have a significant effect on diffusion and reaction rates, conductivity/resistance ratios and crystal morphology of processes occurring within the battery. It is important to learn what processes become rate controlling under such conditions and to determine what may be done through design or regulation to increase the battery efficiency and life under such service. Until recently, no instrumentation has been available to accurately measure watt hours under such conditions.

The Electrochemical Power Laboratory, a section of the Electrochemical Division, MERADCOM, Fort Belvoir, Va., has acquired equipment for this type of measurement and has programmable discharge load banks capable of simulating high current pulsed waveforms. To increase the utility of these tests, the batteries involved were subjected to a post test analysis at the Naval Research Laboratory, Washington, D.C.

Design of Experiment

Initial charge current was limited to 25 amperes per 100 AH (33 amperes)

with crossover from current control to voltage control at 2.55 volts per cell. The voltage is held constant at 2.55 volts by using remote sensing at the battery terminals to correct for voltage drops in the leads. A charge voltage of at least 2.55 volts has been found empirically to be necessary to fully charge electric vehicle batteries. One reason for this found in the literature, is the negative active plate material becomes contaminated by antimony in ordinary operation. Plates having a deposit of antimony can be partially cleared by overcharging at a cell voltage of 2.55 volts or more. The gas then passes off as stibine (1). Next, the charge current is reduced to 5 amperes per 100 AH or 6.6 amperes; this current is held for 3 to 5 hours. Equalization charges were performed whenever cell specific gravities dropped more below 1.270 unless noted otherwise. An equalization charge consisted of a time extension of the 6.6 ampere current charge period until specific gravities were above 1.270.

Capacity discharges were performed periodically. A capacity determining discharge was preceded by an extended or equalization charge. The battery capacity is the number of ampere-hours discharged at 75 amperes to 1.75 volts per cell. Table 1 lists all the types of tests planned for this investigation. Test number 1 is set at 150A. d.c. while test numbers 2,3 and 4 pulsed are at 2MS on with increasing off times. Test 5 is half the frequency of test 3. Test 6 was planned to consist of at least 5 cycles of each of the previous tests (numbers 1 to 5 inclusive). About 70 cycles of each of the numbered tests were planned. However, this was to be contingent on what was learned in the

initial two tests; namely, numbers 1 and 3. The purpose of doing these two tests first was to determine if any significant differences were found between d.c. and pulsed conditions at the same average currents. It was necessary to extend the number of discharges to the "actual cycles" listed in the table since capacity did not decrease as was expected. Since the battery micro-structural examinations showed significant changes for pulse test number 3 (166 Hertz) and only one pulse test station was available, only tests 1, 3 and 6 could be completed within the time frame and resources of this project. Test 6 was considered valuable in order to acquire energies under all the test regimes on the same set of batteries on the same basis.

Battery

EV 106 batteries from ESB were procured for this investigation. These batteries consist of three cell modules, are golf cart type with paper separators and are rated at 75 amperes for 106 minutes to 1.75 volts per cell at 25°C (77°F). This calculates to be 132.5 AH. Unless stated otherwise,³⁻ three cell modules were connected electrically in series for testing.

Test Station

The test station consists of Acme PS² L-1000 programmable load banks which are driven in the constant current mode by a function generator for pulse discharges. Each load bank is rated at a maximum current of 110 amperes with a voltage compliance to 50 volts and a maximum power of 1000 watts. A Hewlett-Packard model 6269B programmable power supply with remote voltage sensing was

used for charge. This supply has a maximum voltage rating of 40 volts and a maximum current rating of 50 amperes. A microprocessor based programmable controller monitors state changes of timers and comparators, and outputs state changes based on its program for termination and initiation of charges, discharges and open circuit periods. Strip chart recorders and data acquisition systems monitor and record data.

Accurate measurement of instantaneous current and power is accomplished by means of a novel wideband Hall-effect multiplier. A 5 microsecond response time of the transducer insures that highly accurate multiplication of 5 kilohertz signals can be readily accomplished (2). The risetime of all pulses was fixed at 0.2 milliseconds to simulate actual electric vehicle waveforms. The worst case overall error was $\pm 1\%$ of reading for all energy values.

A special voltage termination circuit was developed to assure termination of all discharges with a single preset low voltage limit. The circuit monitors a voltage (from a Hall-effect sensor) proportional to current and adds it to the battery voltage during a discharge to compensate for battery internal resistance. The resultant voltage is filtered and then compared to a preset value via a comparator which produces a state change sensed by a controller for termination of discharges. A one hertz low pass filter is incorporated in the termination circuit to prevent premature termination by voltage spikes. The circuit assures termination under pulsed or d.c. conditions at the voltage knee. This approach also avoids selection of a single AH, WH or watt termination value and the readjustments required for a wide range of average current drains. The termination is also independent of battery design as reflected in the internal resistance. Finally, termination occurs at a minimum battery voltage which would allow for reduced but useful performance in a vehicle. In general, with the same average

current, termination will occur at the same state of charge, independent of the pulse frequency.

Results

The following tests were performed:

1. D.C., 145 amperes, 142 cycles, batteries (Wet) numbers 3 and 4 (Preliminary runs).
- 2a. Pulsed, 3MS-50% duty cycle, 145 amperes average, 63 cycles, batteries (Wet) numbers 1 and 2 (Preliminary runs).
- 2b. Pulsed, 3MS-50% duty cycle, 145 amperes average, 92 cycles, batteries (Dry) numbers 18 and 21.
6. Pattern (5 cycle groups of pulsed or d.c. discharges), 108 cycles, batteries (Dry) numbers 22, 23 and 17.

The data from test 1 is graphed in Figure 1. The reference standard energy (75 amperes to 1.75 volts per cell) after cycle 8 was 1564 watt-hours (WH). Equalization charges were performed at cycles 38, 59 and 76. The ratios plotted in Figure 1 are calculated by dividing the energy during a discharge by the standard energy. This facilitates comparison of this set of batteries to others. These ratios ranged from 0.89 to 0.94 with a peak of 0.94 from cycles 55 to 85.

Battery number 2 from preliminary test 2a was analyzed to determine if any significant microstructural differences had been caused by the pulse regime. Since this had, to our knowledge, never been done before; it was not

known that significant reproducible differences between this particular pulsed regime and d.c. at the same average current would occur. The differences were significant and will be described later.

The energy ratio data from test 2b is graphed in Figure 2. The reference standard energy cycle 33 was 1319 WH. An equalization charge was performed at cycle 30. The two batteries were pulsed at 167 hertz with 290 ampere peaks and a 50 percent duty cycle. The average current was 145 amperes. This test was performed to verify the results of the previous pulse test and microstructural analysis. The ratios of the energy during a discharge to the standard energy ranged from 0.75 to 0.84 with peaks ranging from 0.83 to 0.85 from cycle 25 to about 65.

The center cell electrolyte temperature varied typically from 37 to 47°C for the pulsed discharges and from 37 to 42°C for a d.c. discharge. Typical discharge time ranged from 0.7 to 0.9 hours for pulse and d.c. discharges respectively. The temperature excursion for an average current of 145 amperes was about 5°C for d.c. and about twice this for the pulsed case. When a discharge was started at room temperature (26°C), the temperature rise was 13 degrees and equilibrium would be reached after the next cycle. A 75 ampere d.c. discharge lasted about 1.8 hours and the temperature rise was about 2°C.

At least five cycles of each type listed in table 1 were run on three battery modules (numbers 22,23 and 17) connected electrically in series. This series of cycles is referred to as the "Pattern" life cycle run. A summary

of discharge energies is given in Figure 3. Battery module number 22 was removed for analysis after cycle 43. All energies from cycle 44 to 108 were multiplied by 1.5 to compensate for the removed module. The actual energies of cycles 104 to 108 are erratic due to attempts to raise the low specific gravities of the positive terminal cell of battery module number 23. These attempts were not successful and the test was terminated. After very long charges, this cell would accept charge as determined by its specific gravity, very slowly and never reached 1.280 ± 0.01 . The highest specific gravity of this cell was 1.265. Several charge-discharge cycles confirmed this. The module was sent to Exide, the manufacturer, for analysis. An informal report is available on request.

Data from the "Pattern" life cycles are tabulated in table 2. The watt-hour (WH) energies and the corresponding ampere-hour (AH) capacities are given in the table. The AH capacities are all essentially the same 100 ± 2 AH while the energies change as shown in the graph in Figure 4. The graph should be considered cautiously with the trends in Figure 3 in mind. The first cycle of any series is usually significantly low in energy. For this reason, first values were not included in the energies in the graph. Subsequent discharge energies were averaged and the actual values nearest the average used in the graph. The energies vary within a band of roughly 1480 to 1620 initially, rising to 1610 to 1745. The difference is about 140 WH within the banks with an overall rise of about 128 WH from the initial average of 1550 WH to a final of 1678. Since the energies rise as the cycles proceed and variations occur within any set of

similar runs, conclusions (based on Figure 4) should be drawn with care. The Hall-effect watt-hour measurement error was less than $\pm 1\%$ and, therefore, is not a major concern since this would be less than ± 17 WH based on the highest average value of 1678 WH.

The cycle number for the energies in Figure 4 and table 2 ranged from 48 to 79. This is generally a plateau region for cycle life energies. The d.c. energies are, in general, greater than the pulsed energies in this region.

The standard 75 amperes capacities increased from 106 AH (1874 WH) at cycle 12 to 123 AH (2198 WH) at cycle 73. This is indicative of a fundamental increase in capacity within the battery that should be reflected in all discharges.

Pulsed energies versus three average currents are graphed in Figure 5. The corresponding AH capacities for the graphed points in Figure 5 are compared to an idealized equation which relates the current to time of discharge in table 3. Peukerts equation, $I^n t = C$, was selected since it is the most widely used one. In this equation, n and C are constants which were evaluated as noted in the table 3 footnote. The capacity percent error or differences are not large except for an average current of 235 amperes and a frequency of 1000 hertz. The high average current has an AH difference of -11.9 percent that could be attributed to the higher effective ohmic resistance which is not compensated for in the equation. The difference of -7.4 percent at 1000 hertz could be attributed to the tendency of the Hall-effect device to give energy readings at 1000 hertz that are about 1% (of reading) higher than d.c. Also, at higher frequencies, shielding to minimize leakage paths becomes a consideration.

Shielding techniques were used but due to the inherent spread out of the three battery modules and the required high current connections and leads the effects of higher frequencies are difficult to determine.

Battery Examinations

The following three cell batteries were sent to NRL/ILZRO for analysis: Number 4 (d.c. 142 cycles), number 7 (reference), number 2 (pulsed, 63 cycles), number 18 (pulsed, 92 cycles), number 22 (pattern, 43 cycles), number 24 (8 months later, reference), and number 17 (pattern, 108 cycles). Appendix A is a report on batteries 4, 7 and 2. Appendix B is a report on batteries 22, and 17. Battery 18 was cycled essentially the same as number 2 and its analysis confirmed the analysis on battery 2; it is available on request.

The first report (Appendix A) gives the results of three battery examinations. The first battery was an unused dry charged battery to which no electrolyte had been added, and it was included in the examination to determine how the cycled batteries differed from it. The other two batteries were purchased wet and had been cycled but were brought to a fully charged condition before disassembly and examination. The examinations revealed that pulsing might be responsible for a definite accumulative and detrimental effect seen in the pulsed positive plates, and that it might also slightly change the negative in a manner that could be beneficial in effect. The same amount of corrosion seemed to have occurred in the pulsed battery as in the unpulsed battery, after only half as many cycles. This is probably an effect of the pulsing. There is no question

that the large lead sulfate crystals observed in the case of the supposedly fully charged pulsed battery represent a very unusual condition and one that undoubtedly would become progressively worse with each discharge and recharge.

The separators were unusually porous. The open structure probably was responsible for a considerably reduced internal resistance in the batteries.

The second report (Appendix B) gives the results of two dry charged battery examinations. Both batteries were cycled to the "Pattern" discharges previously described and summarized in Figure 3. The first battery was identified as number 22 and at the time it was removed from the test had received a total of 43 discharges. The second battery was number 17 and at the time of its removal had received a total of 108 discharges.

The unusually large lead sulfate crystals that were found in isolated colonies in both the positive and negative plates were also found in a battery that had been pulse discharged at every cycle, whereas a battery that had been discharged each cycle at an equivalent steady state did not show these large crystals. Since the present plates were also pulsed it is reasonable to conclude that this pulsing correlates with the growth of colonies of the very large lead sulfate crystals. The reason for this has not yet been determined.

In the negative plate, the fact that these lead sulfate crystals persist after prolonged charging and show no evidence of partial solution may indicate that they have become detached from the cell circuit.

The situation is different in the positive plates, where normal cycles of charge-discharge allow the crystals to continue to grow in size, while prolonged charges can reconvert them to the lead dioxide structure.

The unusual appearance of the active material immediately above the grid wires may also be a result of pulse type discharges since very high current densities cause the current to proceed by the least resistive path from positive to negative, so that the major portion of the current is carried directly to the grid wires. But in so doing it passes through any intervening active material, which must be adversely affected by this high current.

As to the discrepancy in corrosion product thickness and appearance, no reasonable explanation has been found. For the same alloy material, corrosion rates are usually very similar for batteries experiencing the same cycle regime, except where casting defects and similar externally caused problems may be present. The corrosion product surrounding battery 17 is the more unexpected because it represents less than normal corrosion, and because the corrosion product remains intact and has not separated into layers. This is even more surprising since the appearance of the active material indicates that very high current densities were concentrated at the grid wires.

The smaller lead sulfate crystals observed in the positive and negative plates of both batteries were probably the result of self-discharge during open circuit standing. The larger crystals were probably a result of pulse discharging. Since these large crystals do not reconvert to lead or lead dioxide the

capacity of the battery is gradually reduced during cycling. Prolonged charging can restore the positive plate to its original condition insofar as the lead sulfate crystal removal is concerned. It is evident that this can not be done in the negative, where the large lead sulfate crystals are probably no longer a part of the electrical circuit. Insufficient evidence is available to make a firm prediction, but it seems likely that, if the number of these large lead sulfate crystals increased with increasing pulse discharge cycles, the negative plate will be the primary cause of failure, even if prolonged charges are resorted to as a preventative.

In the present batteries neither the extent of grid corrosion nor the condition of the active material were such as would explain the loss of capacity. The presence of the large lead sulfate crystals in the negative is certainly a contributing, if not the sole, reason for capacity loss.

REFERENCES

1. Vinal, G.W., "Storage Batteries" 1951, Fourth Edition, John Wiley & Sons, Inc., New York, pg. 144.
2. Ohio Semitronics Inc., Watt-Hour Meter Model WH-7, Columbus, Ohio 43212

APPENDICES

Removed

- A. Comparison of Batteries Cycled With, and Without, a Pulsed Type of Discharge.
- B. Examination of Plate Microstructure to Determine the Effect of Pulse Discharge.

FIGURES

1. D.C. - 145 amperes, ratio of discharge WH to capacity WH versus cumulative cycles.
2. Pulse - 145 amperes average, 290 amperes peak, 167 hertz, ratio of discharge WH to capacity WH versus cumulative cycles.
3. "Pattern" life cycle Energies.
4. Energy versus frequency for 150 amperes Average Current.
5. Energy versus Average Current, Duty Cycle and Frequency.

TABLES

1. Types of Tests.
2. Energy Versus Frequency For 150 Amperes Average Current.
3. Average Current and Capacity.

TABLE 1
TYPES OF TESTS

TEST NO.	FREQ (Hz)	ON T (mS)	OFF T (mS)	DUTY CY (%)	IAVG. (A)	IPK. (A)	<u>IPK.</u> IAVG.	PLANNED CYCLES	ACTUAL CYCLES	
1	0	DC	0	100	150	150	1.00	70	142	
2	30	3	30.3	9	27	300	11.11	70		
3	166	3	3	50	150	300	2.00	70	155	
4	267	3	0.75	80	240	300	1.25	70		
5	332	1.5	1.5	50	150	300	2.00	70		
6	AT LEAST 5 CYCLES OF EACH OF THE ABOVE.								>25	108
								TOTALS	375	405

TABLE 2

ENERGY VERSUS FREQUENCY FOR 150 AMPERES AVERAGE CURRENT

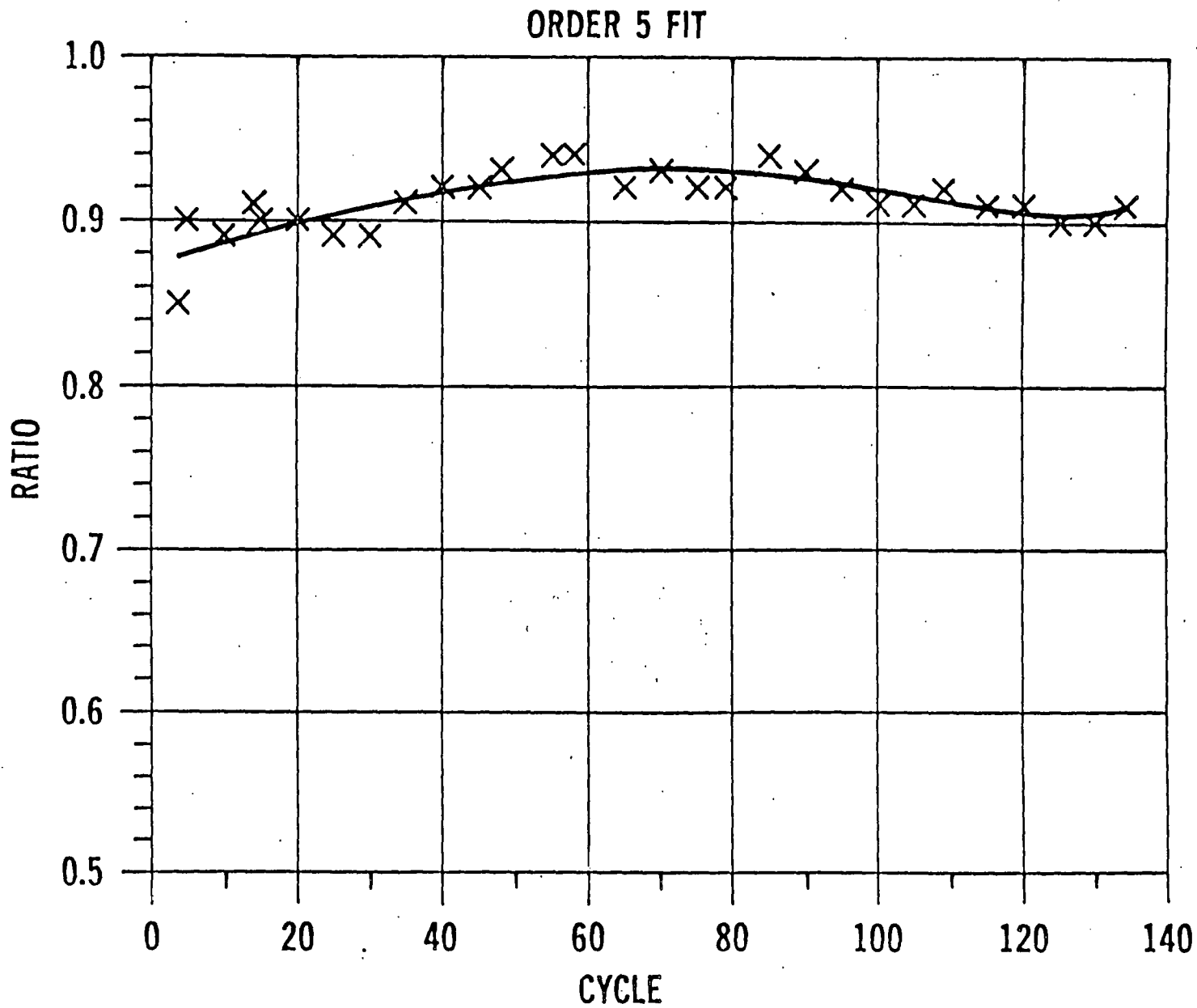
FREQUENCY (HERTZ)	ENERGY (WATT-HOURS)	CAPACITY (AMPERE-HOURS)	CYCLE NUMBER
D.C.	1667	100	48
17	1586	100	79
83	1572	99	74
167	1587	98	51
333	1605	102	69

TABLE 3
AVERAGE CURRENT AND CAPACITY

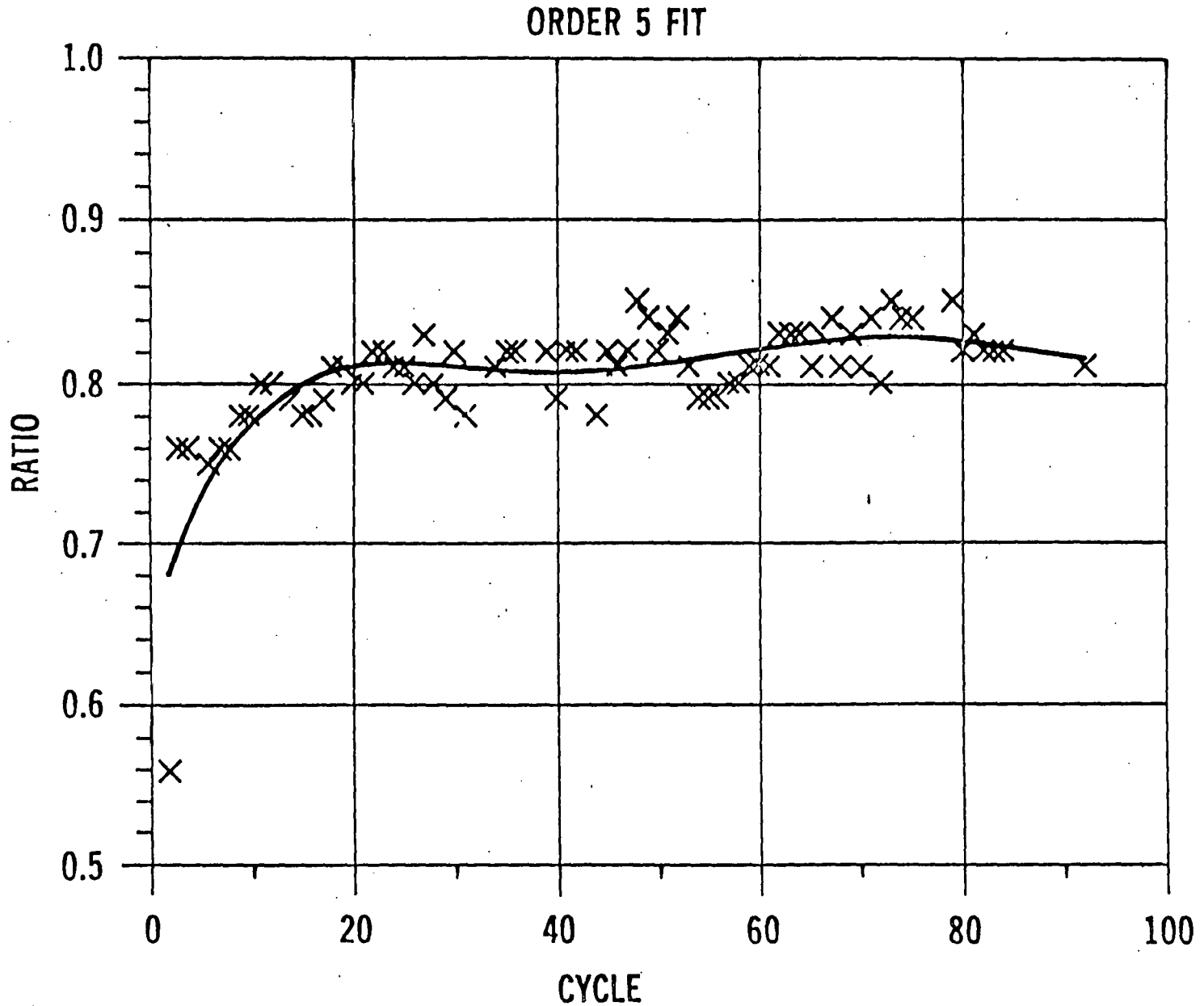
CYCLE NUMBER	FREQUENCY (HERTZ)	DUTY CYCLE (%)	AVERAGE CURRENT (AMPERES)	CAPACITY				ENERGY (WH)
				MEASURED (AH)	MEASURED TEMP. CORR. (AH)	CALCULATED ¹ (AH)	ERROR (%)	
32	30	9	24	159	154	155	-0.6	2663
51	167	50	150	98	93	95	-2.1	1587
22	267	80	235	76	74	84	-11.9	1178
79	16	50	150	102	96	95	+1.1	1592
87	500	50	149	101	95	95	0	1625
90	1000	50	150	94	88	95	-7.4	1692

1. AMPERE-HOUR CALCULATIONS ARE BASED ON PEUKERT'S EQUATION WHICH RELATES CURRENT AND TIME ($I^n t = C$). CONSTANTS n AND C ARE BASED ON TWO d.c. DISCHARGES EACH OF 75A FOR AN AVERAGE OF 1.5265 HOURS AND 150A FOR AN AVERAGE OF 0.634 HOUR.
n = 1.267, C = 362.9

DC - 145 AMPERES, RATIO OF DISCHARGE WH TO CAPACITY WH VERSUS CUMULATIVE CYCLES



PULSE - 145 AMPERES AVG., 290 AMPERES PEAK, 167 Hz., RATIO OF DISCHARGE WH TO CAPACITY WH VERSUS CUMULATIVE CYCLES



CY. 12 106 AH, 1274 WH
CY. 79 723 AH, 2151 WH

PULSE
27A 97%
30 Hz

PULSE
150A 50%
1K Hz

PULSE
150A 50%
16 Hz

PULSE
150A
50%
16 Hz

D.C.
160A

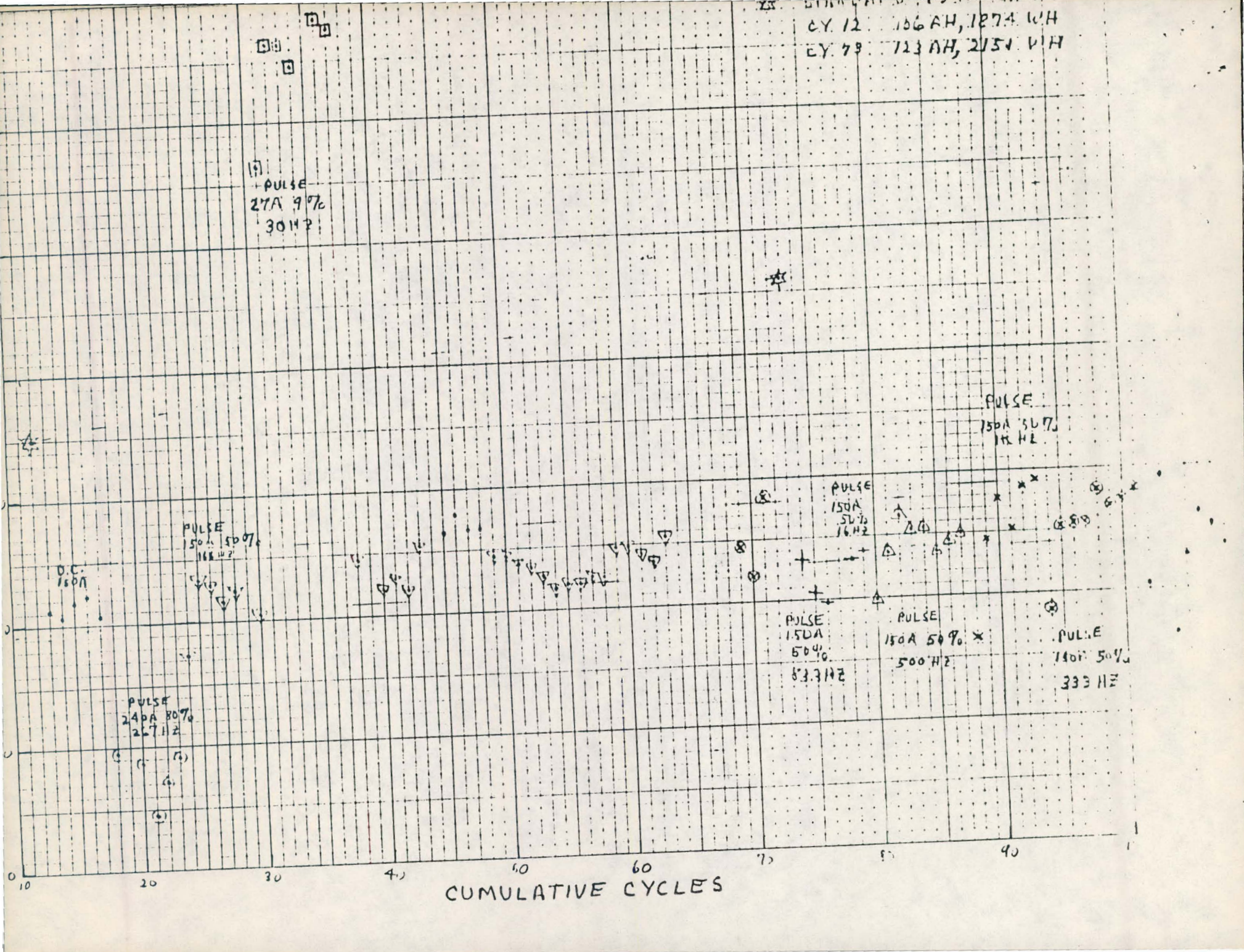
PULSE
150A
50%
63.7 Hz

PULSE
150A 50%
500 Hz

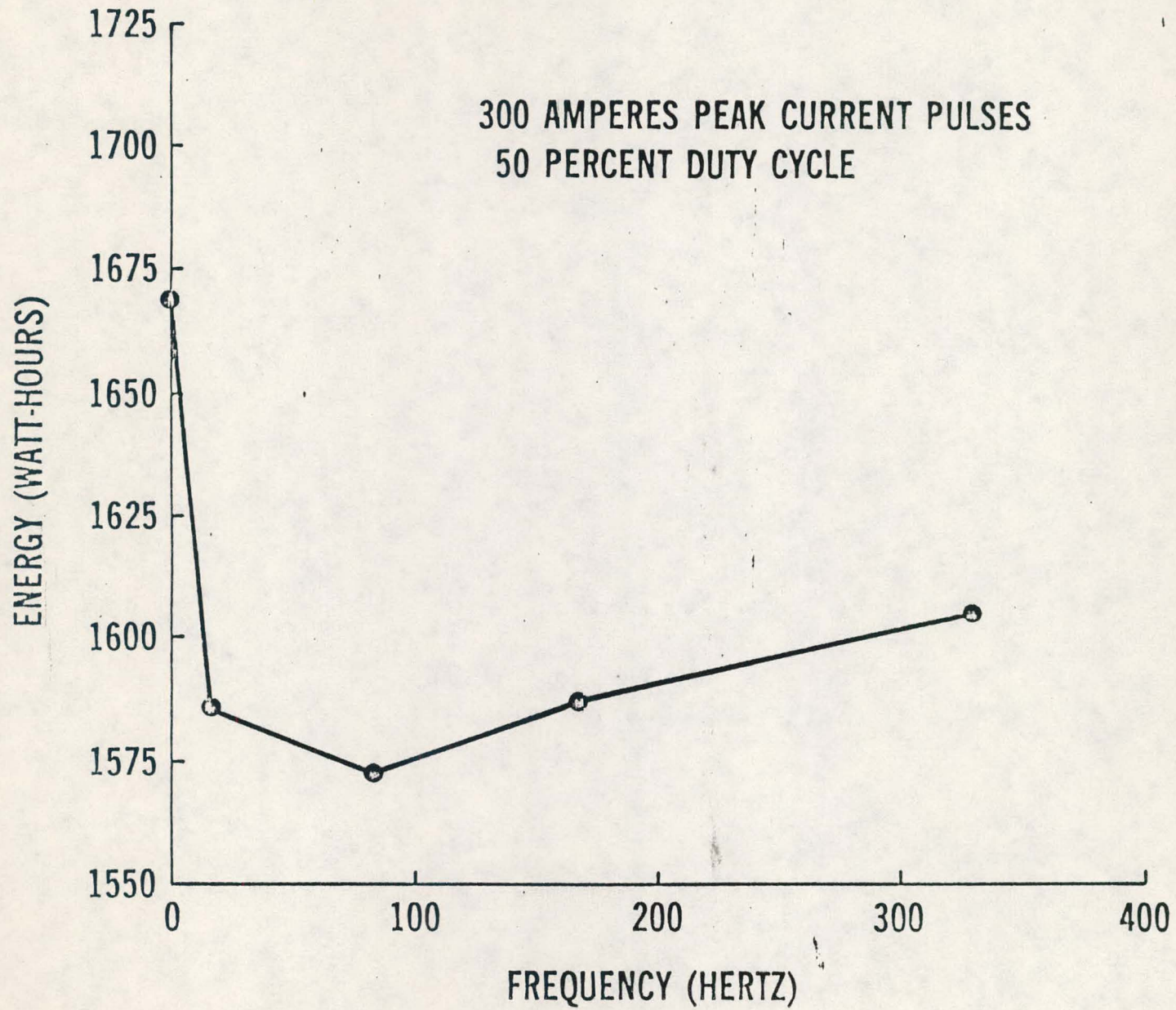
PULSE
140A 50%
333 Hz

PULSE
240A 80%
267 Hz

CUMULATIVE CYCLES



ENERGY VERSUS FREQUENCY FOR 150 AMPERES AVERAGE CURRENT



ENERGY VERSUS AVERAGE CURRENT, DUTY CYCLE AND FREQUENCY

